

# Study on the Preparation of Nanosized Titanium Dioxide with Tubular Structure by Hydrothermal Method and Their Photocatalytic Activity

Yu-Zhen Zeng, Yu-Chang Liu, Yun-Fang Lu, and Jen-Chieh Chung

**Abstract**—In this study, we attempt to synthesize nanosized titanium dioxide with tubular structure for the photocatalytic applications, and self-prepared anatase  $\text{TiO}_2$  powder is the precursor. We demonstrated that nanosized  $\text{TiO}_2$  with tubular structure could be synthesized with a NaOH hydrothermal treatment on  $\text{TiO}_2$  powder and then with a subsequent acid washing. Furthermore different formation mechanism of nanotubes could be got by controlling the pH value of acid washing step. In this research, we investigate the influence of different pH values of acid washing on the crystalline-structure, optical absorption range, porosity, specific surface area, and photo-catalytic activity of nanotubes. The influence of the preparation methods on crystalline-structure of photocatalysts and activities of photocatalytic reaction are obvious. The experimental results show that anatase  $\text{TiO}_2$  nanotubes are produced as the pH value of acid washing is decreased to 1.3. Under this condition, the outer diameter and length of the nanotube is about 10 nm and  $1\mu\text{m}$  respectively, its group is like petals. And it possesses the largest surface area of  $381.2\text{ m}^2/\text{g}$ , band gap of 3.12eV and the best photocatalytic activity.

**Index Terms**—Anatase, hydrothermal method, photocatalytic activity, titanium dioxide nanotube.

## I. INTRODUCTION

Titanium dioxide ( $\text{TiO}_2$ ) has been widely employed in paint, coating, and filler because of its high stability, simple preparation, and non-toxicity. It's also a kind of semiconductor for such applications as optoelectronic device, sensor and alloy materials. And  $\text{TiO}_2$  has excellent photocatalytic properties. In 1972, Fujishima and Honda [1] succeeded for the first time, in the photoelectrochemical decomposition of water under visible light irradiation with n-type  $\text{TiO}_2$  as the anode and without any applied electric power. It has drawn much attention, and numerous efforts have been synthesized nanosize  $\text{TiO}_2$  because of its photocatalytic properties.  $\text{TiO}_2$  had also been fabricated into nanopowders, films, mesoporous  $\text{TiO}_2$  with different methods. Recently, much researchers devoted to the synthesis of nanotubes with large specific surface areas and their structure were demonstrated as  $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$  [2], [3],  $\text{H}_2\text{Ti}_3\text{O}_7 \cdot 0.8\text{H}_2\text{O}$  [4],  $\text{H}_2\text{Ti}_4\text{O}_9 \cdot \text{H}_2\text{O}$  [5], lepidocrocite titanates [6], [7], etc.

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Nanotubes with the diameter of 8~10nm and length of 10~1000nm were produced by alkali reaction for 24~72h [8]. Not only titanium, Oxygen atom but also hydrogen was discovered from the EDX analysis, and its chemical formula was considered as  $\text{H}_2\text{Ti}_n\text{O}_{2n+1}$ , structure as anatase-rutile phase. Seo *et al.* [9] reported that the amount and length of nanotubes was proportional to the reaction temperature. The largest amount of nanotubes was manufactured at  $200^\circ\text{C}$ . It possessed the length of 200-250nm, surface area of  $270\text{ m}^2/\text{g}$ . Tsai *et al.* [10] had prepared  $\text{TiO}_2$  nanotubes with hydrothermal method. The variation of the surface area, diameter, and pore size of nanotubes was investigated by controlling the temperature from 110 to  $150^\circ\text{C}$ . A model of lamellar to tubular structure was proposed for the formation mechanism of  $\text{TiO}_2$  nanotubes after acid rinsing.

In this study, we demonstrated that  $\text{TiO}_2$  nanotubes could be synthesized with a NaOH hydrothermal treatment on self-prepared anatase  $\text{TiO}_2$  powders. And the effects on structure, specific surface area, and photocatalytic activity for KI of  $\text{TiO}_2$  nanotubes were investigated by adjusting different pH values during the acid rinsing process.

## II. MATERIALS AND METHODS

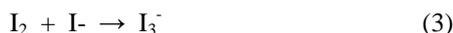
### A. Experiment

The precursor used for nanotube production was self-prepared anatase  $\text{TiO}_2$  powder, which was synthesized from titanium ethoxide by sol-gel method. And the approach for manufacturing  $\text{TiO}_2$  nanotubes was processed with hydrothermal method in autoclave. The preparation was initiated by treating self-prepared anatase  $\text{TiO}_2$  powder with strong base such as a NaOH solution into a Teflon-lined stainless autoclave at  $110^\circ\text{C}$  for 20h. The process was similar to those reports [11], except that the present treatment was conducted hydrothermally, rather than under atmospheric pressure. After this treatment and subsequent cooling, the paste in the bottom layer of Teflon was taken out to pH-value regulation by titrating with HCl solution. The final products were obtained by washing with DI water and subsequent drying.

### B. Characterization of Titanium Dioxide Nanotube

The phase identification of those samples from different synthesis processes was conducted with X-ray diffraction (XRD) using a SIEMENS D8 diffractometer equipped with  $\text{CuK}_\alpha$  radiation. The data were collected for scattering angles ( $2\theta$ ) range from  $20$  to  $80^\circ$  with a step size of  $0.02^\circ$ . The

porosity was characterized by N<sub>2</sub> adsorption at 77K using Micromeritics ASAP2020. And the specific surface area of the nanotube was determined from the Brunauer-Emmett-Teller (BET) equation. The UV-VIS spectrophotometer (Thermo, Eolution 600) was employed to determine the absorbance of light for the photocatalytic powders. The microstructures were explored with a scanning electron microscope (SEM, Hitachi S-4800). The photocatalytic activity was evaluated through the formation of I<sub>3</sub><sup>-</sup> due to oxidation of I<sup>-</sup> to I<sub>2</sub> as a model reaction. Photocatalytic reaction is based on the following reaction.



A reaction system was set up by adding 1g of catalyst powder into 100ml, 0.2M KI aqueous solution in a beaker. And this reactant was irradiated with UV light (500W) at room temperature with constant stirring speed. At regular time intervals, the suspension was extracted and filtered. The concentration of liberated I<sub>3</sub><sup>-</sup> ions in the clear supernatant was monitored by determining the absorbance at 350nm from an UV-Vis spectrophotometer. The result of absorbance was introduced into the Beer-Lambert's Law. Then the formation profiles of I<sub>3</sub><sup>-</sup> in the suspension of the nanotubes prepared at different formation pH value can be obtained as a function of UV irradiation time.

$$A = \epsilon b c \quad (4)$$

A: absorbance

$\epsilon$ : absorptivity coefficient of the solute (26303 dm<sup>3</sup>/cm·mol)

b: path length of light (1cm)

c: concentration of the solute

### III. RESULTS AND DISCUSSION

In this study, we attempted to synthesize anatase TiO<sub>2</sub> nanotubes by hydrothermal method with lower temperature. The powders withdrawn after the reaction were titrated with acid at different pH value of 0.8, 1.3, 2.2, 4, and 6.5, respectively. Lin [12] reported that TiO<sub>2</sub> powders used as the provider of raw material were *corroded* by strong acid, and the formation mechanism of nanotubes were in a dissolution-precipitation-growing procedure. However, Wang *et al.* [13] and T. Kasuga *et al.* [14] discussed that during treatment with NaOH solution, some Ti-O bonds of the TiO<sub>2</sub> precursor were broken, leading to the formation of lamellar fragments that were the intermediate phase in the formation process of the nanotubes material. The tubular structure was achieved by rolling slowly after the acidic post-treatment process, and therefore the acid rinsing step had become very important during the TiO<sub>2</sub> nanotubes formation process.

Crystalline structure is one of the key factors for photocatalytic activity of semiconductor photocatalysts. Fig. 1 shows the XRD patterns taken from initial TiO<sub>2</sub> (precursor) and photocatalysts with HCl washing to different pH values.

This fact indicates that the precursor of reaction is TiO<sub>2</sub> with anatase crystalline-phase the same as the reference of JCPDS 21-1272. In the pH-decreasing course with HCl washing of pH=6.5, there are characteristic peaks positioned at 2 $\theta$ =24° and 28°. These peaks have been assigned to the diffraction of titanates such as Na<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·5H<sub>2</sub>O, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, lepidocrocite titanates. The amount of H<sup>+</sup> ions provided from the acid may not be enough to replace the Na<sup>+</sup>, therefore the formation catalytic powders are still the structure with titanate not titanium dioxide.

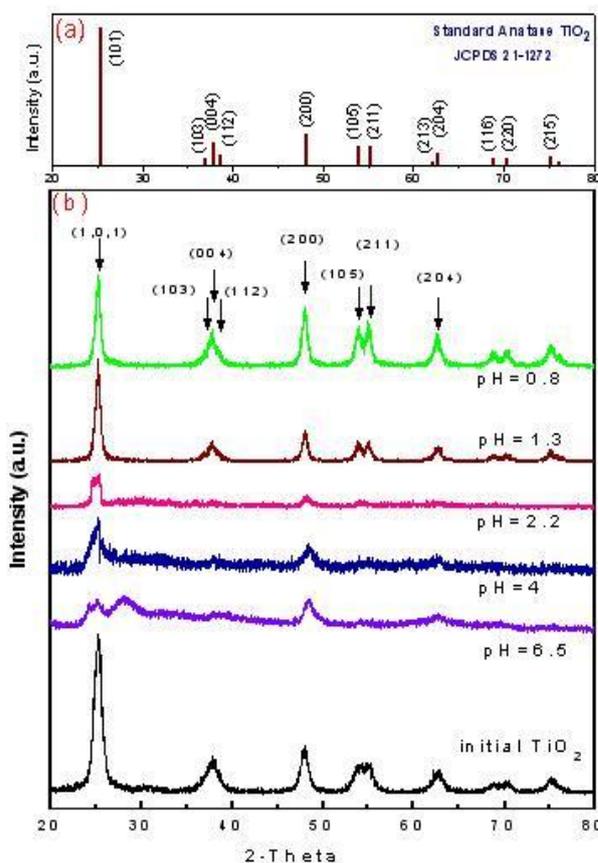


Fig. 1. XRD patterns (a). Standard TiO<sub>2</sub> with crystal structure of anatase from JCPDS 12-1272. (b). Initial TiO<sub>2</sub> and photocatalysts prepared from hydrothermal NaOH treatment, followed by acid rinsing under different pH values.

With the decrease in pH to 4 and 2.2, there appears to be a corresponding decrease in the intensity of the 28° peak relative to that of 24°. This has been ascribed to the decrease in the Na:H ratio of the titanates caused by the replacement of Na<sup>+</sup> with H<sup>+</sup> during acid washing. With the washing pH lowered to 1.3 and 0.8, the 24° peak shifts to 25.2°. The peak at 25.2° should correspond to the diffraction (1, 0, 1) of anatase TiO<sub>2</sub>. And other crystal faces of anatase TiO<sub>2</sub> can also be observed at the specific angles. The preceding results obtained with a progressive pH decrease have demonstrated a phase-transition sequence of Na-containing titanate, protonic titanate, and anatase TiO<sub>2</sub>. For the reason, the controlling of pH value during the acid rinsing process has an effect on the substituting degree of Na<sup>+</sup> ions with H<sup>+</sup>, structure, and crystal phase of products.

The variation of the specific surface area of TiO<sub>2</sub> nanotubes with different washing pH values is described in Fig. 2 and Table I The TiO<sub>2</sub> precursor synthesized by sol-gel method

possesses the specific surface area of  $151\text{m}^2/\text{g}$ . The surface area of catalyst with rinsing pH of 6.5 slightly upgrades to  $161.6\text{m}^2/\text{g}$  because of the shortage in  $\text{H}^+$  ions. The amount of  $\text{H}^+$  ions provided from acid rinsing may not be enough to replace the  $\text{Na}^+$ , therefore the formation of catalytic powders are still lamellar structure not tubular. When the pH value of catalysts during the acid washing process was controlled to 2.2 further, the proportion of  $\text{Na}^+$  ions within the titanate would be decreased due to the increasing of the washing acidity ( $\text{H}^+$ ). The percent of the generated  $\text{TiO}_2$  nanotube would be also increased by scrolling the lamellar titanate or titanium oxide sheets into tubular structure. So the specific surface area can be up to  $294.86\text{m}^2/\text{g}$ .

TABLE I: SPECIFIC SURFACE AREA, POROSITY, AND PORE SIZE OF THE COMMERCIAL  $\text{TiO}_2$  (P25), SELF-PREPARED ANATASE  $\text{TiO}_2$ , AND THE SPECIMENS OBTAINED FROM HYDROTHERMAL  $\text{NaOH}$  TREATMENT ON  $\text{TiO}_2$  WITH SUBSEQUENT POST-TREATMENT WASHING AT DIFFERENT PH VALUES

	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
P25	52.103	0.132	10.117
Self-prepared $\text{TiO}_2$	150.98	0.165	4.369
Photocatalyst pH=6.5	161.6	0.173	4.281
Photocatalyst pH=2.2	294.86	0.242	3.279
Photocatalyst pH=1.3	381.20	0.358	3.761
Photocatalyst pH=0.8	335.13	0.292	3.483

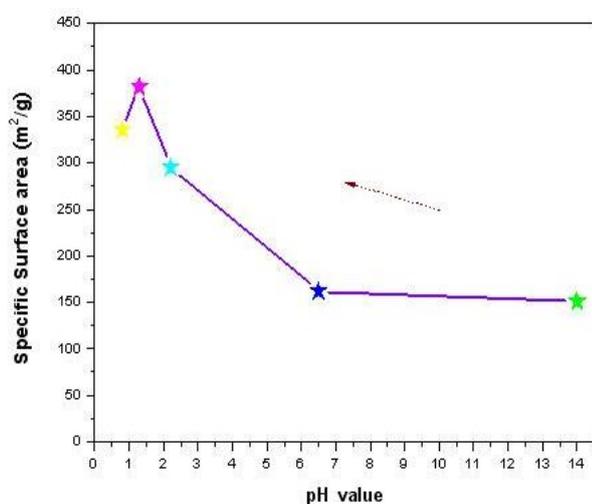


Fig. 2. Surface area of the specimens obtained from post-treatment washing at different pH values.

In the pH-descending course, the area increases to reach a maximum of  $381.2\text{m}^2/\text{g}$  at  $\text{pH}=1.3$ , and it then decreases. At  $\text{pH}=1.3$ , the aggregated nanotubes should be in a loose configuration, because the porosity was contributed to by the internal space as well as the interstice of the nanotubes. When we increased the acidity of the washing step to 0.8, the nanotubes became defective because of the destruction of the acidity. So the area is reduced to  $335.13\text{m}^2/\text{g}$  as well as the porosity. And also the surface area of the synthesized catalysts (titanate powder or  $\text{TiO}_2$  nanotube) are three to seven times larger than commercial  $\text{TiO}_2$  - P25 (25% anatase, 75% rutile) powders.

The UV-VIS absorption spectra of  $\text{TiO}_2$  nanotube or titanate with different pH values of acid washing are shown in Fig. 3. The catalysts of titanate with acid rinsing pH of 6.5 have absorption in the UV region within 400nm, and it possesses the band gap about 3.31eV. With the decreasing of acid rinsing pH value, the absorption range of photocatalysts will shift slightly to high wavelength. Comparing to these five curves, the absorption edge of  $\text{TiO}_2$  nanotubes with  $\text{pH}=1.3$  is observed at the widest wavelength range than others. And the band gap energy is the lowest of 3.12eV ( $\text{pH}=4$  of catalyst with 3.28 eV,  $\text{pH}=2.2$  with 3.28 eV).

However, when the pH value of acid rinsing process is decreased to 0.8, the absorption range of  $\text{TiO}_2$  nanotubes catalyst would shift back UV region. And the band gap energy becomes broad with 3.21eV. It's because the pH value of acid washing is too low that the phenomenon of the defect and disintegration appeared in the structure of nanotubes by the destruction of acidity. At this point, its surface tension becomes larger, lattice distance becomes shorter, resulting in a increase of the vibrational frequency of bond in the nano-particles. Therefore, the absorption spectra will shift to high wavenumber (low wavelength). The experimental results indicate that anatase  $\text{TiO}_2$  nanotubes are produced as the pH value of acid washing is decreased to 1.3. It possesses the largest surface area, the widest absorption range, and may be the best photocatalytic activity.

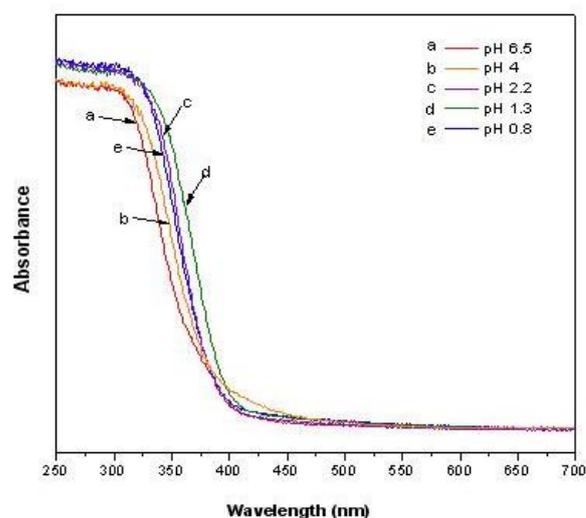


Fig. 3. UV-VIS dispersive reflectance spectra of photocatalysts obtained from post-treatment acid washing at pH value of (a) 6.5, (b) 4, (c) 2.2, (d) 1.3, (e) 0.8.

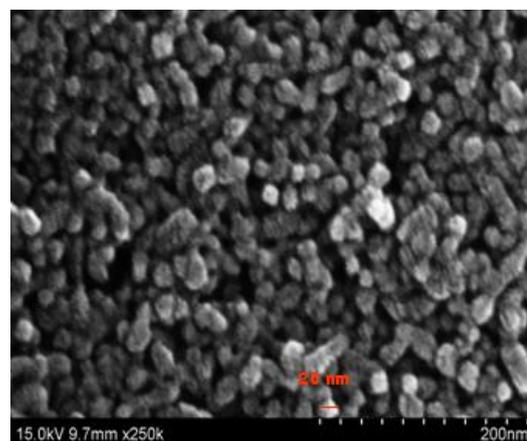


Fig. 4. SEM image of self-prepared anatase  $\text{TiO}_2$  powder via the sol-gel method.

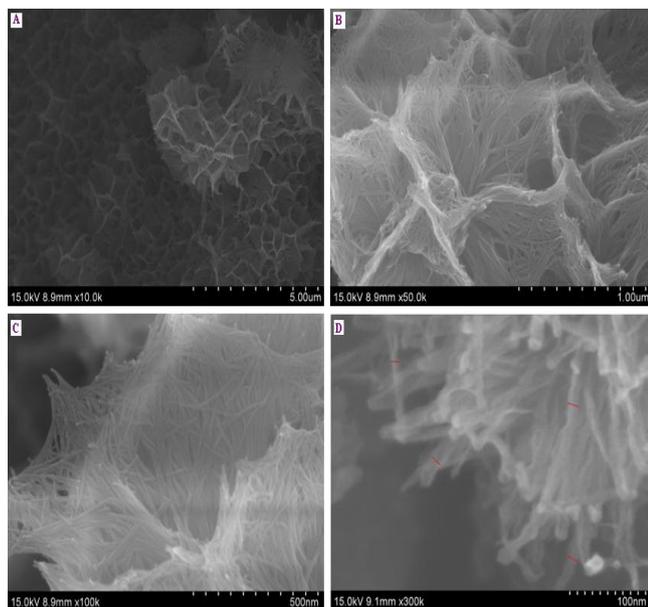


Fig. 5. The SEM image of  $\text{TiO}_2$  nanotube prepared from a NaOH treatment and with a subsequent acid washing of  $\text{pH}=1.3$ . (A) Magnification of 10,000 times, (B) 50,000 times, (C) 100,000 times, (D) 300,000 times.

The SEM image of the  $\text{TiO}_2$  nanopowder obtained by sol-gel method with titanium ethoxide is shown in Fig.4. The morphology explains the uniform distribution of the particles, and its particle size is about 20nm. In this study, self-prepared anatase  $\text{TiO}_2$  powder is the precursor of the synthesized  $\text{TiO}_2$  nanotube.

The SEM images of the samples prepared from a concentrated NaOH treatment and with a subsequent acid washing of  $\text{pH}=1.3$  are shown in Fig. 5. Fig. 5A is the microscopic figure with low-power field. We can observe that the uniformity of the structure distribution inside the catalysts is very excellent, and no particle is remained because of the incomplete reaction. As clearly seen from Fig. 5B and Fig. 5C, numerous fiberlike nanotubes grow from nano-size  $\text{TiO}_2$  particles. Its group is like a petal with bunchy arrangement not disarray. Under this condition, the outer diameter and length of the nanotubes is about 10nm and  $>1\mu\text{m}$  respectively from Fig. 5C and Fig. 5D. The  $\text{TiO}_2$  nanotubes made from nanopowders could improve significantly the specific surface area, increase the efficiency of electron transport and also separate the electron-hole pairs efficiently.

The photocatalytic activity is evaluated through the formation rate of  $\text{I}_3^-$  ions from the photocatalysis reaction of KI after illumination with UV light. By the definition, the higher concentration of  $\text{I}_3^-$  ions, the better photocatalytic activity of photocatalyst. And the properties of those titanate or nanotube with different acid washing pH values are showed in Fig. 6. We can observe that the photocatalytic activity of titanate with the controlling pH value of 6.5 is obviously the lowest than others. With the decreasing of acid washing pH value, the nanotubes are produced gradually, and the photocatalytic activity becomes better. When the washing pH value of nanotubes is lower to 2.2, the photocatalytic activity will be enhanced significantly.  $\text{TiO}_2$  nanotube synthesized with an acid washing treatment of  $\text{pH}=1.3$  possesses the best photocatalytic activity.

However, with the decreasing of pH to 0.8 further, it's seen clearly that the activity is lower than  $\text{pH}=1.3$ . It's because the

pH value of acid washing is too low that the phenomenon of the defect and disintegration appeared in the structure of nanotubes by the destruction of acidity. The variation trend of photocatalytic activity corresponds with the result of specific surface area. In summary, the clear anatase crystalline-phase of  $\text{TiO}_2$  nanotubes prepared with acid washing of  $\text{pH}=1.3$  can result in better efficiency of electron transport, the best porosity, and the largest specific surface area lead to the largest number of active sites which can participate in the reaction. The absorption edge is also observed at the widest wavelength range, so  $\text{TiO}_2$  nanotubes with  $\text{pH}=1.3$  possesses the best photocatalytic activity among those samples.

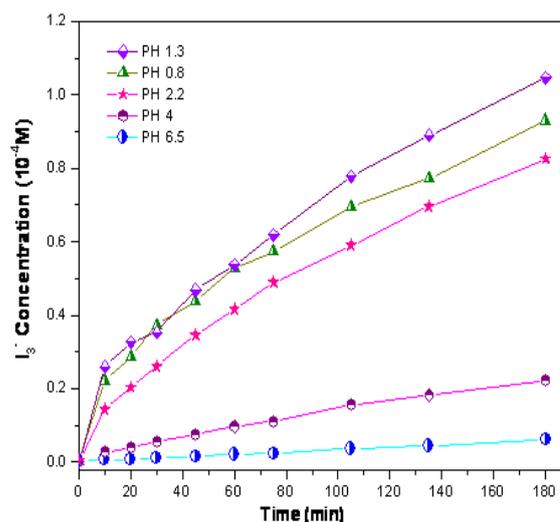


Fig. 6. The photocatalytic activities of photocatalysts evaluated through the formation rate of  $\text{I}_3^-$  ions from the photocatalysis reaction of KI after illumination.

#### IV. CONCLUSIONS

In this study, nanosized  $\text{TiO}_2$  with tubular structure were synthesized and investigated. According to the hydrothermal treatment of anatase  $\text{TiO}_2$  with concentrated NaOH solution, layered or lamellar structures were formed in the present work. After being washed with HCl, the lamellar phase will transform into titanate nanotubes with the gradual substitution of  $\text{Na}^+$  with  $\text{H}^+$ . This lamellar fragments, considered to be the intermediate phase for nanotubes formation, were mainly composed of  $\text{Na}_2\text{Ti}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Ti}_3\text{O}_7$  or lepidocrocite titanates. Then  $\text{TiO}_2$  nanotubes had been proved to be generated with acid washing pH value of 1.3. When we increased the acidity of the washing step to 0.8, the nanotubes become defective because of the formation of an anatase  $\text{TiO}_2$  phase (powder) on some spots of the tubes. They eventually transformed into nanocrystalline anatase with turbostratic stacking. For this reason, the controlling of pH value during the acid rinsing process has an effect on the substituting degree of  $\text{Na}^+$  ions with  $\text{H}^+$ , formation, crystalline structure, and even chemical composition of the final nanotube products.

As for the application of  $\text{TiO}_2$  nanotube, it has been used as the anode electrode of the dye-sensitized solar cell, and better cell efficiency and structure-related characteristics on the charge transport phenomenon have been reported [15]-[17].

Also some studies reported that TiO<sub>2</sub> nanotube exhibits proton intercalation/de-intercalation and resultant photoelectrochromic properties [18], [19], anion doping to develop visible light responsible TiO<sub>2</sub> nanotube for hydrogen generation from water splitting [20]-[23], and the photocatalytic degradation of organic pollutants using TiO<sub>2</sub> nanotube photocatalysts [24], [25]. As mentioned before, one of the future research direction of the TiO<sub>2</sub> nanotube may turn toward the application as the environmental and/or energy creating systems, which would become more important in the near future.

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**Yu-Zhen Zeng** was born in Changhua County, Taiwan on March 31th, 1982. Ms. Zeng obtained a master's degree within two years from Nation Taiwan University of Science and Technology in Taipei city, Taiwan and chemical engineering was her major. The major field was the investigation of modified poly (vinyl alcohol) polymer electrolyte membrane for direct-methanol fuel cells. After graduation, she is engaged in scientific research as an assistant engineer immediately in Institute of Nuclear Energy Research, Atomic Energy Council of Taiwan. She has been working here for seven years. She investigated the electrode materials of the dye-sensitized solar cell, photocatalysts for hydrogen generation from water splitting, and photoelectrochromic devices. And she published the article of "Study of the Nanostructured Mesoporous Titanium Dioxide by Sol-Gel Method for Dye Sensitized Solar Cell" in Materials Research Society-Taiwan 2010 Annual Conference (MRS-T). Now her research fields are about the electrode materials of supercapacitor and shielding materials for high-energy electromagnetic radiation.



**Yu-Chang Liu** was born in Taichung City, Taiwan on July 10th, 1976. He completed a PhD degree in chemical and materials engineering from National Central University in Taoyuan County, Taiwan in 2005. And he studied on the preparation of amorphous nano-sized nickel alloy catalysts and its application for liquid phase selectivity p-chloronitrobenzene hydrogenation reaction during the doctoral research period. After graduation, he went in for the scientific research as an associate engineer in Institute of Nuclear Energy Research, Atomic Energy Council of Taiwan up to now. He investigated the electrode materials of the dye-sensitized solar cell, photocatalysts for hydrogen generation from water splitting, and photoelectrochromic devices. And he published the paper of

“Nanosturctured mesoporous titanium dioxide thin film prepared by sol-gel method for dye-sensitized solar cell” in vol. 10 of Int. J Photoenergy in 2011. Now his interesting research fields are about high-energy electromagnetic radiation shielding materials and the energy storage system of vanadium redox battery.



**Yun-Fang Lu** was born in Tainan County, Taiwan on November 3rd, 1973. He earned a doctor's degree in chemical and materials engineering from Chang Gung University in Taoyuan County, Taiwan in 2009. And he studied on the solute clustering during nucleation and crystal grown in a stirred solution and the operation and control for various crystallizers. At first he worked at USI Corporation as a RD engineer. Then he has gone in for the scientific research as an

associate engineer in Institute of Nuclear Energy Research, Atomic Energy Council of Taiwan since 2004. He investigated the electrode materials of the dye-sensitized solar cell, photocatalysts for hydrogen generation from water splitting and photoelectrochromic devices in INER. And he published the article of “The electrochromic membrane of  $WO_3$  with RF magnetron sputter” in Materials Research Society-Taiwan 2010 Annual Conference (MRS-T). Dr. Liu, Ms. Zeng, and he are all the members of the same research team. So his research fields are the same as both two now.

Institute of Science and Technology, Armaments Bureau, M.N.D. during 1981-1986. Then he was employed as an assistant research fellow by Institute of Nuclear Energy Research, Atomic Energy Council of Taiwan during 1986-1990, associate research fellow during 1991-2000, and senior associate research fellow during 2001-2011. He has been employed under the position of senior research fellow and deputy head of chemical engineering division since 2012. His interesting research fields were hydrometallurgy, ceramic materials and the recovery of valuable metals during 1987-1990, chemical decontamination methods during 1991-1996, development of methods and procedures for soil decontamination during 1997-2003, the development of radioactive organic wastewater treatment technology during 2003-2005, the electrode materials of the dye-sensitized solar cell during 2005-2007, the preparation and technical development of colloidal decontamination solution during 2007-2010. And he has investigated the inorganic adsorbents applied in the radioactive wastewater treatments since 2011. He published the patents of “Method for making metal/titania pulp and photocatalyst” (Patent No. US 8,241,604, B2, Aug. 14, 2012) and “Wastewater treatment apparatus and method with stair-like heat treatment tanks” (Patent No. US 8,187,429 B2, May. 29, 2012). Dr. Chung has already devoted himself to scientific research for 33 years.



**Jen-Chieh Chung** was born in Tainan County of Taiwan on October 3rd, 1958. He completed a PhD degree in chemistry from National Tsing Hua University in Hsinchu City, Taiwan in 1997. And he studied on the decontamination of PCBs wastewater by radiolytic, electrochemical and microwave-Fenton technology during the doctoral research period.

He worked as a research assistant in Chung-Shen