Research Article

Influence of Anodic Oxidation Parameters of TiO$_2$ Nanotube Arrays on Morphology and Photocatalytic Performance

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Titanium dioxide nanotube arrays (TNTAs) were fabricated by electrochemical anodization of Ti foils. The effects of electrolyte, applied voltage, duration of anodic oxidation to morphology, and photocatalytic performance of TNTAs were investigated. TNTAs formed in electrolyte of glycol and DMSO tend to grow along radial direction with flimsy tube wall and weak adhesion on Ti substrate. Those in glycerol, however, easily achieve balance between growth rate and corrosion rate, form orderly arranged array of nanotubes with uniform diameter, moderate length, and strong adhesiveness with substrates then. Although the photocatalytic activity of RhB degradation on TNTAs prepared in glycol and DMSO is higher than those prepared in glycerol, their convenience of recycling and recovery shows the opposite. The optimality condition of anodic oxidation for TNTAs with good morphology and photocatalytic performance was present, which may have potential application in the synthesis of composite nanoarrays.

1. Introduction

Ever since carbon nanotubes were discovered by Iijima, nanomaterials with tube structure have attracted widespread attention from different research area due to its unique geometric structure and advanced physicochemical properties. As one of those nanotube materials, titanium dioxide nanotube arrays (TNTAs) have been applied to many fields, such as photocatalytic hydrogen generation, photovoltaic cells, degradation of organic contaminants, and gas sensor, because of their excellent specific surface area, high adsorption capacity, and less agglomeration [1–13]. Recently, multiple methods of preparation on TNTAs have been proposed: hydrothermal synthesis method, template method, and electrochemical anodic oxidation [14–16]. TNTAs prepared by the first two approaches are dispersed powders, which cannot adhere to the substrate firmly and are hard to be recycled. On the other hand, TNTAs prepared by electrochemical anodic oxidation adhered to the Ti substrate firmly with highly ordered array structures. Furthermore, the morphology of TNTAs can be controlled by adjusting experimental parameters.

Large-scale TNTAs composed of many single and well-arranged TiO$_2$ nanotubes were prepared by potentiostatic anodic oxidation of Ti foils with 0.5 wt% HF electrolyte, as Gong et al. reported at 2001 [17]. After that, the anodic oxidation method of preparing TNTAs has been studied by many researchers; it can be divided into three stages according to length of nanotube or electrolyte composition. The first TNTA generation is produced in strong acid electrolyte containing HF with pH lower than 3; its length is 500 nm below the general length [18]. The second TNTA generation, revolutionarily, uses organic instead of aqueous solvent as electrolyte [14, 16, 19–21]. Macak et al. prepared TNTAs by anodic oxidation and used glycol containing 0.5 wt% NH$_4$F as electrolyte firstly, whose length reaches 7 μm. However, the disadvantages are so fateful that they cannot be ignored: the length of tubes and specific surface area of TNTAs are distributed inhomogeneously. Besides, those tubes hardly adhere on substrates firmly [22–26]. Since then, scientists tried to design and achieve various geometrical
structures, such as stacking-type tube, chain-type tube, Bam-
boo-type tube, branched-type tube, and 3D complicated ... oxidation [27–31]. Nevertheless, to capitalize on TNTAs as
photocatalysts is still a major challenge; that is, efficiencies
of photoinduced processes are very low. This occurs because
photocatalytic reaction rates are not fast enough to compete
with the charge-recombination (electron-hole recombi-
nation). To address these problems, scientists focus on de-
corating TNTAs with noble metals or other nanomaterials
with synergistic effect [14, 32–37]. As the starting point, the
optimum condition of suitable TNTAs for decorating with
materials should be investigated.

In this paper, by employing glycol, DMSO, glycerol, and
(NH_4)_2SO_4 as main electrolytes, respectively, the effects of
electrolyte and applied electric potentials on morphology of
TNTAs were explored. Furthermore, photocatalytic degra-
dation of Rhodamine B (Rh B) on TNTAs prepared from
different electrolytes was compared under UV irradiation.
In addition, the optimum condition TNTAs fabrication for
nanoparticle deposition was discussed.

2. Experimental

2.1. Chemicals. Water used was ion-exchanged at first, dis-
tilled, and then ion-exchanged again by ultrapure water
system. The purified water exhibited the ionic resistivity of
18 MΩ cm in the water system. Other chemicals were of
analytical grade and were used as received.

2.2. Preparation of TNTAs. Well-ordered TNTAs were fabri-
cated by electrochemical anodization in a two-electrode cell
which consisted of Ti foils as working electrode and a Pt foil
as counter electrode. Prior to the anodization, Ti foils (2.0
× 5.0 cm²) were ultrasonically cleaned in acetone, methanol,
and ethanol for 10 min followed, respectively, by deionized
water rinse.

All electrolytes were prepared as a certain propor-
tion; magnetic stirring until complete dissolve is
achieved. In this study, four typical electrolytes were
employed: 0.1 M NH_4F and 0.5 M (NH_4)_2SO_4 mixture solu-
tion; mixture solution composed of 98% dimethyl sulfoxide
(DMSO) and 2% HF in volume; NH_4F with concentra-
tion of 0.075 M dissolved in mixture solvent which is composed of
H_2O (3%, v/v) and glycol (97%, v/v); NH_4F with concentra-
tion of 0.27 M dissolve in mixture solvent composed of water
and glycerol with ratio of 1:1 by volume.

The equipment of anodic oxidation is illuminated as
Figure 1; the anode and cathode electrodes were pretreated
titanium foil and Pt, respectively. The distance between two
electrodes was 2 cm. Applied voltage started from 0 V to a
certain voltage with rate of 250 mV/s and then maintained a
certain time.

The Ti foil was drawn out from electrolyte after the anodic
oxidation process and then washed by deionized water in
order to remove adsorbed electrolyte on the surface, followed
by six times of ultrasonic cleaning every 10 seconds. Then the
resulting TNTAs were dried under room temperature before
next process.

2.3. Characterization. XRD patterns were acquired on a
Bruker Axs D2 PHASER diffractometer with a Cu Kα X-
ray source. Scan range located from 21° to 80°. The mor-
phology of the obtained samples was characterized by a field
emission scanning electron microscope (FESEM, Hitachi S-
4800). The ultraviolet-visible (UV-Vis) spectra analysis was
also performed on a Shimadzu UV-3600 spectrophotometer
equipped with an integrating sphere using BaSO_4 as the
reference.

2.4. Photocatalytic Activity. As shown in Figure 2, the pho-
tocatalytic activities were evaluated based upon the removal
of Rh B solution with an initial concentration of 5 mg L⁻¹
in a glass reactor with a water jacket to control the reaction
temperature. For comparison, the photocatalytic activities of
TNTAs obtained from different electrolytes were also studied.
A 300 W xenon lamp with a 365 nm filter was employed as the
simulated ultraviolet source. The distance between the xenon

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**Figure 1:** Schematic illustration of an electrochemical anodic oxida-
tion cell.

**Figure 2:** Schematic illustration of the photocatalytic reactor.

The dried TNTAs were put into muffle furnace which was
firstly heated up to 200°C with 3°C/min and kept for 30 min,
then was heated up to 450°C with 2°C/min and kept for 3 h,
and was naturally cooled to room temperature at last.
lamp and the TNTAs film was 13 cm. Prior to photocatalytic
degradation, the samples were immersed in 20 mL Rh B
aqueous solution with magnetic stirring in the dark for 1 h
to establish an adsorption-desorption equilibrium at constant
room temperature. After UV irradiation started, the solution
periodically taken from the reactor was analyzed with a UV-
Vis spectrophotometer. The analytical wavelength selected for
optical absorbance measurement was 560 nm.

Based on Lambert-Beer law, there is a proportional relation-
ship between concentration of absorbing material and
absorbance, as shown in the following equation:

\[ A = \log \left( \frac{1}{T} \right) = Kbc \]

(1)
in which \( A \) indicates absorbance; \( T \) indicates transmittance;
\( K \) indicates characteristic constant; \( b \) indicates thickness of
absorption layer with unit of cm; \( c \) indicates concentration of
absorbance with unit of mg L\(^{-1}\). Therefore, change of
absorbance reflects change of concentration of Rh B solution.
Normalized concentration ratio of Rh B solution is close to
normalized maximum absorbance ratio (\( A/A_0 \)); as a result,
\( C/C_0 \) can be replaced by value of \( A/A_0 \).

3. Results and Discussion

3.1. Morphology of TNTAs. We present the SEM results of
TNTAs obtained from four different electrolytes. Figures
3(a) and 3(b) show TNTAs prepared by anodic oxidation
employing NH\(_4\)F and (NH\(_4\))\(_2\)SO\(_4\) mixed aqueous solution
as electrolyte under constant applied voltage of 20 V for 2 h.
Those nanotubes show irregular arrangement with nonuni-
form diameter of about 80 nm.

Figures 3(c) and 3(d) show top and cross-sectional views
of TNTAs prepared by anodic oxidation with DMSO and HF
mixed solution as electrolyte under constant applied voltage
of 35 V for 2 h. Although the length of tubes reached 4 \( \mu \)m,
it is clear that the tube entrance collapses seriously, coupled
with broken surface which may be caused by relatively high
voltage.

Figures 3(e)–3(h) show top, bottom, cross-sectional, and
termination views of TNTAs prepared by anodic oxidation
employing NH\(_4\)F and glycerol mixed aqueous solution as
electrolyte under constant applied voltage of 20 V for 2 h.
Nanotubes obtained under this condition are more compli-
cated. Their surface shows weed-like features and bottom
shows typical hexagon, while the walls are so smooth. The
cross-link between those walls obviously decreased when
compared to other TNTAs. Those nanotubes easily fall off
from Ti substrate although the length of them reaches about
33 \( \mu \)m. Nanotube entrance collapse and broken surface may
be attributed to the inhomogeneity of the tube structure. Fast
growth rate along the tube leads to thinness of tube walls. As
a result, those tubes cannot sustain the weight and thermal
stress of themselves during the drying process.

Figures 3(i) and 3(j) show top and cross-sectional views
of TNTAs prepared by anodic oxidation by employing NH\(_4\)F
and glycerol mixed aqueous solution as electrolyte under
applied constant voltage of 20 V for 2 h. The diameter of
these tubes is uniform with 100 nm for inner and 117 nm for
outer. The length is about 1 \( \mu \)m. Ripples on the tube walls
can be seen, which indicates that the participation of water
into electrolyte is necessary for oxidation corrosion of Ti foils.
The corrosion rate of Ti foils and growth rate of TiO\(_2\) are
affected by the content of water. The formation of nanotubes
with corrugated tube wall needs relative high content of water.
These tubes adhere on the substrate firmly, which performs
good stability of geometric structure and conveniences of
recycling.

Then it can be concluded that NH\(_4\)F and glycerol mixed
aqueous solution is the preferential electrolyte among those
four kinds of electrolytes in this study. Therefore, based on
this electrolyte system, other operating parameters including
applied voltage and duration of anodic oxidation have been
studied.

Figure 4 shows top view of TNTAs prepared at condition
of (a) (20 V, 2 h), (b) (20 V, 6 h), (c) (25 V, 2 h), (d) (25 V,
6 h), (e) (30 V, 2 h), and (f) (30 V, 6 h), respectively. With
the increase of applied voltage from 20 V, the diameter of
nanotubes remains unaffected; however, the tube entrance
becomes uniform and arrangement of nanotubes decreases
seriously. Also the shape of tubes and thinness of tube walls
tend to be inhomogeneous with increase of voltage.

As is seen in Figure 4, with the duration of anodic oxida-
tion from 2 h to 6 h, tubular structure is severely damaged.
The possible explanation might be that two dynamic pro-
cesses contributed to the growth of tube on radial direction:
anodic oxidation of Ti substrate to form fresh TNTAs and
dissolution of tubes on the top part. There is an optimum
duration of oxidation which is defined to be the equilibrium
of those two dynamic processes. Longer time may unbalance
the equilibrium, which forces the growth of tubes to be
affected by diffusion, gravity, viscosity, and so forth.

3.2. Growth Mechanism of TNTAs. The key process of electro-
chemical oxidation can be explained as follows: firstly, oxides
were formed on metal surface under the influence of interac-
tion of oxygen ions or hydroxide ions. After that, those anions
cross through oxidation layer and migrate to metal/oxide
interface to react with metal. Secondly, under the effects of
external electric field, tetravalent titanium ion (Ti\(^{4+}\)) migrates
from metal/oxide surface to oxide/electrolyte surface. Elec-
tric field assisted dissolve will be the third step: under effect of
external electric field, Ti–O bond undergoes polarization and
is weakened, accelerating the dissolution of the metal cations.
After Ti\(^{4+}\) dissolved into electrolyte, free oxygen anions
migrate to metal/oxide intersurface and then interact with
metal as mentioned at the first step. Lastly, chemical dissolve
of metal or oxide occurs in acidic electrolyte. Chemical
dissolve of TiO\(_2\) in fluoride ion electrolyte plays a crucial role
on formation process of nanotubes. Schematic diagram of
ions migration was shown in Figure 5.

At the beginning of anodic oxidation, the initial oxidation
layer was formed by interaction of Ti\(^{4+}\) ions on surface and
O\(^{2-}\) ions in electrolyte, which can also be seen as distributed
homogenously on the surface. The anodic oxidation of metal
to form hydrogen ions and electrons is shown in

\[ Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \]  \hspace{1cm} (2)
Figure 3: FE-SEM images of TNTAs fabricated by different solutions.
Figure 4: FE-SEM images of TNTAs fabricated by glycerol based solutions under different voltage and anodic oxidation time.

Fluorine ions may attack water molecule and oxidation layer; in other words, ions migrating on anode layer under external electric field could react with Ti$^{4+}$ anions:

\[
\begin{align*}
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ & \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \\
\text{Ti} (\text{OH})_4 + 6\text{F}^- & \rightarrow [\text{TiF}_6]^{2-} + 4\text{OH}^- \\
\text{Ti}^{4+} + 6\text{F}^- & \rightarrow [\text{TiF}_6]^{2-}
\end{align*}
\]

(5)  
(6)  
(7)

As shown in Figure 6(a), a thin layer formed on the titanium surface with start of anodic oxidation. Since partial dissolve of oxide may make the barrier layer at the bottom of concave thin, as can be seen in Figure 6(b), the electric field intensity at those remaining barrier layers increased resulting in further growth of pore. As shown in Figure 6(c), pores of tube appear relatively narrow since the field associated dissolve has no influence on formation of pores. However, the electric field distribution at bottom surface of the pore may broaden diameter of tubes as well as deepen cracks, which causes pores of nanotubes formed like a scallop shape. Since the bond energy of Ti–O is rather high, for TiO$_2$, it can be predicted reasonably that pores only can be formed on those thin walls, which can be contributed by relatively low ionic mobility and rather high chemical solubility of oxide in electrolyte. The electric field intensity at protruding metal area will increase with the growth of pores, which may enhance

Hydrogen generated at cathode is as follows:

\[
8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2
\]

(3)

The total oxidation process can be given by

\[
\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2
\]

(4)
the field associated growth of oxide and dissolution of oxide. Meanwhile, uniformly distributed pores and voids between pores formed in Figure 6(d). Subsequently, voids and pores grow together under equilibrium condition. The length will increase until the balance is achieved between electrochemical corrosion rate and chemical dissolve rate on the top surface of nanotubes. Thereafter, the length of nanotubes is finally achieved by given anodic oxidation time, concentration of electrolyte, and anodic oxidation voltage.

3.3. XRD Characterization. As seen in Figure 7, XRD characterization of TNTAs obtained in four different electrolytes has been presented. Five diffraction peaks at 25.2°, 37.8°, 48.1°, 53.9°, and 55.1° indicate crystal phase of anatase at (101), (004), (200), (105), and (211), respectively, according to JCPDS number 21-1272. It is obvious that anatase TNTAs can be obtained by annealing at 450°C. Peak intensities of crystal plane (101) for TNTAs prepared at glycerol aqueous electrolyte and NH₄F and (NH₄)₂SO₄ mixed aqueous electrolyte appear lower than those prepared at glycol electrolyte and DMSO electrolyte. This can be explained by the fact that ratio of TiO₂ is deeply influenced by length of nanotube, which is in accordance with SEM results. Besides, XRD characterization of Ti substrate and TNTAs fabricated in NH₄F and glycerol mixed aqueous solution were presented, respectively, before and after TNTAs are annealed (Figure 8). It can be seen that after anodization process TNTAs are amorphous and upon annealing they become anatase.

Figure 6: Schematic diagram of nanotube evolution at constant anodization voltage: (a) oxide layer formation, (b) pit formation on the oxide layer, (c) growth of the pit into scallop shaped pores, (d) the metallic region between the pores undergoing oxidation and field assisted dissolution, and (e) fully developed nanotubes with a corresponding top view.
3.4. UV-Vis Diffuse Reflection Spectroscopy. The optical properties of TNTAs prepared at different electrolytes were studied by UV-Vis diffuse reflection spectroscopy, as shown in Figure 9. Light response range of all TNTAs reported here is localized in ultraviolet range. However, TNTAs prepared by glycerol electrolyte, in spite of its disadvantage at length of nanotube, show highest intensity of light adsorption at tail. This may benefit from the uniformity of nanotube arrangement and less collapse on nanotube entrance. For those TNTAs obtained by other electrolytes, although length of nanotube may have its edge, collapse on nanotube entrance or structures with weed-like features and disordered orientation result in the fact that the obstacle of incident light could not pass into passageway of nanotubes, eventually.

3.5. Photocatalytic Activity on Degradation of Rh B. TNTAs are one of the most active materials for degradation of contaminants especially for organic pollutants. This may be contributed by the proximity between conduction band edge of TNTAs and redox potentials of the surroundings such as water. Rh B, as one of the most water pollutants, is stable and carcinogenic [38]. The photocatalytic activities of TNTAs fabricated in four different electrolytes were investigated by degrading Rh B.

The variation of \( C/C_0 \) with illumination time is shown in Figure 10(a), in which \( C_0 \) indicates the initial concentration after the adsorption equilibrium is established, while \( C \) indicates concentration of reaction solution extracted out every 30 minutes. It can be seen from blank curve of Figure 10(a) that the Rh B molecule is extremely stable under UV irradiation without the presence of catalysts. Also, after irradiation of 210 minutes by UV, Rh B shows no evidence of decomposition, which indicates impossibility of self-degradation. The degradation efficiencies of TNTAs prepared in electrolytes of glycol, DMSO, glycerol, and (NH\(_4\))\(_2\)SO\(_4\) are 75.14%, 49.82%, 34.26%, and 25.82%, respectively. The kinetics equation of catalytic reaction on these TNTAs photocatalysts has been studied by using first-order kinetics equation \( \ln(C/C_0) = -kt \), in which \( k \) indicates the first kinetics equation constant. As shown in Figure 10(b), the catalytic rate constant in electrolyte of glycol, DMSO, glycerol, and (NH\(_4\))\(_2\)SO\(_4\) is \( 6.45 \times 10^{-3} \), \( 3.37 \times 10^{-3} \), \( 2.03 \times 10^{-3} \), and \( 1.42 \times 10^{-3} \) min\(^{-1} \), respectively. The order of catalytic rate constant is in accordance with the order of the length of nanotubes. For photocatalytic degradation on TiO\(_2\) nanotube arrays, it is common sense that the amount of TiO\(_2\) crystals will increase with increase of length of nanotube, which would exhibit better photocatalytic activity.

In order to further more effective composites by loading nanoparticles, however, those nanotubes prepared in electrolyte of glycol, DMSO shows their disadvantage of poor...
recycling efficiency. Firstly, the entrance of these tubes tends to collapse and snarl, which brings a great difficulty to decorate other nanoparticles on more widespread surface of TNTAs. Secondly, the overlong nanotubes increased the burden of Ti substrates, which makes nanotubes vulnerable and easier to fall off from substrates, when compared with other nanotubes having moderate length. And this will go against recycling and recovery of effective part of photocatalyst. To make composites by depositing nanoparticles on TNTAs, TNTAs prepared in glycerol under voltage of 20 V for 2 h are the best loading substrate, contributing by their uniform diameter, moderate length, and close adhesiveness with Ti foils.

4. Conclusions

The formation process of TNTAs strongly depends on the electrolytes. TNTAs formed in the electrolytes of glycol and DMSO grow along radial direction with flimsy tube wall and weak adhesion on Ti substrate. These TNTAs are not appropriate to assemble composite photocatalyst with other nanomaterials, although they show, respectively, higher catalytic activities. Those made in glycerol, however, easily achieve balance between growth rate and corrosion rate and form orderly arranged array of nanotubes with homogenous diameter, moderate length, and strong adhesiveness with substrates.

In addition, applied voltage and anodic oxidation duration crucially affect nanotube formation. Generally, longer time and higher voltage of oxidation will enhance length of nanotubes. However, the oxidation rate of Ti substrate and dissolve rate of nanotubes will be well balanced at condition of 20 V for 2 h. Consequently, TNTAs prepared in this condition will be the most appropriate loading substrates to further assemble functional composite nanomaterials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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