S & M 1786

# Analyses of Growth Parameters of TiO<sub>2</sub> Nanotube Arrays and Their Effect on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S Methyl Orange Degradation

Shang-Te Tsai, <sup>1</sup> Chi-Yu Lin, <sup>2</sup> Yu-Xiang Dong, <sup>3</sup> Cheng-Fu Yang, <sup>3\*</sup> and Hong-Yu Shih <sup>4</sup>

Department of Economics and Management, Ningde Normal University,
 No. 1, College Rd., Ningde City, Fujian 352100, China
Department of Aero-Electronic Engineering, Air Force Institute of Technology,
 No. 198. Jieshou W. Rd., Gangshan Township, Kaohsiung 820, Taiwan
Department of Chemical and Materials Engineering, National University of Kaohsiung
 No.700, Kaohsiung University Rd., Nan-Tzu District, Kaohsiung 811, Taiwan
Department of Leisure, Recreation, and Tourism Management, Southern Taiwan University,
 No. 1, Nan-Tai Street, Yungkang Dist., Tainan City 710, Taiwan

(Received May 31, 2018; accepted October 18, 2018)

Keywords: hydrothermal method; Eu<sup>3+</sup>-doped ZnO nanowires, photoluminescence

In this study, we analyzed the growth and annealing parameters of TiO<sub>2</sub> nanotube (TNT) arrays and their effect on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation. At first, the TNT arrays were grown on Ti metal by the anodic oxidation method under DC voltages of 10-30 V. Surface observation was used to judge the effect of the grown TNT arrays, and we found that 20 V was the optimum voltage in this study. After the TNT arrays were grown under the DC bias of 20 V, the TNT arrays were annealed at temperatures in the range of 400-500 °C for time durations of 1–3 h. From the X-ray diffraction (XRD) patterns, we found that the as-grown TNT arrays have an amorphous phase. Because different annealing temperatures and annealing times were used, the XRD patterns showed that only the anatase TiO<sub>2</sub> phase and Ti phase were observed. The TNT arrays with different annealing parameters were used to carry out experiments on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation. The transmittance spectra of C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange has one strong and wide absorption band located at 463-464 nm and a small absorption band located at 270-271 nm. The C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange solutions under only UV-light irradiation were almost unchanged with the increase in irradiation time. After the annealed TNT arrays were used to degrade the C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange, we found that the TNT arrays grown at 20 V and annealed for 1 h at 450 °C had the best effect on the C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation.

## 1. Introduction

Textile and paint industries require the largest group of chemical materials produced in the world, and during their production and usage, many harmful contaminants enter rivers and the environment. Dye compounds being released as effluent from textile and paint factories are

<sup>\*</sup>Corresponding author: e-mail: cfyang@nuk.edu.tw https://doi.org/10.18494/SAM.2019.2103

significant sources of pollution and eutrophication in aquatic ecosystems and the environment. (1) With the progression of global industrialization, environmental pollution has become a more serious issue; thus, the degradation and conversion of chemical materials into harmless mineral compounds are important issues and have received considerable attention. Many physical and chemical methods are used to reduce the harmful dye compounds inflict on the environment, and the most important methods include reverse osmosis, adsorption, precipitation, and coalescence. (2) Not only do these methods only transfer pollution from one phase to another and concentrate them, but they also are nondestructive processes. In recent years, advanced oxidation processes (AOPs) have been used as substitutes in regular purification. (3) In these processes, unstable materials with high reactivity, particularly free hydroxyl radicals, are used to degrade pollutants and convert them into harmless mineral materials. The development of photocatalysis has attracted considerable attention in recent years, with photocatalysis being used in various products across a broad range of research areas, including environmental and energy-related fields. (4-6) So far, many different photocatalyst materials, such as GaAs, PbS, CdS, Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, ZnO, TiO<sub>2</sub>, and their composites, have been investigated to decompose different dyes and minimize their pollution potential.

TiO<sub>2</sub>-based materials possess a wide range of applications owing to their excellent properties, such as nontoxicity, excellent catalytic activity, low cost, and long-term stability. Of the many different photocatalysts, TiO2-based materials are the most widely studied and used in many applications because of their strong oxidizing abilities<sup>(7)</sup> for the decomposition of organic pollutants, super-hydrophilicity, chemical stability, long durability, nontoxicity, low cost, and transparency to visible light. (8) Consequently, the decomposition of a color photocatalyst by using a TiO2-based catalyst with a UV beam is among the AOPs that will be further studied. (8) Materials of nanoscale size have a high surface area, and a high fraction of surface atoms has been studied because of their exclusive properties such as optic, electronic, and catalytic properties. TiO<sub>2</sub>-based materials of nanoscale size have a significant degradation effect, making them good photocatalysts of organic and inorganic pollutants in air and water, that have broad application prospects. (9) For example, Dariani et al. designed and made a novel laboratory photocatalytic reactor. They then studied the photocatalytic properties of TiO<sub>2</sub> nanoparticles using UV-A light. Then, the photodegradation of methylene blue as a water pollutant was evaluated until the photocatalytic process was optimized by adjusting the process parameters. (2) Chin et al. used the thermal decomposition of titanium tetraisopropoxide (TTIP) to generate TiO<sub>2</sub> nanoparticles using a tubular electric furnace at various synthesis temperatures (700–1300 °C) and TTIP heating temperatures (80–110 °C). They also determined the photocatalytic degradation effect of TiO2 nanoparticles on methylene blue and compared it with the photocatalytic degradation effect of the nanoparticles produced by a thermal decomposition process with a commercial photocatalyst. In the past, many researchers also investigated TiO<sub>2</sub>based nanoparticles as photocatalyst materials to degrade industrial dyes. (11,12)

We grew TiO<sub>2</sub> nanotube (TNT) arrays and used the grown TNT arrays to fabricate dyesensitized solar cells (DSSCs). We also extensively investigated the effect of the TNT array length on the measured photovoltaic performance of DSSCs.<sup>(13)</sup> Also, the TNT-based materials and array can be used as sensor materials to detect different gases. For example, Galstyan *et al.*  studied the growth process of TNTs and investigated their gas sensing properties using two different approaches, namely, chemoresistive and Kelwin probe methods. (14) N. Kılınc *et al.* investigated the TNT/copper octakisalkylthiophthalocyanine [(C<sub>6</sub>S)<sub>8</sub>PcCu] hybrid structure as a volatile organic compound (VOC) sensor and investigated its sensing properties at room temperature. (15)

Only a few researchers have used TNT arrays as photocatalyst materials to degrade pollutant dyes. There are two different types of methylene blue,  $C_{16}H_{18}N_3ClS$  and  $C_{37}H_{27}N_3Na_2O_9S_3$ . Previously, we used anodic-oxidized TNTs to degrade the  $C_{16}H_{18}N_3ClS$  methylene blue. In this study, we analyzed the growth and annealing parameters of TNT arrays and their effect on  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation. First, we investigated the effects of the growth and annealing parameters on the characteristics of grown TNT arrays. The  $C_{16}H_{18}N_3ClS$  methylene blue has three strong absorption bands at 246, 293, and 664 nm. Therefore, the  $C_{14}H_{14}N_3NaO_3S$  methyl orange has one strong and wide absorption band located at 463–464 nm and a small absorption band located at 270–271 nm. Next, we investigated whether the annealing parameters (time and temperature) have a strong effect on the crystallization of TNT arrays, which would lead to large differences in the effectiveness for  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation. The photocatalytic activity of grown TNT arrays was examined through experiments on  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation under UV light irradiation. We showed that the grown and annealed TNT arrays had effectively degraded over 90% of the  $C_{14}H_{14}N_3NaO_3S$  methyl orange at 120 min of exposure time.

# 2. Experimental Procedure

In this research, highly ordered TNT arrays were fabricated by the electrochemical anodic oxidation method, using Ti foils as the anode and cathode and changing the amount of fluoride (NH<sub>4</sub>F) in the solution. Ti foils of 0.25 mm thickness were degreased by ultrasonication in acetone and then isopropanol for about 30 min, followed by rinsing with deionized (DI) water, and finally, drying in air before being used. The ordered TNT arrays were oxidized on Ti foil (Aldrich, 99.7% purity) with an area of 20 × 20 mm<sup>2</sup> at the constant voltages of 10, 20, and 30 V. The electrolyte solutions contained ammonium fluoride (NH<sub>4</sub>F, 99.9%) in ethylene glycol (EG) in the presence of H<sub>2</sub>O (2 vol%, pH 6.8) with anodization under various conditions. All anodization experiments were carried out at room temperature. After being grown, the TNT arrays were rinsed with ethanol, dried in air, and annealed at 150 °C for 2 h to remove organic solvents. The detailed processes for preparing the TNT arrays are described in Refs. 13 and 16.

The grown TNT arrays were then crystallized further at different temperatures (400–500 °C) for different durations in air. X-ray diffraction (XRD) patterns were used to characterize the crystalline structure of the anodized TNT arrays under different annealing parameters. The XRD analysis of the prepared TNT arrays was carried out using a Bruker diffractometer with Cu-K X-rays with a wavelength ( $\lambda$ ) of 1.5406 Å, and data were taken for the  $2\theta$  range of 20 to 80°. The TNT arrays prepared with different annealing parameters were used to carry out the experiments on  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation. A 10 ppm solution of  $C_{14}H_{14}N_3NaO_3S$  methyl orange was prepared and  $10 \times 10 \text{ mm}^2$  TNT arrays were dipped

in a 5 ml solution. After that, the samples were put under UV light of 265 nm wavelength for different durations from 0 to 120 min. The absorbance spectra of the supernatant of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solutions were subsequently measured using a UV–Vis spectrophotometer in the 200 to 700 nm wavelength range, and were used to judge the effectiveness of  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation. To determine the variation in the concentration of  $C_{14}H_{14}N_3NaO_3S$  methyl orange, the values of five samples were analyzed and the average value was obtained.

#### 3. Results and Discussion

Figure 1 shows the surface morphologies of TNT arrays grown under different DC voltages. As Fig. 1(a) shows, when the applied voltage was 10 V, the TNT arrays were not clearly observed. This result suggests that 10 V is too small and the current is also too low for the self-organization process to occur, and the Ti and TiO<sub>2</sub> on the surfaces of the Ti foil are not removed; thus, the TNT arrays cannot be observed. When the applied voltage was 20 V, as Fig. 1(b) shows, highly ordered TNT arrays consisting of very regular tubes with uniform inner diameters of ~57 nm were obtained. When the applied voltage was 30 V, as Fig. 1(c) shows, even highly ordered TNT arrays consisting of very regular tubes with uniform inner diameters of ~111 nm were obtained; residual TiO<sub>2</sub> powders remained on the surfaces of the TNT arrays. This result suggests that when 30 V is used, the voltage and also the current are too high, and the Ti oxidation process is quicker than the TiO<sub>2</sub> consumption process. Consequently, residual TiO<sub>2</sub> powders will exist on the TNT arrays. We will show, in the next sudy, that 20 V is the best applied voltage in this study because TNT arrays grown under this voltage have the optimal effect on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation.

To achieve a high degradation effect on organic pollutants, the growth of TNT array crystalline phases is very important, because the crystallinity of TNT will influence their photocatalytic effect. Figure 2 shows the XRD patterns of the prepared TNT arrays under different growth and annealing conditions. For the as-grown and unannealed TNT arrays, only the Ti phase could be observed and no TiO<sub>2</sub> phases were observed (not shown here). As Fig. 2(a) shows, the TNT arrays were grown under different applied voltages and annealed at 450 °C for 1 h. The diffraction intensity of the (101) peak of the anatase phase, which occurred

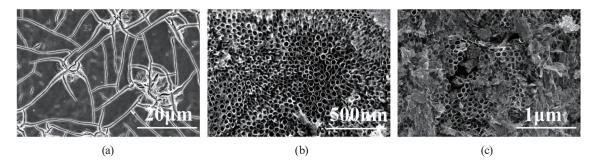


Fig. 1. TNT arrays grown under different DC voltages by the anodic oxidation method: (a) 10, (b) 20, and (c) 30 V.

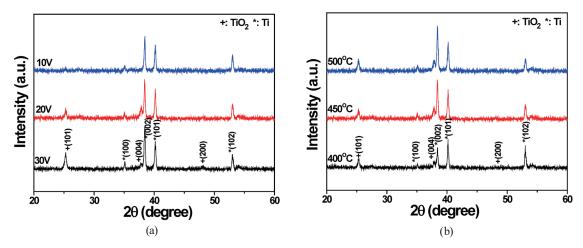


Fig. 2. (Color online) XRD patterns of TNT arrays (a) grown under different voltages and annealed at 450 °C for 1 h and (b) annealed at different temperatures for 1 h.

at around 25.5°, increased with increasing applied voltage. Such a (101) diffraction peak of the anatase phase was almost nonexistent when 10 V was used as the growth voltage. Figure 2(a) also shows that for the TNT arrays grown under 20 V, the (004) diffraction peak of the anatase phase, which had the maximum intensity, occurred at around 37.8°. These results suggest that the growth voltage is important in  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation.

The transmittance spectra of methyl orange solutions under only UV light irradiation are depicted in Fig. 3. These results reveal that the absorption spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange has one strong and wide absorption band located at 463-464 nm and a small absorption band located at 270-271 nm. These are different from the three strong absorption bands of  $C_{16}H_{18}N_3ClS$  methylene blue, which are located at 246, 293, and 664 nm. When only UV light was used to irradiate the solution of  $C_{14}H_{14}N_3NaO_3S$  methyl orange, the intensities of transmittance spectra remained almost unchanged with increasing irradiation time. These results prove that the irradiation of only UV light has no effect on the degradation of  $C_{14}H_{14}N_3NaO_3S$  methyl orange.

We have established the effects of growth and annealing parameters on the UV–visible transmittance spectra to determine their effects on the degradation of  $C_{14}H_{14}N_3NaO_3S$  methyl orange. The degradation experiment was carried out at a fixed concentration of  $C_{14}H_{14}N_3NaO_3S$  methyl orange, TNT arrays of 2 × 2 cm² area, neutral initial pH, and in equal time intervals. Figure 4 shows absorbance spectrum versus wavelength for  $C_{14}H_{14}N_3NaO_3S$  methyl orange at a concentration of 10 ppm with different exposure times. According to the absorbance spectra of all the samples, the maximum absorbance bands of all the samples occur at wavelengths of 463-464 and 270-271 nm.

At first, 20 V was used as the growth voltage and 1 h and 450 °C were used as the annealing parameters of the TNT photocatalyst materials. The absorbance spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solutions are depicted in Fig. 4(a). At first, the absorbance spectrum was taken at zero time (i.e., before the illumination of UV light and the addition of  $TiO_2$  photocatalyst materials) and the peak had the highest value. After the start of UV light illumination at

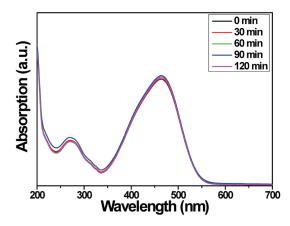


Fig. 3. (Color online) UV–visible spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution as a function of time of only UV light irradiation.

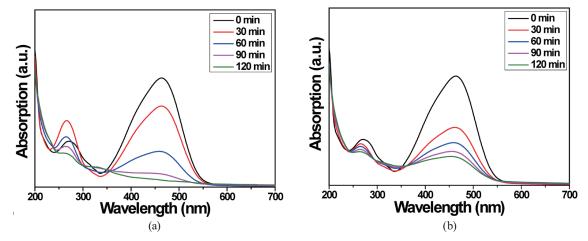


Fig. 4. (Color online) UV–visible spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution as a function of TNT array annealing temperature and UV light irradiation time. Annealed at (a) 450 and (b) 500 °C.

intervals of 30 min, the absorbance spectrum was recorded, and the intensities of two strong absorption bands of  $C_{14}H_{14}N_3NaO_3S$  methyl orange apparently decreased gradually with increasing UV light irradiation time. Compared with the results in Fig. 3, the addition of annealed TNT arrays into the  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution resulted in an improved photocatalytic response owing to the degradation of MB under UV light illuminations. Figure 4(a) also shows that during the experiment, the maximum value of the absorbance band decreased with increasing exposure time. As the exposure time was equal to 120 min, the absorbance peak became nearly smooth. The  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution changed from orange to colorless and became nearly transparent during the degradation process.

Next, 20 V was used as the growth voltage and 1 h and 500 °C were used as the annealing parameters of the TNT photocatalyst materials. The relationship between absorbance and irradiation time in the degradation of  $C_{14}H_{14}N_3NaO_3S$  methyl orange under UV light irradiation is also shown in Fig. 4(b). The strong absorption bands of  $C_{14}H_{14}N_3NaO_3S$  methyl orange also

decreased gradually with increasing irradiation time, and the absorbance was not zero even after 120 min of irradiation. In addition, the strong absorption bands in Figs. 4(a) and 4(b) do not shift with irradiation time, indicating that the degradation of  $C_{14}H_{14}N_3NaO_3S$  methyl orange is due to chromophore destruction.

The rate of C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation was estimated using

Degradation rate = 
$$100 \times (C_0 - C)/C$$
, (1)

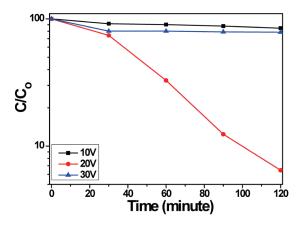
where  $C_0$  is the initial concentration of the dye solution and C is the concentration of the dye solution after photocatalytic degradation. The degradation rate was calculated using the concentration determined from the absorbance of  $C_{14}H_{14}N_3NaO_3S$  methyl orange at 463–464 nm. The determination of  $C_{14}H_{14}N_3NaO_3S$  methyl orange concentration can also be described in terms of the Beer–Lambert Law. When a monochromatic light beam passes through the solution, the amount of light absorbed by the dye solution is directly related to its concentration, as  $^{(2,16)}$ 

$$A = \log\left(C_{\text{o}}/C\right) = abc,\tag{2}$$

where A is the absorption ratio,  $C_0$  is the incident light, C is the transmission light, a is the molar absorptivity in units of  $L \cdot mol^{-1} \cdot cm^{-1}$ , b is the path for light transmission (this is the width of the quartz used to hold the methyl orange liquid), and c is the analyzed concentration of the compound in solution, expressed in  $mol \cdot L^{-1}$ . The equation is commonly applied to chemical analysis measurements and used to understand the attenuation for photons, neutrons or rarefied gases in physical optics. According to the Beer–Lambert Law, the relationship between the dye concentration and the absorbed light is linear.

However, our measurements for the determination of the C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange concentration were carried out at intervals of 0–120 min and the relationship was not linear. When the UV light irradiation times were 30, 60, 90, and 120 min, and 10 (20, 30) V was used as the voltage in the anodic oxidation method, the average intensity of the strong absorption band located at 463–464 nm was decreased to 91.6% (74.3%, 80.2%), 90.2% (32.8%, 80.2%), 87.8% (12.4%, 79.1%), and 84.6% (6.45%, 78.6%), respectively. These results prove that the transmittance spectra can be used to judge the degradation effect of the C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange solutions. These results in Fig. 5 also prove that the different growth parameters of TNT arrays will cause them to have different crystalline structures and thus different effects on methyl orange degradation.

These results suggest that 20 V is the optimum growth voltage for the TNT arrays to degrade C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange. We will show, in our next study, that when 20 V is used as the growth voltage, different annealing parameters will cause the TNT arrays to have different effects on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation. The relationship between absorbance ratio (calculated using the peak at 463–464 nm) and irradiation time in the degradation of C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange using TNT arrays prepared with different annealing temperatures under UV light irradiation is shown in Fig. 6. With exposure to UV light, the



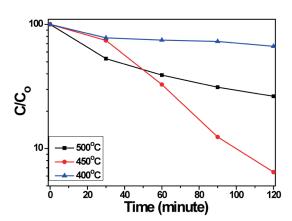


Fig. 5. (Color online) UV–visible spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution as a function of TNT array growth voltage and UV light irradiation time. The TNT arrays were annealed at 450 °C for 1 h.

Fig. 6. (Color online) UV-visible spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution as a function of TNT array annealing temperature and UV light irradiation time. The TNT arrays were grown using 20 V bias and annealed for 1 h.

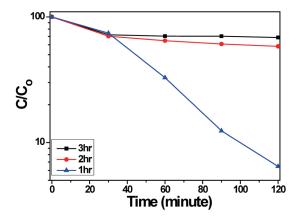


Fig. 7. (Color online) UV–visible spectra of  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution as a function of TNT array growth time and UV light irradiation time. The TNT arrays were annealed at 450 °C for 1 h.

absorbance ratio of the 463–464 nm peak decreased monotonically with increasing UV light irradiation time. The use of 450-°C-annealed TNT arrays as the photocatalyst materials resulted in a larger slope than when using TNT arrays annealed at other temperatures. This means that the 450-°C-annealed TNT arrays have the optimum photocatalytic effect on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation. Comparison of the results in Figs. 2, 5, and 6 suggests that the appearance and diffraction intensity of the (004) peak are the key points of C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation.

Figure 7 also shows the UV-visible spectra of the  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution as a function of TNT array growth time (1–3 h) and UV light irradiation time. The TNT arrays were annealed at 450 °C for 1 h. The photodegradation process starts when TNT arrays absorb UV radiation of energy equal to or higher than its band gap. The energy band gap for the anatase phase is 3.2 eV and that for the rutile phase is 3.0 eV. Free electrons ( $e^-$ ) are formed in the conduction band and holes ( $h^+$ ) are formed in the semiconductor valence band when

the TNT arrays are irradiated with photon energy higher than the band gap. These energized electrons will either recombine with the holes or the electron-hole pairs will proceed through redox reactions with electrons adsorbed on the surfaces of the photocatalyst (TNT arrays). (17) We believe that after TNT arrays are grown and annealed to obtain a better aspect ratio, less residual impurity, or highly crystalline anatase phase, they become capable of absorbing more UV light energy and more electrons and holes are formed. This is the reason behind the higher degradation ratio of TNT arrays.

#### 4. Conclusions

In this study, the photocatalytic effect of TNT arrays annealed under different conditions was successfully proved by experiments on  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation. At first, when a different bias voltage was used to grow the TNT arrays, we found that 20 V was best because the nanotube structure was actually observed and no residual  $TiO_2$  particles remained on the surface of the TNT arrays.  $C_{14}H_{14}N_3NaO_3S$  methyl orange has one strong and wide absorption band located at 463–464 nm and a small absorption band located at 270–271 nm. The TNT arrays grown at a bias voltage of 20 V and annealed at 450 °C for 1 h had an optimum effect on  $C_{14}H_{14}N_3NaO_3S$  methyl orange degradation. Even if the concentration of the  $C_{14}H_{14}N_3NaO_3S$  methyl orange solution is only 10 ppm, it can be decreased to 6.45% after 254 nm UV light irradiation for 120 min.

# Acknowledgments

The financial support from the National Science Council (MOST 106-2622-E-390-002-CC3, MOST 106-2221-E-390-019, and MOST 106-2622-E-390-004-CC3) is deeply appreciated.

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### **About the Authors**



**Shang-Te Tsai** received his Ph.D. in information management from Taiwan University of Science and Technology. Professor Tsai's research focuses on multimedia data analysis and system integration, large data analysis and application, embedded system development and design, application of ANSYS simulation software, and analyses of the growth and annealing parameters of TiO<sub>2</sub> nanotube (TNT) arrays and their effects on C<sub>37</sub>H<sub>27</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>3</sub> methylene blue and C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradations. He has published more than 20 seminar papers and SCI, SSCI, and EI international journal articles. (feilongzz@gmail.com)



Chi-Yu Lin received his Ph.D. degree in aeronautics and astronautics from National Cheng Kung University, Tainan City, Taiwan, R.O.C., in 2013. He now works at the Air Force Institute of Technology. His current research interests include flow control, unmanned aerial vehicles, experimental fluid mechanics, analyses of the growth and annealing parameters of TiO<sub>2</sub> nanotube (TNT) arrays and their effects on C<sub>37</sub>H<sub>27</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>3</sub> methylene blue and C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradations, and fluorescent materials. (takiincku@yahoo.com.tw)



**Yu-Xiang Dong** was an undegraduate student in the Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung, Taiwan. He is now with the Thin-film and Optical Materials Laboratory of Professor Cheng-Fu Yang to learn the fabrication technology of TiO<sub>2</sub> nanotube (TNT) arrays and investigate their effect on C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S methyl orange degradation. (maltesel114@gmail.com)



Cheng-Fu Yang received his B.S., M.S., and Ph.D. degrees in 1986, 1988, and 1993 from the Department of Electrical Engineering of Cheng Kung University. He has vast experience in different areas of materials and electrical applications, including ferroelectric ceramics, microwave ceramics, dielectric thin films, nonvolatile ferroelectric random access memories, transparent conduction oxide (TCO) thin films, ceramic-polymer composites, silicon-based thin-film solar cells, CIGS or CIS solar cells, inorganic optical ceramics, microwave antennas, and microwave filters. Since 1990, he has published more than 210 SCI and SSCI journal papers and more than 140 EI journal papers, as well as more than 260 domestic and international conference papers. (cfyang@nuk.edu.tw)



Hong-Yu Shih received his B.A. in 1991 from National Taiwan University, M.S. in 1994 from Rutgers University, and Ed.D. from the University of South Dakota in 2000. He has vast experience and interests in different areas of quantititve analysis of culture, including culture image analysis, culture-diversity research design, and foreseen culture conflicts. Since 2002, he has published more than 50 papers in prestigious journals and domestic/international conferences. (hongyushih@stust.edu.tw)