

Article

Preparation of Gd-Doped TiO₂ Nanotube Arrays by Anodization Method and Its Photocatalytic Activity for Methyl Orange Degradation

Rui Li ¹, Jin Yang ¹, Shiyin Xu ¹, Yushun Zhou ¹, Xuan Wang ¹, Hailong Peng ^{1,2,*}  and Jun Du ^{1,2,*}

¹ School of Resources, Environmental, and Chemical Engineering, Nanchang University, No.999 Xuefu Avenue, Nanchang 330031, China; lr3132@sina.com (R.L.); yangjin199501@sina.com (J.Y.); xsy870260363@163.com (S.X.); yushun985@163.com (Y.Z.); 63125wx@sina.com (X.W.)

² Key Lab of Poyang Lake Ecology and Bio-resource Utilization (Ministry of Education), Nanchang University, No.999 Xuefu Avenue, Nanchang 330031, China

* Correspondence: penghailong@ncu.edu.cn (H.P.); dujun@ncu.edu.cn (J.D.); Tel.: +86-791-83969985 (J.D. & H.P.)

Received: 13 February 2020; Accepted: 3 March 2020; Published: 5 March 2020



Abstract: Gd-doped TiO₂ nanotube arrays with 3D ordered and high specific surface (176 m²/g) area are successfully prepared on a Ti foil surface via an anodizing method. The characterizations of Gd-doped TiO₂ nanotube arrays are carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectrometer (EDX), optical contact angle measurer, and ultraviolet (UV) fluorescence spectrophotometer, respectively. The results reveal that the Gd-doped TiO₂ nanotube arrays form on the Ti foil surface with a length of about 50.5 μm and 100 nm in diameter, and the growth direction grown along the (101) direction of anatase crystal. Under the optimized reaction conditions (60 V, 10 h, 0.01mol/L Gd³⁺), the crystal phase of Gd-doped TiO₂ show an excellent nanotube structure, possess a beneficial photocatalytic performance for methyl orange (MO) (Degradation rate was 95.8%) and an excellent hydrophilic property (The optical contact angle was 4.9°). After doping with Gd, the hydrophilic and photocatalytic properties of the TiO₂ nanotubes are further improved.

Keywords: Gd-doped TiO₂; nanotube arrays; anodization; photocatalysis; hydrophilicity

1. Introduction

Recently, as an emerging green advanced oxidation technology [1], the photocatalytic oxidation technique is widely used in the treatment of organic wastewater due to its mild reaction condition, simple operation, high efficiency, low energy consumption, and environmentally friendly characteristics [2,3]. Among these photocatalytic materials, TiO₂ is an inorganic photosensitive semiconductor material which has the advantages of high photocatalytic activity, good stability, non-toxicity, and low cost. Therefore, TiO₂ has been applied to prepare many semiconductor photocatalysts and attracts widespread attention [4–8]. Nano-TiO₂ has been prepared into a layered structure, like nanoparticles [9], nanobelts [10], nanowires [11], nanorods [12], nanotubes [13], and nano-flowers [14]. Compared with nanospheres or two-dimensional nanofilms, one-dimensional TiO₂ nanotubes have a larger specific surface area [15] and a stronger adsorption capacity [16]. TiO₂ nanotube arrays have highly ordered and size-controllable properties [17]. The large surface energy enables them to enhance the interface separation effect of electron-hole pairs and the directional transport efficiency of carriers [18–20].

Nowadays, the preparation methods of nano-TiO₂ materials mainly include a template synthesis method [21], a hydrothermal synthesis method [22], and an anodizing method [23–27]. Anodizing refers

to the process of forming an oxide film on the surface of the anode material as a consequence of electric current reaction in the electrolyte solution. TiO₂ nanotube arrays prepared by this anodizing method have a neat arrangement, a large specific surface area, and equivalent aperture. Moreover, a dense TiO₂ barrier layer is formed between the nanotube arrays and the metal Ti substrate, the prepared photocatalyst has strong adsorption capacity and has the electrical characteristics of non-linear diodes [28]. Gong [24] prepared TiO₂ nanotube arrays with a uniform surface arrangement and high order by anodic oxidation with a hydrofluoric acid solution as the electrolyte. Then, after successive researches on anodic oxidation by Ruan [29] and Macak [30], to enhance the comprehensive properties of the TiO₂ nanotube arrays, the secondary anodic oxidation method has been used to produce a more orderly TiO₂ nanotube array [31,32].

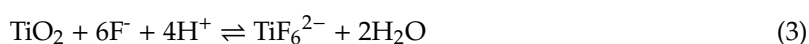
Unfortunately, as a wide band gap semiconductor material (3.20 eV for anatase and 3.03 eV for rutile [33]), the defects of TiO₂ are very obvious. A high recombination rate of photogenerated electron-hole pairs [34], a lower conductivity [35] and photoelectric conversion efficiency [36] have become the main obstacles hindering the development and application of TiO₂. Therefore, study on the modification of TiO₂ nanomaterials has become a popular direction in the field of photocatalyst research, and the most commonly used method is metal ion doping. Previous results [37,38] show that the surface properties and photocatalytic performances of TiO₂ nanomaterials are greatly improved. Additionally, there also is doping-TiO₂ research with the use of Ag [39], Pd [40], Pt [41] and Au [42]. As a rare earth element, gadolinium (Gd) has a special 4f electronic structure, which can replace part of Ti in TiO₂ allowing TiO₂ to expand its spectral response range to sunlight without reducing the photoactivity under ultraviolet light and improve its operating factor of visible light. Moreover, Gd-doped nanomaterials have unique optical and magnetic properties which are easy to recycle and do not cause secondary pollution. Presently, Gd-doped TiO₂ nanotubes prepared using an anodization method for photocatalytic degradation of organic wastewater has never been published, to the best of the authors' knowledge.

During this study, the highly ordered and neatly arranged Gd-doped TiO₂ nanotube arrays are successfully prepared on a Ti foil substrate by an anodizing method. The originality of this paper has been investigated as follows: (1) TiO₂ nanotube arrays are synthesized directly on the Ti foil surface using an anodization method with a beneficial photocatalytic performance and hydrophilic property; (2) The influence of different reaction times and voltages on the growth of TiO₂ nanotube arrays are illustrated; (3) The Gd-doped TiO₂ nanotube arrays are prepared, and the photocatalytic performance and hydrophilic property are further carried out. (4) The TiO₂ nanotube arrays are tightly grown on the surface of the Ti foil, and the Gd has strong magnetic properties, making the catalyst easy to recycle in the application is and environmentally friendly.

2. Results and Discussion

2.1. Formation and Photocatalytic Mechanism of Gd-Doped TiO₂ Nanotube Arrays

An anodization method was applied to prepare Gd-doped TiO₂ nanotube arrays. The growth of nanotubes was completed under the combination of anodic oxidation and chemical dissolution, and the chemical reaction occurring during the process is conveyed by the following Equations:



The formation mechanism of TiO₂ nanotubes is illustrated in Figure 1. The anodic oxidation current-time (I-t) curve can directly explain the growth processes of TiO₂ nanotubes. Figure 1a is the I-t curve of an anodized Ti foil with 10 V in 0.5 wt % HF aqueous solution at room temperature (25 °C). According to the above-mentioned equation and I-t curve, the generation of nanotubes can be divided

into three stages. During the initial stage of oxidation (I), the metal Ti foil is rapidly oxidized and dissolved in an acid electrolyte containing F^- to generate a large amount of Ti^{4+} , which corresponds to Equation (1). Regarding the second stage (II), Ti^{4+} reacts with oxonium ions in the electrolyte to form a dense TiO_2 oxide film with the current rapidly decreasing, which corresponds to Equation (2). Meanwhile, as shown in Figure 1b, the TiO_2 oxide film interacts with F^- in the electrolyte under an electric field, and the TiO_2 barrier layer is partially etched to generate micropores, which causes the anode current to rise slowly. Concerning the third stage (III), TiO_2 nanotubes grow steadily and the anode current is provided by ion migration on both sides of the TiO_2 barrier layer, thus forming a relatively stable current curve.

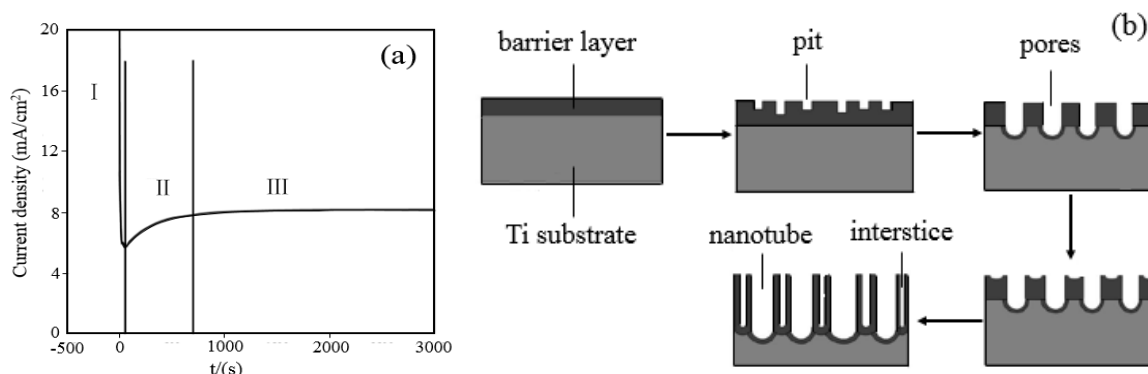
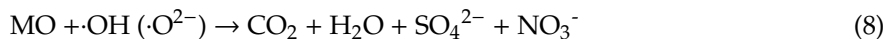


Figure 1. Schematic diagram of (a) current density-time curve of anodization [43], (b) TiO_2 nanotube formation mechanism [44].

The photocatalytic mechanism of TiO_2 is demonstrated in the following Equations. When ultraviolet light irradiates the surface of TiO_2 , electrons in the valence band are stimulated to the conduction band, thereby generating highly active carriers (e^-) and holes (h^+). Dissolved oxygen (O_2) on the catalyst surface captures electrons to form a superoxide anion radical ($O_2^{\cdot-}$), and the holes oxidize H_2O and OH^- into a highly oxidative hydroxyl radical ($\cdot OH$), which can degrade organic matter. The degradation mechanism of MO by TiO_2 in this experiment is how the holes and H_2O react to generate a hydroxyl radical and superoxide anion radical, then the azo bond and benzene ring of MO are broken by oxidation and, finally, MO is degraded into CO_2 , H_2O , SO_4^{2-} , NO_3^- .



2.2. Characterizations of TiO_2 and Gd-Doped TiO_2 Nanotube Arrays

2.2.1. XRD

XRD patterns of TiO_2 samples prepared at different conditions are shown in Figure 2. According to Figure 2a, the 2θ angles of pure titanium at 38.43° , 40.35° , 53.10° and 62.96° , corresponding to the (002), (101), (102), and (110) crystal planes of titanium (standard card PDF NO. 44–1294), respectively. However, the 2θ angles of the annealed TiO_2 samples at 25.49° , 37.11° , 37.95° , 48.21° , 54.09° , 55.16° and 69.02° appear, which correspond to the (101), (103), (004), (200), (105), (211), and (116) crystal planes, respectively. There is a maximum in the peak intensity when the 2θ angle was 25.49° (XRD standard card PDF NO. 78–2486). These results prove that the reaction produces anatase phase TiO_2 .

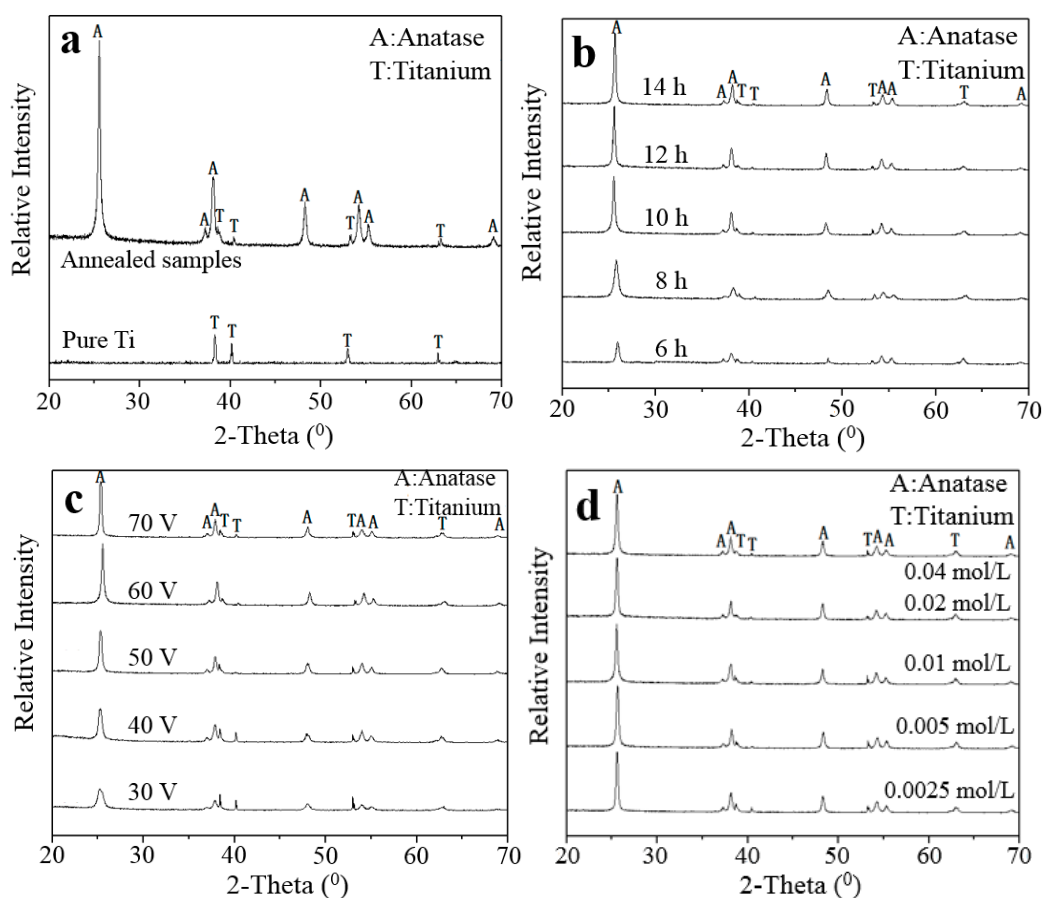


Figure 2. XRD patterns of (a) Ti, annealed samples, (b) and (c) TiO₂ prepared at different times (6–14 h) and voltages (30–70 V), (d) different Gd concentrations (0.0025–0.04 mol/L).

Figure 2 also shows the effect of different reaction times and voltages on the crystal structure of TiO₂ nanotube arrays. Under the environment of no Gd ions existing, when the reaction time is shorter than 8 h, the new diffraction peaks with weak intensity at 25.49°, 37.11°, 37.95°, 48.21°, 54.09°, 55.16° and 69.02° appears, which corresponds to the (101), (103), (004), (200), (105), (211) and (116) crystal planes of the anatase phase (Figure 2b). Accompanying the increase in the reaction time, the diffraction peak intensity of the anatase TiO₂ strengthens. It is believed that the anodic oxidation rate of the titanium substrate and the chemical dissolution rate of the oxide layer reach a dynamic equilibrium at a reaction time of 10 h. Shown in Figure 2c, the peaks of 37.11°, 37.95°, 48.21°, 54.09°, 55.16°, and 69.02° correspond to the (101), (103), (004), (200), (105), (211), and (116) crystal planes of anatase TiO₂, respectively. The diffraction peak of the titanium substrate weakens as the reaction voltage increases, and the TiO₂ diffraction peak of the anatase phase is enhanced. Additionally, we can observe a maximum in the XRD peak intensity at 60 V. When the voltage continuously increases, the generated TiO₂ crystal is rapidly dissolved, so the intensity of the corresponding anatase phase TiO₂ diffraction peak is slightly reduced.

Figure 2d reveals the XRD spectra of TiO₂ nanotube samples with different Gd ion concentrations. The diffraction peaks appear at 2θ angles of 25.49°, 37.11°, 37.95°, 48.21°, 54.09°, 55.16°, and 69.02°, corresponding to the anatase phase of TiO₂. The presence of XRD diffraction peaks in the crystal structure of the doped phase is not detected in the samples, which proves that the doped Gd³⁺ has good dispersity in the crystal lattice of the samples. It can be seen from Figure 2c that the curves and diffraction peak intensities of samples prepared with different Gd³⁺ concentrations are generally consistent and each diffraction peak corresponds to the standard anatase TiO₂ spectrum

chart (standard card PDF NO.78–2486), indicating that doping Gd^{3+} with different concentrations has no significant effect on the structure of the sample.

2.2.2. SEM

Figure 3 shows the SEM images of the samples at different reaction stages. Figure 3a shows the surface morphology of the pure titanium sheet. It can be seen that the surface of the titanium sheet is uneven, but there is no tubular structure. Figure 3b,c are SEM images of the samples after the reaction. It is known that dense TiO_2 nanotube arrays have been formed, and the diameter of a single nanotube is about 100 nm. Figure 3d shows a cross-sectional view of the samples where the neatly arranged tubular structure can be clearly seen.

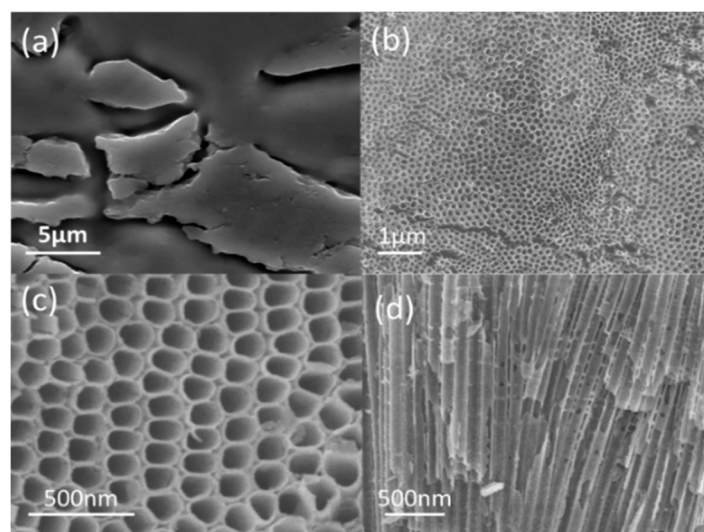


Figure 3. SEM images of (a) Ti, (b) (c) TiO_2 nanotube arrays under different magnifications, (d) cross-sectional view of TiO_2 nanotube arrays

Figure 4 contains SEM images of samples at different reaction times. It is found that different reaction times have little effect on the surface morphology of TiO_2 nanotube arrays—nanotubes with 100 nm diameters and neatly arranged surfaces were formed—but different reaction times have a significant effect on the nanotube length of arrays. Shown in Figure 4a, when the reaction time is 6 h, the length of the generated nanotubes is approximately 18.6 μm. When the time increased to 10 h, the tubes grew obviously and reached 50.5 μm. However, when the reaction time continues to increase, the change of tube length is no longer palpable, as seen in Figure 4d,e. This is because the growth of TiO_2 nanotubes is accompanied by the increase of H^+ concentration in the electrolyte; however, the chemical corrosion rate of TiO_2 nanotubes is carried out at a faster rate. After comprehensive analysis from the perspective of characterization and economics, the 10 h anodic oxidation reaction time is the best time for TiO_2 nanotube arrays.

Meanwhile, the SEM images of the samples prepared at different reaction voltages are shown in Figure 5. Different reaction voltages only have a significant effect on the length of the nanotubes. The length of the nanotubes reaches a peak value of 50.5 μm at the reaction voltage of 60 V. The increase of the electric field strength improves the growth rate of the nanotubes, but the excessive voltage causes the H^+ concentration in the electrolyte to increase sharply and corrode the nanotubes.

It can be seen from Figure 6 that the surfaces of the TiO_2 nanotube arrays generate at different Gd^{3+} concentrations are clear and neat, and the nanotubes are arranged closely and orderly together. The generated nanotubes are approximately 50.5 μm in length and 100 nm in diameter. Gd_2O_3 is a kind of transparent semiconductor material, thus the existence of doping phase particles cannot be seen intuitively in the SEM diagram. The experimental results indicate that the doped treatment will not

destroy the highly ordered tubular structure of the TiO_2 nanotube arrays, and the introduction of the rare earth element Gd will not affect the surface morphology and microstructure of the nanotube arrays.

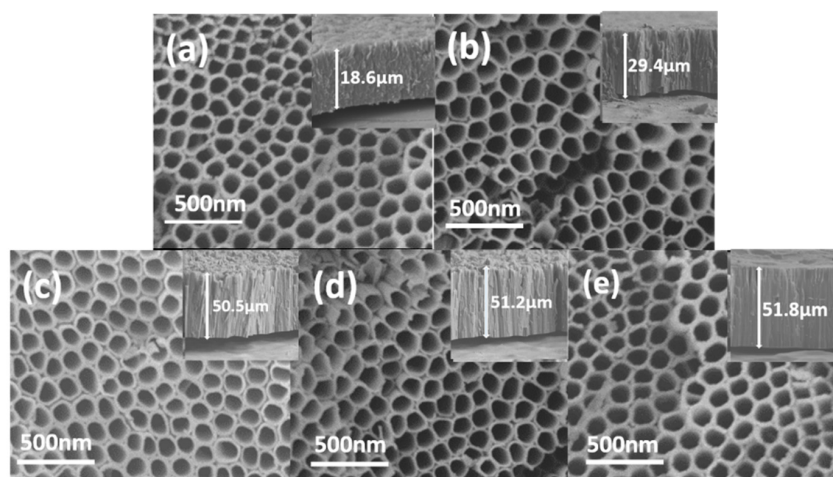


Figure 4. SEM images of TiO_2 nanotube arrays at different times. (a) 6 h, (b) 8 h, (c) 10 h, (d) 12 h, and (e) 14 h.

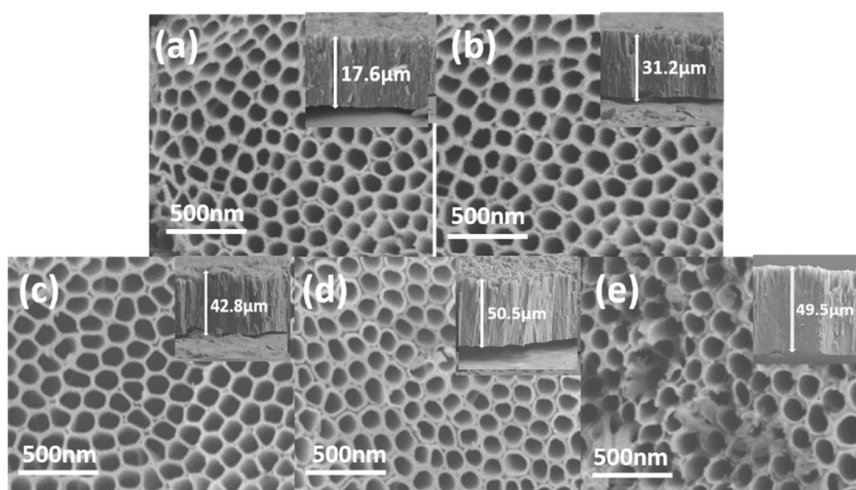


Figure 5. SEM images of TiO_2 nanotube arrays at different voltages. (a) 30 V, (b) 40 V, (c) 50 V, (d) 60 V, (e) 70 V.

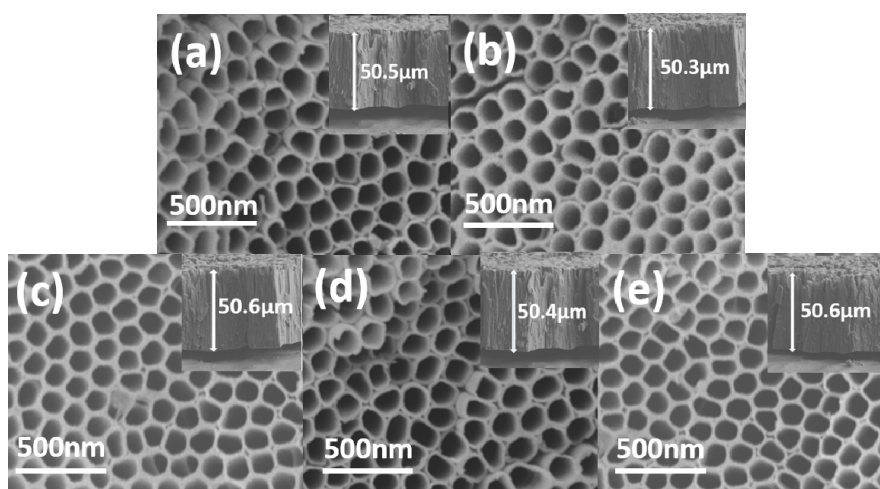


Figure 6. SEM images of samples with different gadolinium concentrations. (a) 0.0025 mol/L, (b) 0.005 mol/L, (c) 0.01 mol/L, (d) 0.02 mol/L, and (e) 0.04 mol/L.

2.2.3. TEM

EDX spectra (Figure 7a) shows that the TiO_2 nanotubes have four elements of C, Cu, Ti and O, in which C and Cu come from C film and Cu net on copper grid, respectively. Ti and O elements form TiO_2 nanotubes. The TEM image of a single TiO_2 nanotube (Figure 7b) shows a clearly tubular structure with the diameter of this nanotube about 100 nm, which is consistent with the SEM results. Figure 7c reveals the electron diffraction pattern of the TiO_2 nanotubes and a clear diffraction ring d1 can be seen. The crystal plane spacing is 0.35 nm, corresponding to the (101) crystal plane, indicating that the TiO_2 nanotube has high crystallinity. It also can be seen that three dim diffraction rings, d2, d3 and d4, are 0.24 nm, 0.19 nm and 0.17 nm, which correspond to the (004), (200), (105) crystal planes of anatase TiO_2 , respectively. Clear and ordered lattice stripes are observed in the HRTEM image of a single TiO_2 nanotube (Figure 7d), and the nanotubes grow along the (101) crystal plane, which is consistent with the results of the electron diffraction patterns.

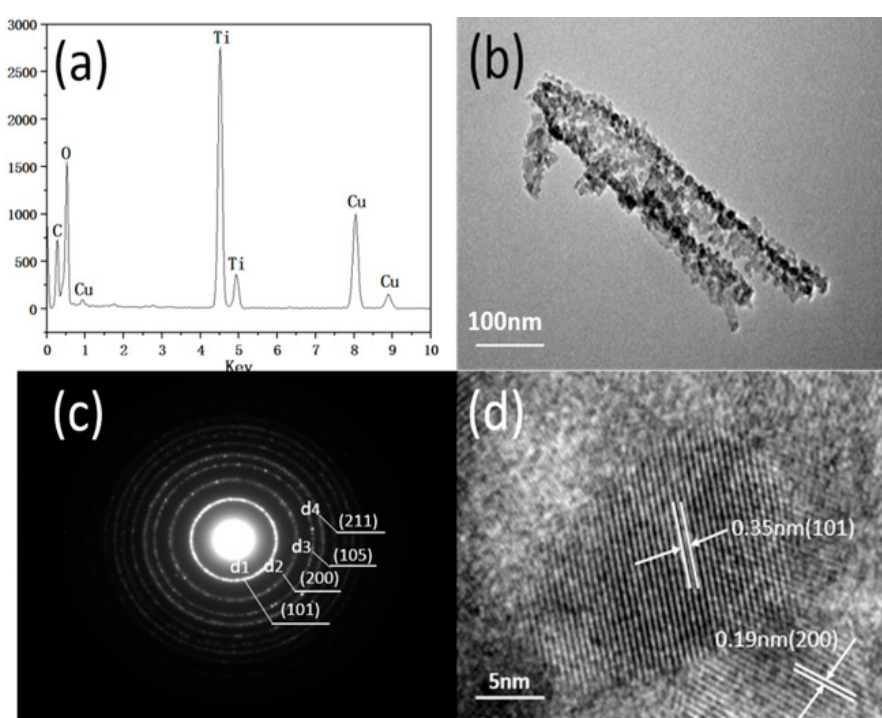


Figure 7. Characterization of TiO_2 nanotubes. (a) EDX spectra of TiO_2 samples. (b) TEM image of TiO_2 samples. (c) Electron diffraction pattern of TiO_2 samples. (d) HRTEM image of TiO_2 samples

2.2.4. XPS

Figure 8 is the XPS spectrum of the TiO_2 and Gd-doped TiO_2 nanotube arrays. It can be seen that the undoped sample contain three elements of C, Ti, and O, whereas Gd-doped TiO_2 samples contain not only Ti, C, and O elements but also certain amounts of the Gd element, indicating that the Gd is successfully doped into the TiO_2 samples. Shown in Figure 8b, the characteristic peak of $\text{Ti}2p_{3/2}$ in the undoped samples appears at 458.7 eV, while Gd-doped TiO_2 appears at 458.4 eV, and the characteristic peak of $\text{Ti}2p_{1/2}$ in the undoped sample appears at 464.5 eV while Gd-doped TiO_2 is 464.2 eV. The distance between the two characteristic peaks of $\text{Ti}2p_{3/2}$ is about 5.8 eV and the peak content of $\text{Ti}2p_{3/2}$ is much higher than $\text{Ti}2p_{1/2}$, indicating that Ti in Gd-doped TiO_2 mainly exists in the form of Ti^{4+} [45]. The Ti peak of the Gd-doped sample shifts toward the low binding energy compared to the undoped sample. The reason might be that Gd^{3+} replaces part of the Ti^{4+} doped into the oxide lattice and combines with oxygen, causing an imbalance of the electric charge. The XPS spectrum of O1s is shown in Figure 8c. It can be seen that the characteristic peaks of O1s are wide and asymmetric, indicating that the oxygen is in more than one chemical state. The characteristic peaks of

O1s in Gd-doped samples appear at 529.7 eV (Ti–O) and 531.4 eV (O–H). Figure 8d is the XPS spectrum of Gd 4d. The characteristic peaks of Gd-doped samples appear at 142.1 eV and 148.1 eV, indicating that the Gd element will exist as Gd–O in TiO_2 , which would increase the carrier lifetime and improve the ability to transfer photogenerated electrons.

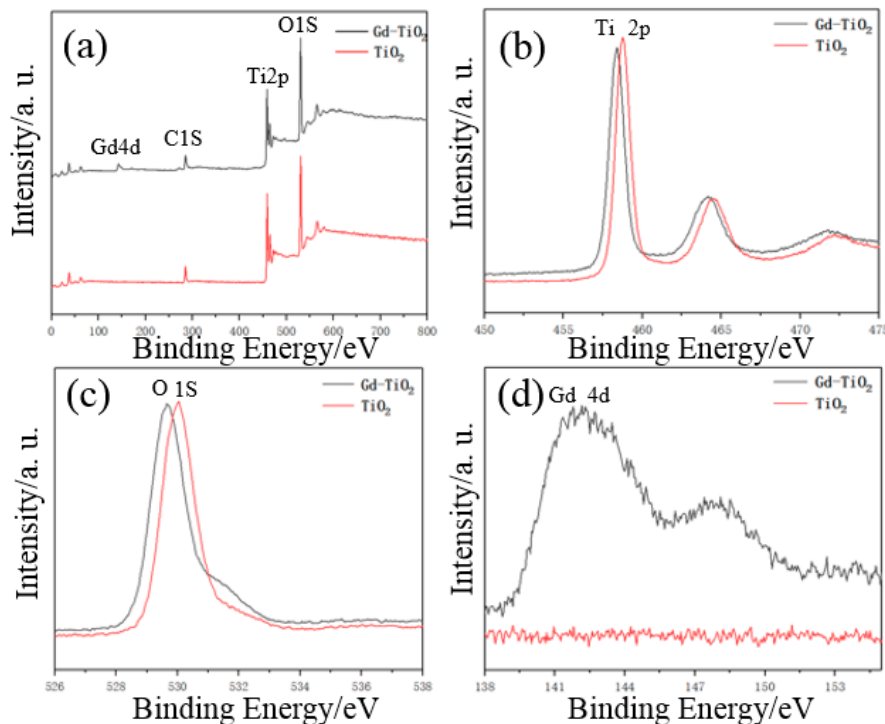


Figure 8. XPS of (a) full spectrum, (b) Ti2p, (c) O1s and (d) Gd4d.

2.2.5. EDX

An EDX spectrum of the sample before and after the rare earth element Gd doping is shown in Figure 9. Undoped samples contain four elements of C, O, Cu, and Ti while, after doping, samples contain five elements: C, O, Cu, Ti, and Gd. Among them, C and Cu come from carbon film and copper mesh, and O and Ti form TiO_2 . The inclusion of Gd in the doped sample indicates that the Gd is successfully doped into the TiO_2 lattice structure, which further confirms the successful preparation of the Gd-doped TiO_2 nanotube arrays.

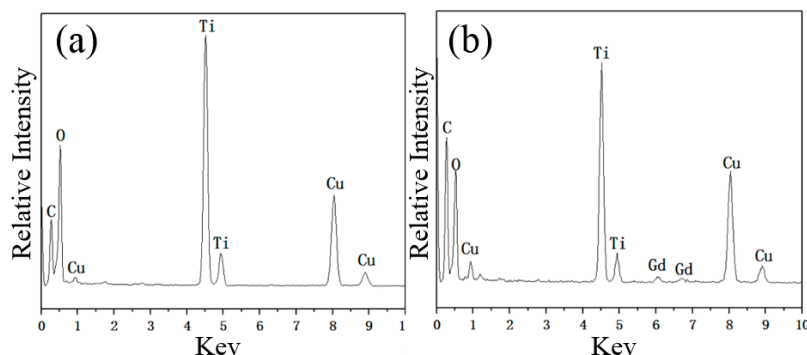


Figure 9. EDX spectra of (a) TiO_2 and (b) Gd-doped TiO_2 nanotubes

2.2.6. BET

The specific area and porosity analyzer are used to calculate the specific surface area of the prepared Gd-doped TiO_2 nanotube arrays. Shown in Figure 10, Gd-doped TiO_2 nanotube arrays with

a large BET area and more reactive sites are successfully prepared by anodization under the conditions of 60 V voltage, 10 h and 0.01 mol/L Gd^{3+} concentration. Figure 10 shows that the specific surface area of the prepared TiO_2 nanotube arrays is $176 \text{ m}^2/\text{g}$, while the TiO_2 (P-25) is $56 \text{ m}^2/\text{g}$. Large specific surface area is considered to be an important factor that could improve the photocatalytic performance of the catalyst.

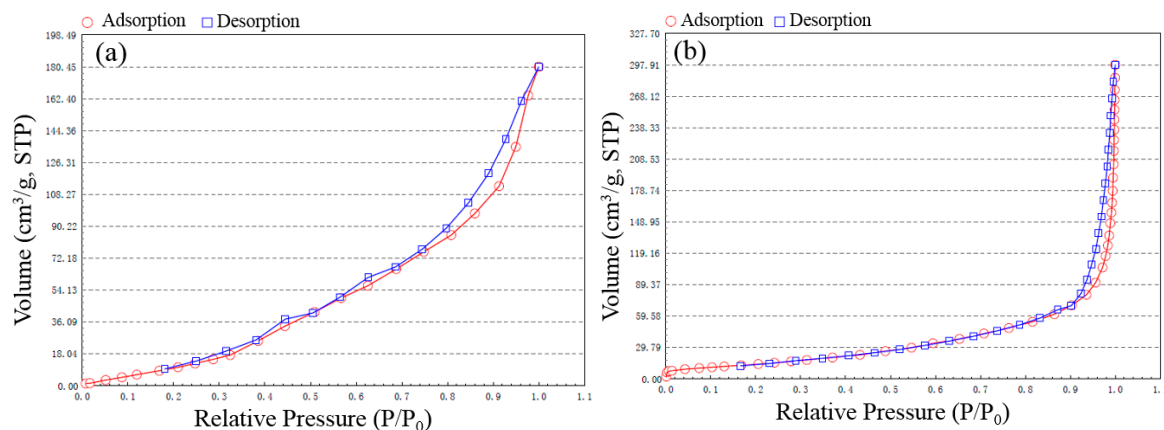


Figure 10. CO_2 adsorption-desorption curves of (a) Gd-doped TiO_2 nanotube arrays and (b) titanium dioxide (P-25)

2.3. Photocatalytic Reaction of TiO_2 and Gd-Doped TiO_2 Nanotube Arrays

Figure 11 demonstrates that the different reaction conditions have significant effects on the degradation rate of the MO solution. Figure 11a shows that the photocatalytic performance of the prepared TiO_2 improves rapidly with the increase of the reaction time, and the degradation rate of the MO is increased from 54.8% to 90.8%. The short reaction time makes the lower crystalline phase content of TiO_2 and the shorter length of the TiO_2 nanotubes, thus the photocatalytic property of the sample is poor under such a condition. When the reaction time increases, the TiO_2 crystal phase content and the specific surface area of the nanotubes is improved, and the sample's degradation rate of the MO become better. Considering the crystalline phase structure, surface morphology and economy, the optimal reaction time is determined to be 10 h. The effect of reaction voltages on photocatalytic performance is roughly consistent with reaction time (Figure 11b). Accompanying the increase in the reaction voltage, the driving force of the anodization reaction is enhanced, and the degradation rate of the MO also is increased obviously. Taking all factors into consideration, 60 V is the best condition for the TiO_2 nanotube array to obtain the best photocatalytic performance.

Figure 11c demonstrates photocatalytic degradation curves of the concentration change of the MO solution by TiO_2 nanotube arrays with different Gd concentrations. It can be seen that the photocatalytic performance of TiO_2 nanotubes is further enhanced by the doping of Gd^{3+} . Compared with the non-doped 79.8%, continuously increasing the concentration of Gd^{3+} to 0.01 mol/L, the degradation rate of the MO reaches a maximum of 95.8%. It is not easy to further improve the degradation rate on the basis of the original high degradation rate. The enhancement of the photocatalytic performance is due to the doping of the Gd, which helps to generate strong oxidizing hydroxyl groups on the surface of the TiO_2 photocatalyst, and reduces the recombination rate of electrons and holes.

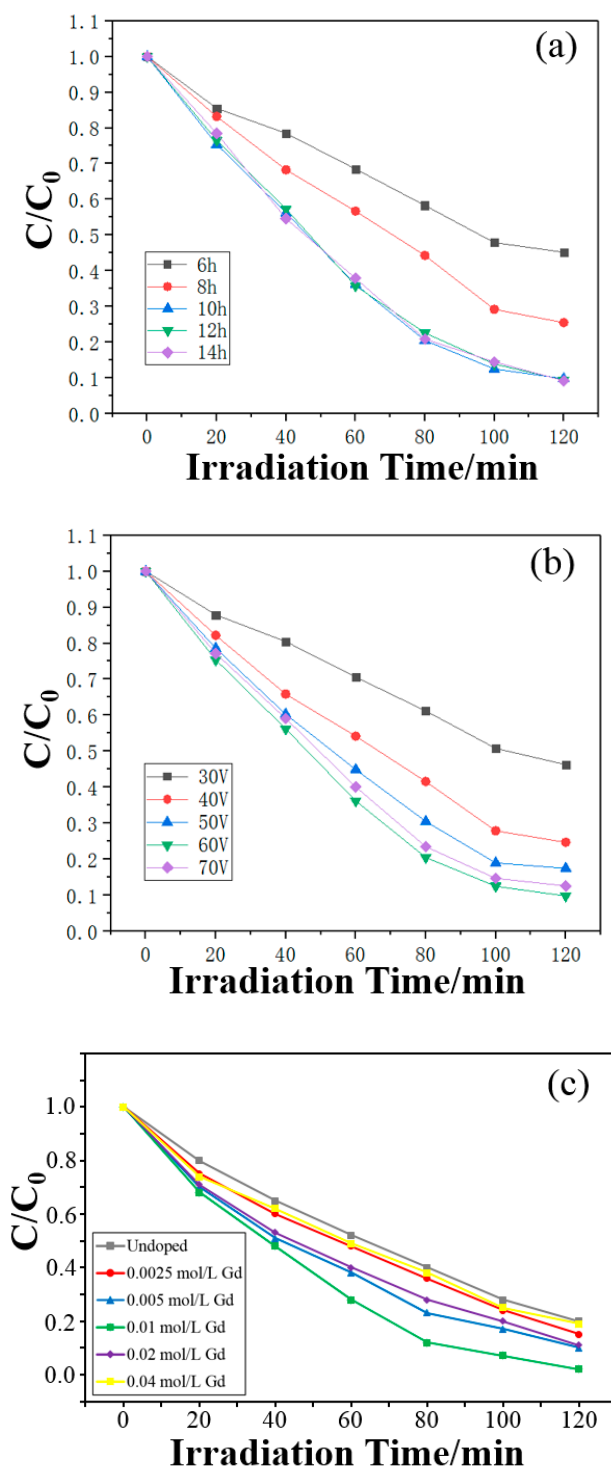


Figure 11. Concentration change of MO solution by TiO₂ nanotube arrays and Gd-doped TiO₂ at (a) different times (6–14 h), (b) different voltages (30–70 V) and (c) different Gd³⁺ concentrations (0.0025–0.04 mol/L).

2.4. Hydrophilicity of TiO₂ and Gd-Doped TiO₂ Nanotube Arrays

The hydrophilic properties of TiO₂ nanotube arrays prepared in different conditions are shown in Figure 12. The optical contact angle of the samples is 6.7° and 6.8° when the reaction time and voltage is 10 h and 60 V, respectively. Figure 12a shows that when the reaction time increases, the length of the generated nanotubes becomes longer, the sample has better crystallinity and a larger specific surface

area, which greatly improves the ability for chemically and physically adsorbed water, as well as an excellent hydrophilic property. Similarly, as shown in Figure 12b, when the reaction voltage is low, the driving force obtained by the reaction is small and it is more difficult for ions to pass through the barrier layer to form TiO₂ nanotubes, indicating that the hydrophilic property of the sample is worse. However, the excessively high reaction voltage makes the anodic oxidation rate too fast and corrodes the surface of the nanotubes, which causes the hydrophilic performance to decrease.

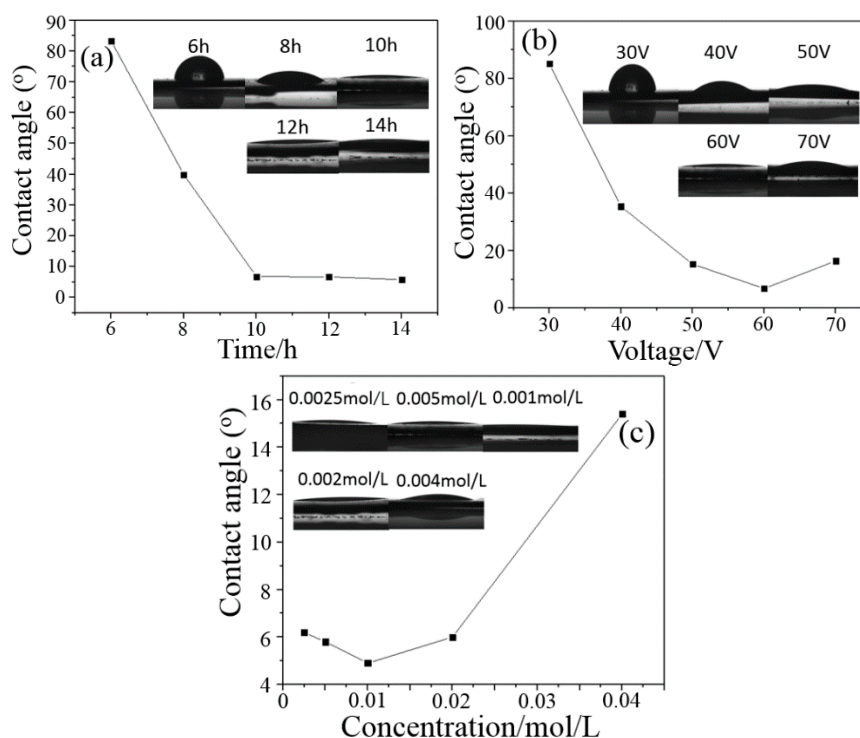


Figure 12. Hydrophilic property of TiO₂ nanotube arrays and Gd-doped TiO₂ nanotube arrays prepared at (a) different times (6–14 h), (b) different voltages (30–70 V) and (c) different Gd³⁺ concentrations (0.0025–0.04 mol/L).

Figure 12c shows the hydrophilic property of TiO₂ nanotube arrays with different Gd³⁺ concentrations. It can be observed that, when the doping concentration of Gd³⁺ is 0.01 mol/L, the contact angle reaches a minimum value of 4.9°. The doped rare earth oxide is hydrophobic and the hydrophilic property of the samples becomes worse when the concentration of Gd³⁺ continues to increase. Compared with the undoped samples (6.7°), it can be seen that the hydrophilic properties of the samples doped with Gd³⁺ (4.9°) are significantly better. This is because the samples after doping can lead the small content of the Gd³⁺ to enter the Ti⁴⁺ position of the TiO₂ crystal lattice, resulting in lattice distortion and causing an imbalance of the electrical charge with generating hydrophilic hydroxyl groups.

3. Experimental Section

3.1. Materials

Pure Ti foil was obtained from the Tenghui Titanium Corporation (Jinhua, China). Ammonium fluoride (NH₄F) and ethylene glycol (C₂H₆O₂) were purchased from the Xilong Science and Technology Co., Ltd (Shantou, China). Hydrofluoric acid, nitric acid and anhydrous ethanol (C₂H₅OH) were purchased from the Da Mao chemical reagent Corporation (Tianjin, China). Acetone (C₃H₆O) was acquired from the Shanghai Yanchen Chemical Industrial Co., Ltd (Shanghai, China). Methyl orange (MO)

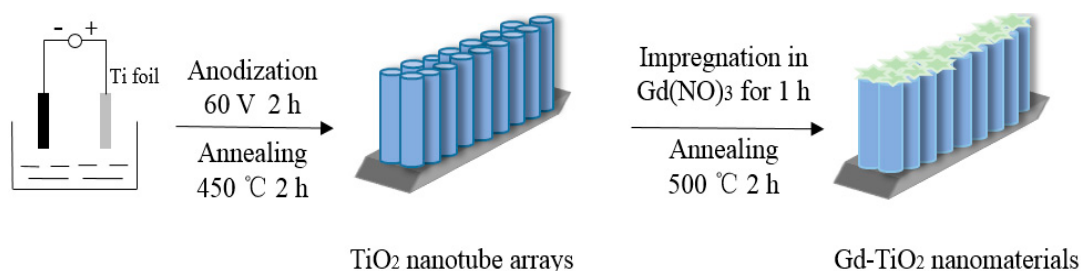
powders were acquired from the Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China). The ultrapure water was acquired from a Mili-Q Ultrapure water depurator (Millipore, Bedford, MA, USA).

3.2. Preparation of TiO_2 Nanotube Arrays

The polished titanium foil was ultrasonicated in an acetone solution, anhydrous ethanol, and ultrapure water for 10 minutes to eliminate surface oil and oxide. Hydrofluoric acid, nitric acid, and deionized water were prepared into a chemical polishing solution at a volume ratio of 1:3:5, the sonicated titanium foil was placed in the solution for 30 seconds, and then washed with pure water. A titanium foil was used as an anode, a graphite sheet as a cathode, and an ethylene glycol solution of ammonium fluoride was used as an electrolytic solution. The reaction was carried out for 10 h after commencing power. The titanium foil was washed with ethanol and annealed at $450\text{ }^\circ\text{C}$ for 2 h in a muffle furnace. Afterward, the TiO_2 nanotube arrays were generated on the Ti foil surface.

3.3. Fabrication of Gd-Doped TiO_2 Nanotube arrays

Different concentrations of a Gd nitrate solution ($0.025\text{--}0.04\text{ mol/L}$) was prepared. The TiO_2 nanotube arrays were immersed in the Gd nitrate solution for 1 h at $30\text{ }^\circ\text{C}$ by an impregnation method. Then, the sample was taken out and placed in a muffle furnace and annealed at $500\text{ }^\circ\text{C}$ for 2 h, and Gd-doped TiO_2 composite nanotube arrays were prepared successfully on the Ti substrate surface. The preparation processes were as follows (Scheme 1):



Scheme 1. Preparation processes of Gd-doped TiO_2 nanotube arrays

3.4. Characterizations

The morphology of TiO_2 nanomaterials was observed by an environmental scanning electron microscope (ESEM, FEI Quanta200F, FEI, Hillsboro, USA) and high resolution transmission electron microscope (HRTEM) (200 kV, JEOL, Tokyo, Japan). X-ray diffractometry (XRD, D8 ADVANCE, Bruker, Germany) was performed to identify the phase structure of TiO_2 samples. Elemental analysis was measured by X-ray photoelectron spectroscopy (XPS) (ESCALAB250Xi, ThermoFisher Scientific, USA). The specific surface area data of the catalyst was calculated by the Specific Area and Porosity Analyzer (JW-BK132F, Beijing, China). The photocatalytic degradation process of methyl orange was performed in a photochemistry reactor (BL-GHX-V, BILON, Shanghai, China). Hydrophilic properties were calculated by an optical contact angle meter (Zheke, DSA 100, Zheqi Technology, Beijing, China).

3.5. Photocatalytic Oxidation of Gd-Doped TiO_2 Nanotube arrays

Gd-doped TiO_2 nanotube array samples were cut into squares with a 10 mm length and placed in a quartz test tube for the photocatalytic degradation process. To obtain photocatalytic performance data, an MO solution with a concentration of 20 mg/L was prepared as simulated pollutants for photodegradation reactions [46]. The 500 W high-pressure mercury lamp with a main wavelength of 365 nm was used as the luminous source, and the light intensity measured during the reaction was 160 mW/cm^2 . The absorbance of residual MO was detected every 20 min. The photocatalytic

performance of the catalyst was evaluated by degradation rate (η). Related calculation is shown in Equation (9):

$$\eta = C_0 - \frac{C_t}{C_0} \times 100\% = A_0 - \frac{A_t}{A_0} \times 100\% \quad (9)$$

where the initial concentration and absorbance of the catalyst were C_0 and A_0 , and the concentration and absorbance at a certain time were C_t and A_t . A_t was the absorbance that was observed under 466 nm ultraviolet (UV) light irradiation. The same method was used to calculate the absorbance of the catalyst at different voltages (30–70 V), different times (6–14 h) and different concentrations (0.0025–0.04 mol/L).

4. Conclusions

During this study, tightly ordered anatase TiO_2 nanotube arrays were successfully prepared using anodizing technology, which was then doped with the rare earth element Gd to fabricate a novel photocatalyst of Gd-doped TiO_2 nanotube arrays. Reaction times, voltages, and Gd concentrations were proved to be the vital factors affecting the crystal phase and microstructure of the TiO_2 nanotube arrays. When the reaction voltage was 60 V, the reaction time was 10 h and the concentration of Gd^{3+} was 0.01 mol/L, the Gd-doped TiO_2 nanotube arrays exhibited the larger specific surface area ($176 \text{ m}^2/\text{g}$), a beneficial hydrophilic property (optical contact angle was 4.9°), and an excellent photocatalytic performance (degradation rate of MO was 95.8%). The hydrophilic and photocatalytic properties of the TiO_2 nanotube arrays were greatly improved after doping with Gd. Gd-doped TiO_2 nanotube arrays may be a potential photocatalyst in applications for water pollution.

Author Contributions: Conceptualization, J.D.; data curtain, S.X.; formal analysis, Y.Z.; funding acquisition, J.D.; methodology, R.L.; project administration, R.L.; resources, J.Y.; supervision, J.D. and H.P.; validation, X.W.; writing – original draft, R.L.; writing – review & editing, H.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Natural Science Foundation of China, grant number 51162022 and 31660482; Test Foundation of Nanchang University, grant number 2012019, and The APC was funded by National Double First-class Discipline Construction Fund of China, grant number 2704000104”.

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (Grant No. 51162022 and 31660482), National Double First-class Discipline Construction Fund of China (Grant No. 2704000104), and Test Foundation of Nanchang University (Grant No.2012019).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Chong, M.N.; Jin, B.; Chow, C.W.K. Recent developments in photocatalytic water treatment technology: A review. *Water Res.* **2010**, *44*, 2997–3027. [[CrossRef](#)]
2. Alfano, O.M.; Bahnemann, D.; Cassano, A.E.; Dillert, R.; Goslich, R. Photocatalysis in water environments using artificial and solar light. *Catal Today.* **2000**, *58*, 199–230. [[CrossRef](#)]
3. Rajeshwar, K.; Osugi, M.E.; Chanmanee, W.; Chenthamarakshan, C.R.; Zaroni, M.B.; Kajitvichyanukul, P.; Krishnan, A.R. Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. *J. Photochem. Photobiol. C Photochem. Rev.* **2008**, *9*, 171–192. [[CrossRef](#)]
4. Khan, S.; Al-Shahry, J.M.; Ingler, W.B. Efficient photochemical water splitting by a chemically modified n- TiO_2 . *Science* **2002**, *297*, 2243–2245. [[CrossRef](#)]
5. Murdoch, M.; Waterhouse, G.I.N.; Nadeem, M.A. The effect of gold loading and particle size on photocatalytic hydrogen production from ethanol over Au/ TiO_2 nanoparticles. *Nat. Chem.* **2011**, *3*, 489–492. [[CrossRef](#)] [[PubMed](#)]
6. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278. [[CrossRef](#)] [[PubMed](#)]
7. Li, X.; Li, Z.; Yang, J. Proposed photosynthesis method for producing Hydrogen from dissociated water molecules using incident near-infrared light. *Phys. Rev. Lett.* **2014**, *112*, 018301. [[CrossRef](#)] [[PubMed](#)]

8. Zhu, K.; Neale, N.R.; Miedaner, A. Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO₂ nanotubes arrays. *Nano Lett.* **2007**, *7*, 69–71. [[CrossRef](#)] [[PubMed](#)]
9. Jeong, N.C.; Farha, O.K.; Hupp, J.T. A convenient route to high area, nanoparticulate TiO₂ photoelectrodes suitable for high-efficiency energy conversion in dye-sensitized solar cells. *Langmuir* **2011**, *27*, 1996–1999. [[CrossRef](#)] [[PubMed](#)]
10. Zhou, Y.; Zhu, Q.; Tian, J.; Jiang, F. TiO₂ nanobelt@Co₉S₈ composites as promising anode materials for lithium and sodium ion batteries. *Nanomaterials* **2017**, *7*, 252. [[CrossRef](#)]
11. Hwang, Y.J.; Hahn, C.; Liu, B.; Yang, P. Photoelectrochemical properties of TiO₂ nanowire arrays: A study of the dependence on length and atomic layer deposition coating. *ACS Nano* **2012**, *6*, 5060–5069. [[CrossRef](#)] [[PubMed](#)]
12. Zhang, H.; Liu, X.; Li, Y.; Sun, Q.; Wang, Y.; Wood, B.J.; Liu, P.; Yang, D.; Zhao, H. Vertically aligned nanorod-like rutile TiO₂ single crystal nanowire bundles with superior electron transport and photoelectron catalytic properties. *J. Mater. Chem.* **2012**, *22*, 2465–2472. [[CrossRef](#)]
13. Mancic, L.; Osman, R.F.M.; Costa, A.M.L.M.; d’Almeida, J.R.M.; Marinkovic, B.A.; Rizzo, F.C. Thermal and mechanical properties of polyamide 11 based composites reinforced with surface modified titanate nanotubes. *Mater. Des.* **2015**, *83*, 459–467. [[CrossRef](#)]
14. Kusior, A.; Kollbek, K.; Kowalski, K.; Borysiewicz, M.; Wojciechowski, T.; Adamczyk, A.; Trenczek-Zajac, A.; Radecka, M.; Zakrzewska, K. Sn and Cu oxide nanoparticles deposited on TiO₂ nanoflower 3D substrates by inert gas condensation technique. *Appl. Surf. Sci.* **2016**, *380*, 193–202. [[CrossRef](#)]
15. Leary, R.; Westwood, A. Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis. *Carbon* **2011**, *49*, 741–772. [[CrossRef](#)]
16. Meng, S.; Ren, J.; Kaxiras, E. Natural dyes adsorbed on TiO₂ nanowire for photovoltaic applications: Enhanced light absorption and ultrafast electron injection. *Nano Lett.* **2008**, *8*, 3266–3272. [[CrossRef](#)] [[PubMed](#)]
17. Thompson, T.L.; Yates, J.T., Jr. Surface science studies of the photoactivation of TiO₂-new photochemical processes. *Chem. Rev.* **2007**, *106*, 4428–4453. [[CrossRef](#)]
18. Takata, Y.; Yidakal, S.; Masuda, M. Pool boiling on a superhydrophilic surface. *Int. J. Energy Res.* **2003**, *27*, 111–119. [[CrossRef](#)]
19. Liao, J.Y.; Lei, B.X.; Chen, H.Y. Oriented hierarchical single crystalline anatase TiO₂ nanowire arrays on Ti-foil substrate for efficient flexible dye-sensitized solar cells. *Energy Environ. Sci.* **2012**, *5*, 5750–5757. [[CrossRef](#)]
20. Fujishima, A.; Rao, T.; Tryk, D. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C Photochem. Rev.* **2000**, *1*, 1–21. [[CrossRef](#)]
21. Lu, J.; Li, H.; Cui, D. Enhanced enzymatic reactivity for electrochemically driven drug metabolism by confining cytochrome P450 enzyme in TiO₂ nanotube arrays. *Anal. Chem.* **2014**, *86*, 8003–8009. [[CrossRef](#)] [[PubMed](#)]
22. Wang, D.; Liu, Y.; Yu, B. TiO₂ nanotubes with tunable morphology, diameter, and length: Synthesis and photo-electrical/catalytic performance. *Chem. Mater.* **2009**, *21*, 1198–1206. [[CrossRef](#)]
23. Michailowski, A.; Almawlaw, D.; Cheng, G. Highly regular anatase nanotube arrays fabricated in porous anodic templates. *Chem. Phys. Lett.* **2002**, *349*, 1–5. [[CrossRef](#)]
24. Gong, D.; Grimes, C.A.; Varghese, O.K. Titanium oxide nanotube arrays prepared by anodic oxidation. *J. Mater. Res.* **2001**, *16*, 3331–3334. [[CrossRef](#)]
25. Lin, C.J.; Yu, Y.H.; Chen, S.Y. Anodic growth of highly ordered titanium oxide nanotube arrays: Effects of critical anodization factors on their photocatalytic activity. *World Acad. Sci. Eng. Technol.* **2010**, *38*, 41–48.
26. Marien, C.B.D.; Cottineau, T.; Robert, D. TiO₂ nanotube arrays: Influence of tube length on the photocatalytic degradation of paraquat. *Appl. Catal. B Environ.* **2016**, *194*, 1–6. [[CrossRef](#)]
27. Wei, O.; Feng, T.; Xiao, F. High performance BiOCl nanosheets/TiO₂ nanotube arrays heterojunction UV photodetector: The influences of self-induced inner electric fields in the BiOCl nanosheets. *Adv. Funct. Mater.* **2018**, *28*, 1707178.
28. Roy, P.; Berger, S.; Schmuki, P. TiO₂ nanotubes: Synthesis and applications. *Angew. Chem. Int. Ed.* **2011**, *50*, 2904–2939. [[CrossRef](#)]
29. Ruan, C.M.; Paulose, M.; Varghese, O.K. Fabrication of highly ordered TiO₂ nanotube arrays using an organic electrolyte. *J. Phys. Chem. B* **2005**, *109*, 15754–15759. [[CrossRef](#)]

30. Macak, J.M.; Tsuchiya, H.; Taveira, L. Smooth n-doped TiO₂ nanotubes. *Angew. Chem. Int. Ed.* **2005**, *44*, 7463–7465. [\[CrossRef\]](#)
31. Li, S.; Zhang, G.; Guo, D. Anodization and fabrication of highly ordered TiO₂ nanotubes. *J. Phys. Chem. C* **2009**, *113*, 12759–12765. [\[CrossRef\]](#)
32. Wu, H.; Zhang, Z. Photoelectrocatalytic degradation of organic pollutant on highly smooth and ordered TiO₂ nanotube arrays. *J. Solid State Chem.* **2011**, *184*, 3202–3207. [\[CrossRef\]](#)
33. Wei, Z.; Hai, H.; Yong, T.; Dong, Z. Synthesis of uniform ordered mesoporous TiO₂ microspheres with controllable phase junctions for efficient solar water splitting. *Chem. Sci.* **2019**, *10*, 1664.
34. Tan, L.; Chai, S.; Mohamed, A.R. Synthesis and applications of graphene-Based TiO₂ photocatalysts. *Chem. Sus. Chem.* **2012**, *5*, 1868–1882. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Scanlon, D.O.; Dunnill, C.W.; Buckeridge, J.; Shevlin, S.A.; Logsdail, A.J.; Sokol, A.A. Band alignment of rutile and anatase TiO₂. *Nat. Mater.* **2013**, *12*, 798–801. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Li, Z.; Qing, C.; Ai, W.; Jia, D.; Wei, Z.; Yuan, S.; Hong, L. Iron oxide embedded titania nanowires—An active and stable electrocatalyst for oxygen evolution in acidic media. *Nano Energy*. **2018**, *45*, 118–126.
37. Ghicov, A.; Schmidt, B.; Kunze, J. Photoresponse in the visible range from Cr doped TiO₂ nanotubes. *Chem. Phys. Lett.* **2007**, *433*, 323–326. [\[CrossRef\]](#)
38. Tu, Y.F.; Huang, S.Y.; Sang, J.P.; Zou, X.W. Preparation of Fe-doped TiO₂ nanotube arrays and their photocatalytic activities under visible light. *Mater. Res. Bull.* **2010**, *45*, 224–229. [\[CrossRef\]](#)
39. Xing, H.; Yun, C.; He, Z. Photocatalytic degradation of organic pollutants with Ag decorated freestanding TiO₂ nanotube arrays and interface electrochemical response. *J. Mater. Chem.* **2011**, *21*, 475–480.
40. Zhong, Z.; Yan, Y.; Peng, W. Hierarchical top porous/bottom-tubular TiO₂ nanostructures decorated with Pd nanoparticles for efficient photoelectrocatalytic decomposition of synergistic pollutants. *ACS Appl. Mater. Inter.* **2012**, *4*, 990–996. [\[CrossRef\]](#)
41. Xin, F.; Sloppy, J.D.; LaTepa, T.J. Synthesis and deposition of ultrafine Pt nanoparticles within high aspect ratio TiO₂ nanotube arrays: Application to the photocatalytic reduction of carbon dioxide. *J. Mater. Chem.* **2011**, *21*, 13429–13433.
42. Zhi, G.; Hai, L.; Cheng, L. Biotemplated synthesis of Au nanoparticles-TiO₂ nanotube junctions for enhanced direct electrochemistry of heme proteins. *Chem. Commun.* **2013**, *49*, 774–776.
43. Qing, Z.; Bao, Z.; Jing, B. TiO₂ nanotube arrays and its applications. *Prog. Chem.* **2007**, *19*, 117–122.
44. Mor, G.K.; Varghese, O.K.; Paulose, M.; Mukherjee, N.; Grimes, C.A. Fabrication of tapered, conical-shaped titania nanotubes. *J. Mater. Res.* **2003**, *18*, 2588–2593. [\[CrossRef\]](#)
45. Fortes, A.D.; Suard, E.; Knight, K.S. Negative Linear Compressibility and Massive Anisotropic Thermal Expansion in Methanol Monohydrate. *Science* **2011**, *331*, 742–746. [\[CrossRef\]](#)
46. Barton, I.; Vlastimil, M.; Josef, M. Photocatalytic activity of nanostructured TiO₂ coating on glass slides and optical fibers for methylene blue or methyl orange decomposition under different light excitation. *J. Photochem. Photobiol. A* **2016**, *317*, 72–80. [\[CrossRef\]](#)



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).