

Photo-electrocatalytic activity of TiO₂ nanotubes prepared with two-step anodization and treated under UV light irradiation

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ABSTRACT: To improve the photo-catalytic degradation of salicylic acid, we reported the fabrication of ordered TiO₂ nanotube arrays by a simple and effective two-step anodization method and then these TiO₂ nanotubes were treated in a methanol solution under UV light irradiation. The TiO₂ nanotubes prepared in the two-step anodization process showed better photo-catalytic activity than those prepared in one-step anodization process. Also, compared with TiO₂ nanotubes without the UV pretreatment, the TiO₂ nanotubes pretreated in a methanol solution under UV light irradiation exhibited significant enhancements in both photocurrent and activity. The treated TiO₂ nanotubes exhibited a 5-fold enhancement in photocurrent and a 2.5-fold increase in the photo-catalytic degradation of salicylic acid. Also, the effect of addition of persulfate and periodate on the photo-catalytic degradation of salicylic acid was investigated. The results showed that the degradation efficiency of salicylic acid is increased with increasing persulfate and periodate concentrations. These treated TiO₂ nanotubes are promising candidates for practical photochemical reactors.

Keywords: Nanotubes; Nanostructures; Anodization; Photodegradation; Salicylic acid

INTRODUCTION

It is known that salicylic acid (SA) has an ototoxic effect and can induce transient hearing loss in zinc-deficient individuals. It can also cause fetal abnormalities and central nervous system depression if swallowed, inhaled or absorbed through skin. Salicylic acid has been identified as a water pollutant which originates from the manufacturing activities of paper milling, cosmetic industries and as a landfill leachate. Thus, there is great interest in developing advance oxidation techniques to effectively treat the salicylic acid pollutant for the purification of wastewater and groundwater [1]. A variety of techniques have been proposed for wastewater treatment. Heterogeneous photocatalysis is a promising alternative technique for eliminating organic pollutants from wastewater. Among various oxide semiconductor photocatalysts, TiO₂ is one of the most promising photocatalysts because of its biological

and chemical inertness, cost effectiveness, and the strong oxidizing power of its photo-generated holes [2,3]. TiO₂ has been intensively investigated as a photocatalytic material for solar energy conversion and environmental purification since Fujishima and Honda discovered the photo-catalytic splitting of water on TiO₂ electrodes in 1972 [4-8]. It is well known that TiO₂ is an excellent and high efficient photocatalyst. However, it only absorbs the ultraviolet light with a wavelength no longer than 387 nm due to its large band, which means the low utilization ratio of solar light for applications in photo-catalysis. Generally, TiO₂ with a large specific surface area can improve the photo-catalytic performance. Therefore, many efforts have been made to obtain nano-structured TiO₂-based materials with a large specific surface area [9]. Nano-structured titanium dioxide has been attracting attention from both fundamental and applied perspectives, driven by its unique photo-activity in a broad range of applications, extending from photocatalysis of hazardous chemicals, self-cleaning surfaces, to solar energy conversion, gas sensors, and hydrogen storage [7-17].

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One-dimensional TiO₂ nanostructures, particularly TiO₂ nanotubes, have received great attention because of their superior photocatalytic and photo-electronic performance over TiO₂ nanoparticles. TiO₂ nanotubes have been synthesized *via* various approaches, including using a template of nanoporous alumina, sol-gel processes, seeded growth method, hydrothermal techniques and the anodizing of titanium [18-20]. Among these, anodizing of titanium is a relatively simple process for the fabrication of TiO₂ nanotubes. Since Zwillig *et al.* reported the growth of TiO₂ nanotubes through the electrochemical anodization of titanium, many results on TiO₂ nanotubes have been reported to control the length, morphology, orientation, and the pore size of the TiO₂ nanotubes by tailoring the electrochemical conditions during anodizing process.

In the present work, we report a facile and effective approach for the enhancement of the photocatalytic activity of TiO₂. The TiO₂ nanotubes prepared in the two-step anodization process were treated in a methanol solution under UV light irradiation. The treated TiO₂ nanotubes showed considerable enhancements for photocatalytic oxidation of salicylic acid.

EXPERIMENTAL

Chemicals and Solutions

Ethylene glycol (EG), ammonium fluoride (NH₄F), Salicylic acid (SA) and methanol of analytical grade were obtained from Aldrich or Merck and used as received. All other chemicals were of analytical grade and were used as received without further purification. Distilled water was used throughout. Stock solutions were made by dissolving the salicylic acid in 0.5 M H₂SO₄ solution. Subsequent concentrations were obtained by diluting the stock solution with 0.5 M H₂SO₄ solution.

Fabrication of TiO₂ Nanotube Film Electrode

A two-step electrochemical anodizing method was used to fabricate the TiO₂ nanotube. Prior to anodizing, a piece of titanium sheet (99.99% purity, 1-mm thick) was cut into small rectangular pieces 10 × 40 mm and the titanium electrodes were first mechanically polished with different emery type abrasive papers, rinsed in a bath of distilled water, and then chemically etched by immersing in a

mixture of HF and HNO₃ acids for 1 min. The ratio of components HF/HNO₃/H₂O in the mixture was 1:4:5 in volume. The last step of pretreatment was rinsing with acetone and distilled water. The anodizing experiments were carried out using a conventional two-electrode system with titanium foil as anode and a platinum foil with about 20 cm² geometric area as cathode, respectively. All electrolytes consisted of 0.3 wt% NH₄F in an aqueous EG solution (2 vol% water in EG). All the anodizing experiments were carried out at room temperature. In the first-step anodizing, the titanium foil was anodized at 50 V for 1 h, and the nanotube layer was grown on the Ti surface. The nanotube layer was removed by sonicating in distilled water, and a mirror surface of titanium was exposed. Then, the pretreated titanium was used as anode again for the second-step anodizing at 50 V for 30 min. After the anodizing processes, the sample was cleaned with distilled water. To crystallize the as-anodized TiO₂ nanotubes, all samples were annealed at 450 °C for 3 h in air with heating and cooling rate of 30 °C min⁻¹. For the UV pre-treatment, a TiO₂ sample was placed in a quartz tube containing 5 ml of 50% methanol-H₂O (v/v) and it was irradiated under UV light for 30 min.

Characterization of TiO₂ Nanotube Film

The morphology and composition of the titanium oxide nanotube films were characterized by a scanning electron microscope (Philips, Model XL30) and an energy dispersive X-ray spectroscopy (EDX). XRD analyses were performed with a XRD using Simens 5000 diffractometer with a Cu-K α radiation source in scan mode.

Photo-electrocatalytic Experiments

At first, we designed a reactor system constructed from a quartz reactor, a TiO₂ nanotube film electrode as photo-anode (working electrode) and a platinum foil electrode as cathode (counter electrode). A 400 W Hg lamp was used as the UV light source. The distance between the light source and the electrode surface was 2 cm. The lamp was positioned vertically outside the reactor. The anode and cathode were placed in parallel and a saturated calomel electrode (SCE) served as the reference electrode. The solution in the cell was continuously stirred with a magnetic stirrer bar. An EG&G 2273 potentiostat/galvanostat was

used to apply an anodic potential bias during the photocatalytic degradation of salicylic acid.

RESULTS AND DISCUSSION

Characterization of the Electrode Morphology

Scanning electron microscopy (SEM) image of TiO₂ nanotubes prepared in the two-step anodizing process is shown in Fig. 1. The titanium oxide nanotubes are well aligned and organized into a highly oriented array. The tops of the tubes are open, similar to that of porous alumina obtained by anodic oxidation on aluminum. The average diameters of these tubes are approximately 20-70 nm. Figure 2 shows images of the titanium oxide nanotubes pretreated in a methanol solution under UV light irradiation. Figure 3 shows the XRD patterns of the prepared titanium oxide nanotubes. Except for the peaks (marked with stars) derived from Ti substrate, all of the diffraction peaks are attributed to those of the anatase TiO₂, revealing that the formed TiO₂ nanotubes exist in the anatase phase.

Photocatalytic Activity

The photocatalytic activity of the samples was evaluated by photocatalytic degradation of salicylic acid aqueous solution under UV light irradiation. However, under dark conditions without light illumination, the salicylic acid concentration does not change for every measurement using TiO₂ nanotube samples. Illumination in the absence of TiO₂ nanotube sample does not result in the degradation of salicylic acid. Therefore, the presence of both illumination and TiO₂ nanotube sample is necessary for the efficient degradation. These results also suggest that the degradation of salicylic acid aqueous solution is caused by photocatalytic reactions on TiO₂ nanotube sample surface under the UV illumination.

Figure 4 shows time dependence of the spectral absorbance of 100 ppm salicylic acid in 0.1 M H₂SO₄ taken at 5-min intervals during the photo-degradation process. The absorbance of salicylic acid on TiO₂ nanotubes prepared in one-step anodization process (curve a) at 205 nm decreased with time and after 20 min of photocatalytic degradation, 18% of the salicylic acid was removed from the solution. For comparison, the photocatalytic oxidation of salicylic acid was also carried out using TiO₂ nanotubes

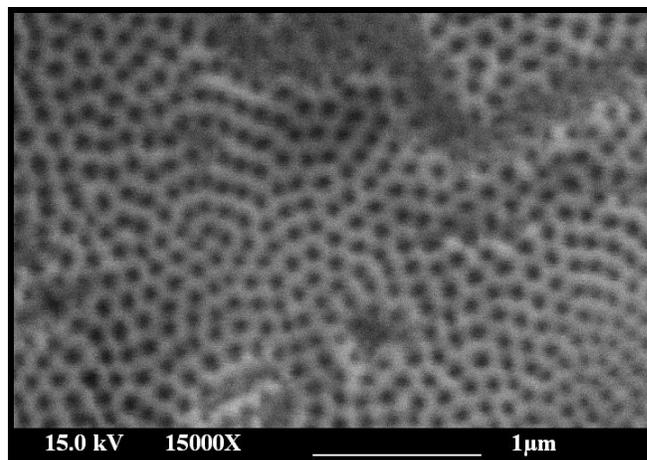


Fig. 1. Surface morphology of the TiO₂ nanotubes prepared in the two-step anodization process.

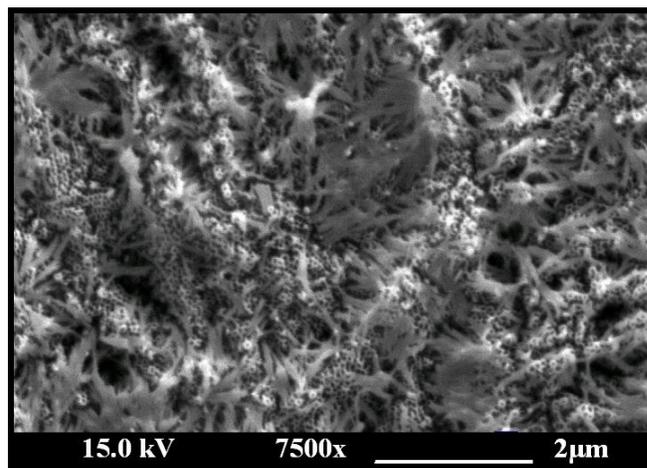


Fig. 2. Surface morphology of the TiO₂ nanotubes prepared in the two-step anodization process and treated in a methanol solution under UV light irradiation.

prepared in 2-step anodization process (curve b) and TiO₂ nanotubes prepared in 2-step anodizing process with the UV pretreatment in methanol (curve c); *ca.* 36% and 88% removal of the salicylic acid from solution was observed, respectively.

Figure 5 depicts the photocatalytic degradation profiles of salicylic acid as a function of time with (a) TiO₂

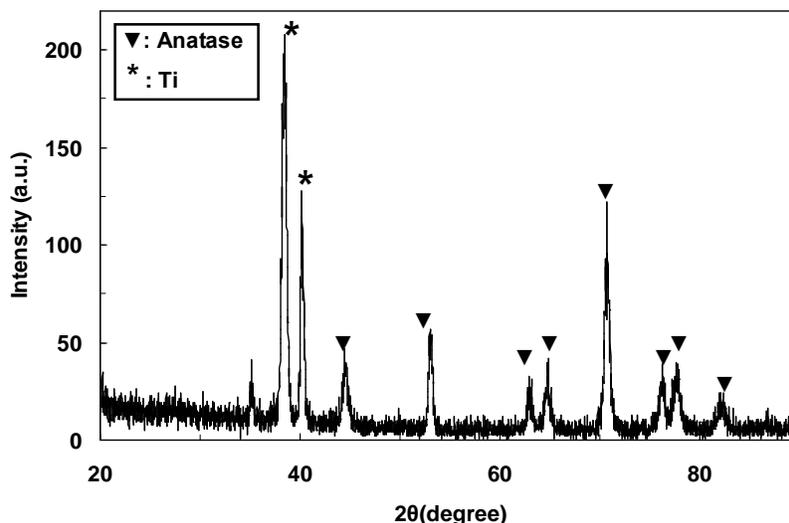


Fig. 3. XRD patterns of TiO₂ nanotubes prepared in 2-step anodization process.

nanotubes prepared in one-step anodizing process (b) TiO₂ nanotubes prepared in 2-step anodizing process and (c) TiO₂ nanotubes prepared in 2-step anodizing process with the UV pretreatment in methanol. The experimental data of Fig. 5 were found to fit approximately a pseudo-first-order kinetic model by the linear transforms $\ln(C_0/C) = kt$ (k is rate constant). The reaction rate of photocatalytic oxidation process of salicylic acid on TiO₂ nanotubes prepared in 2-step anodizing process with the UV pretreatment in methanol (0.0615 min^{-1}) was more than 2.9 times higher than that of photocatalytic oxidation process of salicylic acid on TiO₂ nanotubes prepared in 2-step anodizing process (0.0213 min^{-1}), indicating a significant enhancement of photocatalytic activity by the pretreatment in methanol solution under UV irradiation. This significant enhancement of the photocatalytic performance may be attributed to the inhibition of charge recombination of photo-induced electrons and holes, creation of oxygen vacancies, improvement in conductivity, and the promotion of interfacial charge-transfer kinetics at TiO₂ nanotubes [21].

Photo-electrochemical Properties of the TiO₂ Nanotubes

To further study, the transient photocurrent responses of the TiO₂ nanotube samples prepared at different conditions

are measured by switching the UV light on and off. Figure 6 shows a comparison of I-t curves of different samples. It can be seen that the photocurrent value rapidly decreases to zero as soon as the irradiation of light turns off, and the photocurrent comes back to a constant value when the light is on. This indicates that under UV light irradiation, most of the photo-generated electrons are transported to the walls of TiO₂ nanotubes and then transferred to titanium substrate to produce photocurrent. As depicted in Fig. 6, the response of the photocurrent under UV irradiation is very rapid, and the photocurrents for TiO₂ nanotubes prepared in one-step anodizing process (a), TiO₂ nanotubes prepared in 2-step anodizing process (b), and TiO₂ nanotubes prepared in 2-step anodizing process with the UV pretreatment in methanol (c) are 266 (curve a), 802 (curve b) and 3580 (curve c) $\mu\text{A cm}^{-2}$, respectively. The steady-state photocurrent of the TiO₂ nanotubes with the pretreatment is *ca.* 4.5 times higher than that of the un-pretreated TiO₂ nanotubes.

We further tested the stability of the pretreated TiO₂ nanotubes in a 0.1 M H₂SO₄ solution containing 100 ppm salicylic acid. The photo-current transients were recorded at an applied electrode potential of 0.56 V *vs.* SCE by several on-off cycles of intermittent irradiation. The duration of light pulses was set at 100 s, followed by dark current measurements for 50 s. As seen in Fig. 7, for the UV

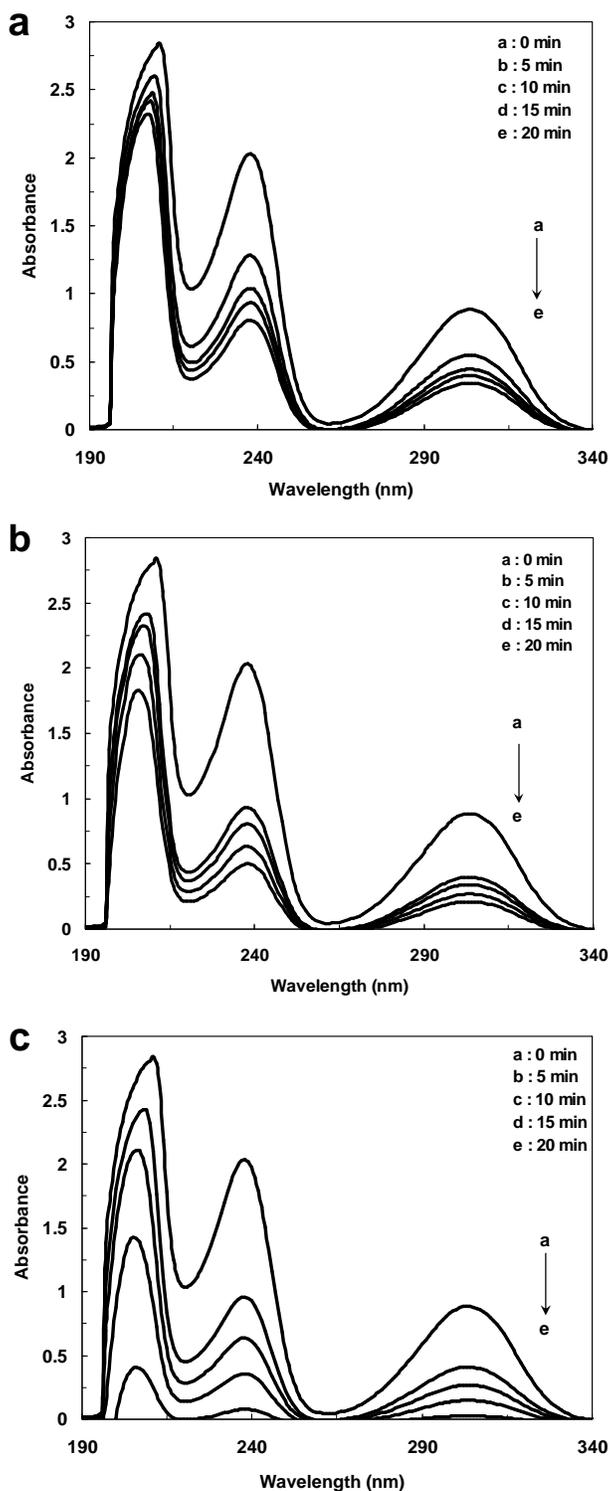


Fig. 4. UV-Vis absorbance spectra during the photo-catalytic degradation of salicylic acid using: (a) TiO₂ nanotubes prepared in one-step anodization process, (b) TiO₂ nanotubes prepared in 2-step anodization process and (c) TiO₂ nanotubes prepared in 2-step anodization process with the UV pretreatment in methanol.

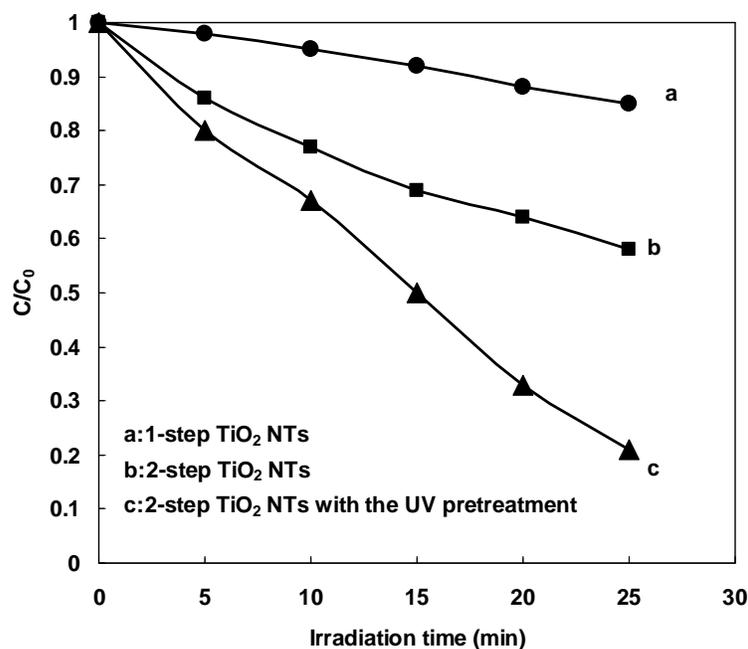


Fig. 5. Comparison of photo-catalytic activity of the samples prepared at various conditions for the photo-catalytic degradation process of salicylic acid.

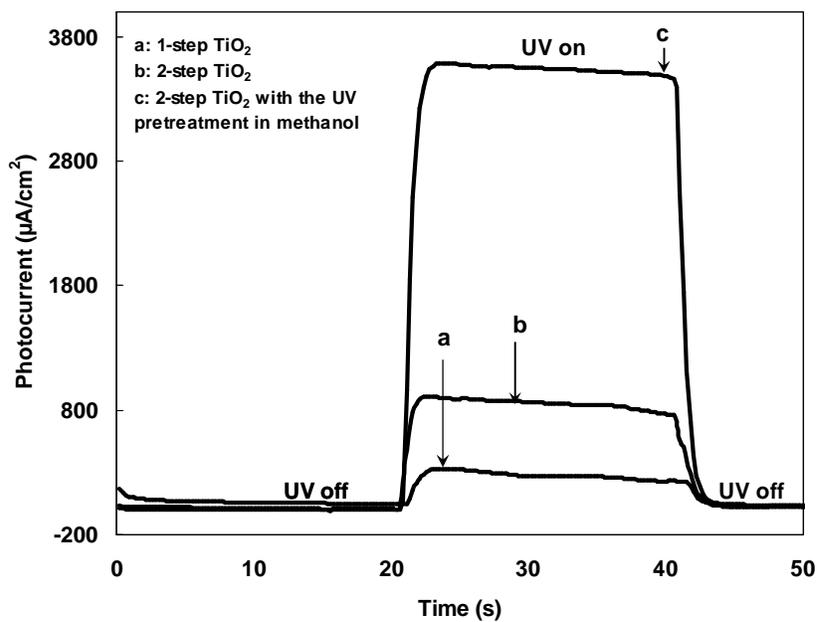


Fig. 6. The transient photocurrent-time profiles of (a) TiO_2 nanotubes prepared in one-step anodization process, (b) TiO_2 nanotubes prepared in 2-step anodization process and (c) TiO_2 nanotubes prepared in 2-step anodization process with the UV pretreatment in methanol.

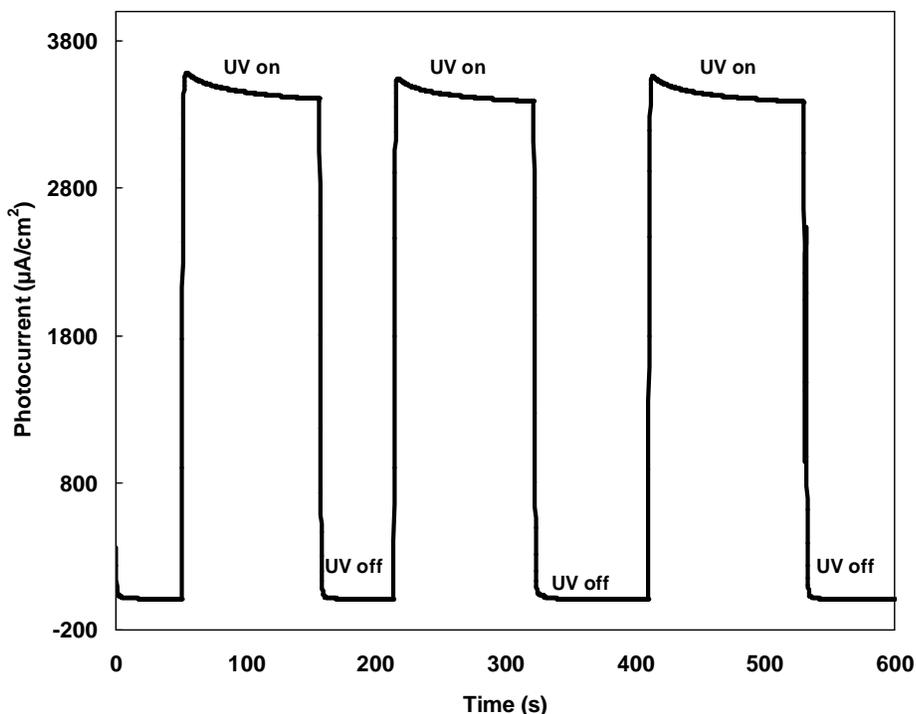


Fig. 7. Stability test for TiO₂ nanotubes with the UV pretreatment in methanol.

Table 1. Comparison of the Photocatalytic Activity of the Present Study with Similar Studies

Photocatalyst	Light sources	Pollutants	Degradation rate (%)	Ref.
Cu ₂ O/TiO ₂	Visible light	AO-I I	90	[24]
ZnTe/TiO ₂	Solar light	9-AnCOOH	100	[25]
WO ₃ /TiO ₂	UV light	Cr (VI)	100	[26]
Ag-N/TiO ₂	Visible light	AO-II	37	[27]
WO ₃ /TiO ₂	Visible light	MB	97	[28]
Fe/TiO ₂	Visible light	MB	50	[34]
Pretreated TiO ₂	UV light	SA	88	This work

pretreated TiO₂ nanotubes, there is almost no change in photocurrent, and the relative standard error for the photocurrent is *ca.* 1%, indicating the remarkable stability of the UV pretreated TiO₂ electrode. A comparison of the photocatalytic activity of the present study with similar studies is presented in Table 1.

Effect of Addition of Persulfate and Periodate on the Degradation of Salicylic Acid

The effect of addition of S₂O₈²⁻ and IO₄⁻ on the photocatalytic degradation of salicylic acid has been investigated by varying the amount of (NH₄)₂S₂O₈ and NaIO₄ from 0-100 mg l⁻¹. The results are shown in Figs.

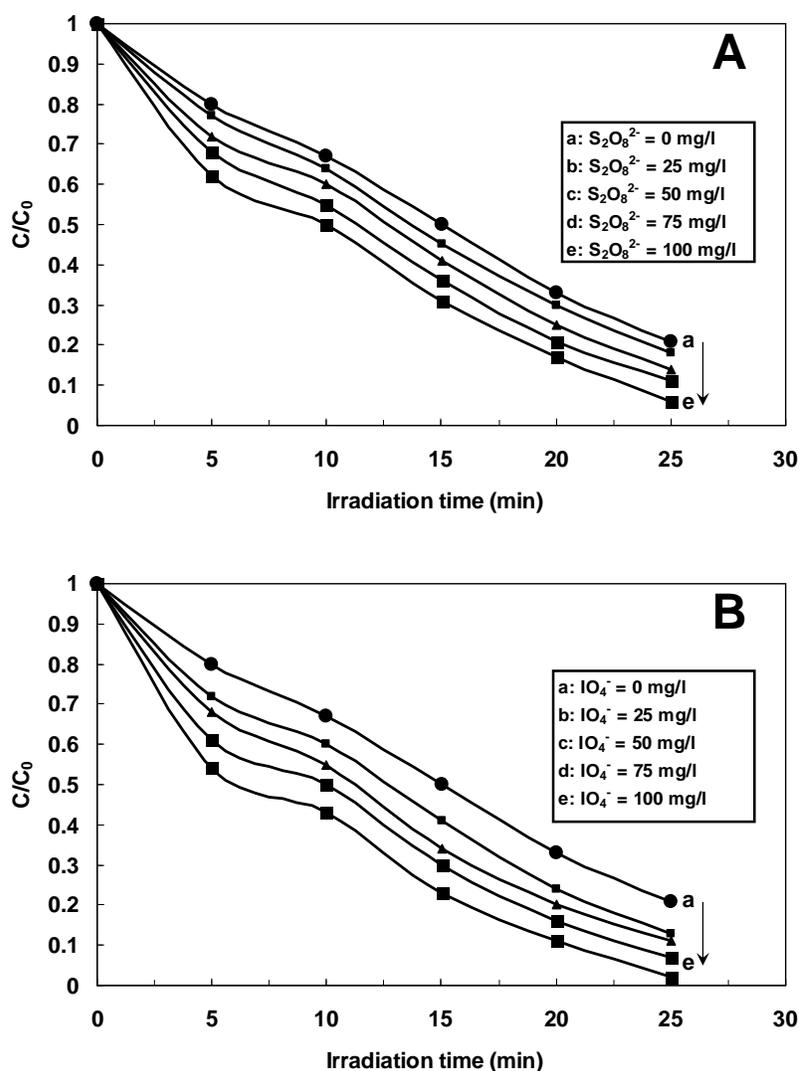


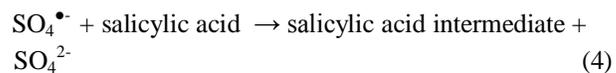
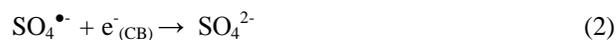
Fig. 8. Effect of addition of persulfate and periodate on the degradation of salicylic acid in solution containing 100 ppm salicylic acid in 0.1 M H_2SO_4 .

8A,B. It can be seen from Fig. 8A that increasing of persulfate concentration causes the increasing of degradation of salicylic acid. Addition of persulfate to photocatalytic processes enhances the degradation rate by two ways [22,23]:

(I) $S_2O_8^{2-}$ scavenges the conduction band electron and promotes the charge separation and production of other oxidizing species namely sulphate radical anion (Eq. (1)).



(II) $S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet-}$) both thermally and photocatalytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following pathways (Eq. (2-5)):



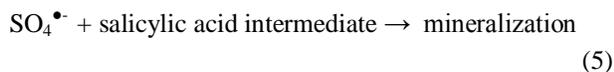


Figure 8B shows the effect of addition of IO₄⁻ on the photocatalytic degradation of salicylic acid. It can be seen that increasing of periodate concentrations increases the degradation efficiency of salicylic acid. IO₄⁻ increases the degradation of salicylic acid by capturing the electrons ejected from TiO₂ so that the probability of recombination of electrons and holes will decrease, *i.e.* the available number and the survival time of holes will be higher and thus react effectively with adsorbed water molecules to produce more hydroxyl radicals [23].



Also, the photocatalytic degradation of periodate under UV irradiation involves the formation of a number of highly reactive radical and non-radical intermediates as follows:



Comparison of UV/TiO₂/IO₄⁻ and UV/TiO₂/S₂O₈²⁻ processes on the photocatalytic degradation of salicylic acid shows that the efficiency of salicylic acid degradation using UV/TiO₂/IO₄⁻ is higher than UV/TiO₂/S₂O₈²⁻ because IO₄⁻ is one group of oxidants, which has more than two atoms of oxygen and one atom of halogen (I) as a central atom. Polarizability difference in oxidant atoms makes its central atom extremely electropositive. Therefore, IO₄⁻ can capture the electrons ejected from photo-catalyst more than other oxidants [23].

CONCLUSIONS

In summary, we have successfully demonstrated a facile

and effective approach for enhancing the activity of TiO₂ nanotubes. Compared with TiO₂ nanotubes without the UV pretreatment, the TiO₂ nanotubes pretreated in a methanol solution under UV light irradiation exhibited substantial enhancements in both photocurrent and activity. The degradation rate of salicylic acid using UV/TiO₂/oxidant was higher than that for UV/TiO₂ and increased with increasing oxidant concentration. The rate of degradation of salicylic acid using UV/TiO₂/IO₄⁻ was higher than UV/TiO₂/S₂O₈²⁻. The facile and effective approach proposed in this study opens many opportunities to develop highly active TiO₂ photo-catalysts for the pressing energy and environmental applications, ranging from water splitting, solar energy, and air purification to wastewater treatment.

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