

Photocatalytic degradation of microcystin-LR using TiO₂ nanotubes under irradiation with UV and natural sunlight

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In order to investigate the catalytic performance of anodic TiO₂ nanotubes and their practical application in the treatment of refractory microcystins (MCs) in natural-water samples, TiO₂ nanotubes of diameter of 50–80 nm were fabricated by anodization in C₂H₂O₄ · 2H₂O containing NH₄F. Under irradiation with natural sunlight, MC-LR was totally degraded after 1 d using the anodic TiO₂ nanotubes. In contrast, the removal efficiency without TiO₂ nanotubes was as low as 47.7% within 20 d. In addition, a mixture of anatase and rutile TiO₂ gave higher photocatalytic activity than the single phase did. The pH also influenced the adsorption capacity of the TiO₂ nanotubes. The order of MC-LR degradation efficiencies at different pH values was 3.5 > 8.0 > 10.0. After five repeated experiments on the degradation of MC-LR for 7 h, the degradation efficiency was still stable.

TiO₂ nanotube, microcystin, photocatalysis, sunlight irradiation

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TiO₂ has attracted significant attention because of its high oxidative power and low toxicity-features that have good potential for degrading many organic materials [1]. The hydroxyl radicals (•OH) produced by TiO₂ photocatalysis are much more oxidizing (2.8 V vs. NHE, normal hydrogen electrode) than many of the oxidants that are commonly used for disinfection of water, such as ozone (2.07 V vs. NHE), hydrogen peroxide (1.78 V vs. NHE), hypochlorous acid (1.49 V vs. NHE), and chlorine (1.36 V vs. NHE) [2]. It has been reported that microcystin (MC)-LR can be rapidly degraded by photocatalysis using TiO₂ [3–5]. The photocatalysts used in previous studies were TiO₂ powders and films. Generally, the separation of powdery TiO₂ from water is difficult and the suspended TiO₂ powder tends to aggregate, especially at high concentrations [6].

Recently, TiO₂ nanotubes have attracted particular interest because of their higher performances in pollutant degradation compared with TiO₂ films. The immobilized TiO₂

nanotubes are directly grown from a titanium substrate using an electrochemical anodization method and, as a result, they possess good mechanical adhesion strength [7–10]. In previous studies, TiO₂ nanotubes displayed excellent photocatalytic performance in the degradation of organic pollutants [7,11]. Most of the previous studies have focused on laboratory experiments rather than on applications in natural environments. Investigations of the photocatalytic activity of anodic TiO₂ nanotubes in natural environments could therefore provide useful information with respect to assessing their potential practical applications.

MCs, generated by *Microcystis aeruginosa*, can produce toxins that damage the nervous system or liver and hence are harmful to animal and human health [12]. MCs are relatively stable across a range of pHs and temperatures because of their cyclic structures. Consequently, conventional water treatment methods are not effective in removing MCs from drinking-water supplies [13]. Over 80 types of MC have been identified to date; MC-LR is the most common type found worldwide [14]. To the best of our knowledge,

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the degradation of refractory MC-LR using anodic TiO₂ nanotubes, especially under natural sunlight, has never been reported.

In this work, we investigated the photocatalytic degradation of MC-LR using TiO₂ nanotubes under irradiation with simulated/natural sunlight in natural-water samples. Highly ordered TiO₂ nanotubes were obtained by anodization in a solution of C₂H₂O₄·2H₂O and NH₄F with aqueous electrolytes. The samples were characterized and the photocatalytic degradations of MC-LR by TiO₂ nanotubes under UV light and natural sunlight were investigated. It is encouraging to find that under irradiation with natural sunlight, the MC-LR removal efficiency was significantly enhanced by the TiO₂ nanotube photocatalyst, especially under irradiation with natural sunlight.

1 Experimental

Exposure to MCs through ingestion, inhalation, and skin contact can cause acute and chronic health effects. All the experiments were therefore conducted in a biological safety cabinet with a fume hood. Appropriate laboratory clothing, safety gloves, and protective goggles are important when handling toxin solutions.

Titanium sheets (99.60% purity) were degreased in an ultrasonic bath with acetone, and rinsed in deionized water. The titanium sheet was used as the anode and a nickel sheet was used as the cathode. The titanium sheet was anodized at 20 V for 2 h in different concentrations of an oxalic acid + NH₄F electrolyte, using a direct-current power supply. After anodization, samples were annealed in the temperature range 400 to 700°C for 2 h. Field-emission scanning electron microscopy (FE-SEM; LEO1530VP) was used for morphological characterization of the TiO₂ nanotubes. The crystal structure was identified by X-ray diffractometry (XRD; Rigaku, D/max 2550PC) using a diffractometer with Cu K α radiation.

The photocurrent magnitude was measured in situ using an electrochemical station (CHI660C, CH Instruments Co., China) interfaced to a computer. TiO₂ nanotubes were used as the photoanode, nickel sheet was used as the counter electrode, and a saturated calomel electrode (SCE) electrode was used as the reference electrode. The experiments were performed under the following conditions: UV light irradiation (100-W high-pressure mercury lamp), vigorous bubbling, 0.1 mol/L sodium sulfate as electrolyte.

The MC-LR for the degradation experiments was purified from a naturally occurring bloom of *Microcystis aeruginosa*, using a previously reported method [15]. The photocatalytic degradation laboratory experiments on MC-LR were performed in a photochemical reactor under the following conditions: UV irradiation (100-W high-pressure mercury lamp, Beijing Tianmai-Henghui Light Co. Ltd.), an initial concentration of 5 mg/L (denoted by C₀), and aera-

tion with air at a flow rate of 0.5 L/min. The nanotubular photocatalysts were placed in the photochemical reactor, with a 50-mL cylindrical quartz-tube containing the MC-LR. The distance between the UV lamp and the reactor was 20 cm, and the area of the TiO₂ nanotubes was 20 cm². Experiments under irradiation with sunlight were also performed, in an outdoor balcony in May 2011. The quartz-tube was sealed and aerated with air. The air temperature was between 20 and 26°C. The other conditions were the same as in the laboratory experiments.

The concentration of MC-LR during the reaction (C) was monitored using high-performance liquid chromatography (Agilent 1120 HPLC) with the following conditions: Agilent TC-C18 (2) reversed-phase chromatography column; variable wavelength detector; chromatograms were analyzed and integrated at 238 nm; column temperature 30°C. Gradient elution involved a mobile phase of acetonitrile (A) and ultrapure water containing 0.05% trifluoroacetic acid (B). The program for the gradient elution was 0 min with A:B = 30:70, followed by 15 min with A:B = 40:60. Spectra of all the peaks were compared with those reported results.

2 Results and discussion

Figure 1 shows the SEM images of TiO₂ nanotubes anodized in electrolytes containing different NH₄F contents: (a) 1/12 mol/L oxalic acid + 0.2 wt.% NH₄F; (b) 1/12 mol/L oxalic acid + 0.5 wt.% NH₄F; and (c) 1/12 mol/L oxalic acid + 1.0 wt.% NH₄F. We can clearly see that a tubular morphology is obtained from electrolytes (b) and (c). The diameters of the TiO₂ nanotubes from electrolytes (b) and (c) are 50–80 nm, and those from electrolyte (a) are smaller and more uneven. In addition, the tubular length increases from 350 to 900–1000 nm with increasing NH₄F content. It can be seen that the tube wall from electrolyte (c) suffers from striking disintegration of morphological integrity; this is ascribed to localized chemical dissolution of the oxide surface as a result of a higher concentration of F⁻ [16].

The XRD patterns of the TiO₂ nanotubes annealed at 400, 500, 600, and 700°C for 2 h in an air atmosphere and an unannealed sample are shown in Figure 2. It is apparent that all the peaks of the unannealed sample pertain to the titanium substrate, indicating amorphous forms of TiO₂. After annealing at 400°C, anatase TiO₂ ($2\theta = 25.3^\circ$) is dominant; a mixture of rutile ($2\theta = 27.3^\circ$) and anatase phases appears when the annealing temperature is over 500°C. Moreover, the amount of rutile phase increases with increasing annealing temperature. Generally, TiO₂ (101) is the main crystal face of anatase, whereas TiO₂ (110) dominates the crystal faces of rutile. These two crystal faces of TiO₂ show both similarities and differences, resulting in both similar and different adsorption behaviors with water. They have different contact angles with a water interface, but produce a variety of hydroxide radicals in common [17,18].

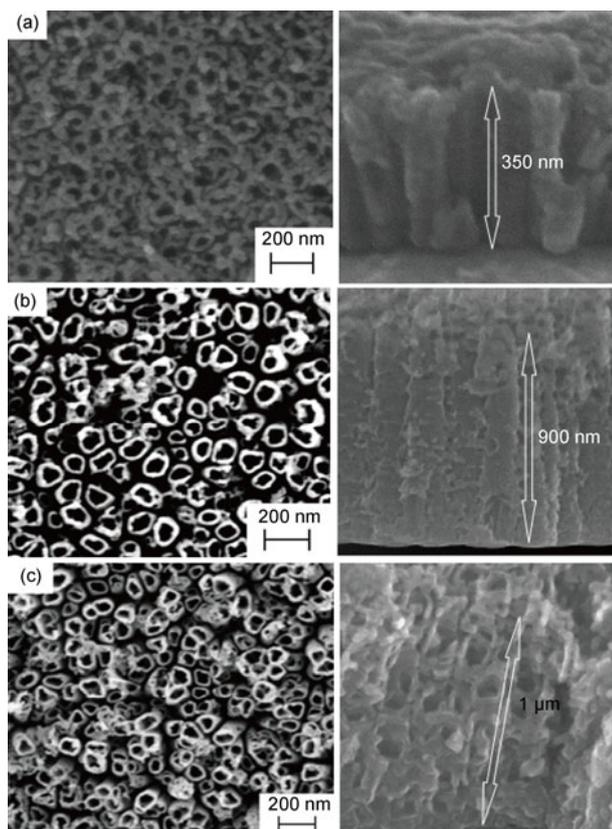


Figure 1 SEM images of TiO₂ nanotubes anodized at 20 V for 2 h in electrolytes of (a) 1/12 mol/L oxalic acid + 0.2 wt.% NH₄F, (b) 1/12 mol/L oxalic acid + 0.5 wt.% NH₄F, (c) 1/12 mol/L oxalic acid + 1.0 wt.% NH₄F.

Figure 3(A) shows the photocurrents of TiO₂ nanotubes anodized in electrolytes (a), (b), and (c) under different applied potentials (vs. SCE). It is apparent that the photocurrents of the samples anodized in electrolytes (b) and (c) are higher than that in electrolyte (a). Figure 3(B) presents the photocatalytic efficiencies of MC-LR removal under UV irradiation using TiO₂ nanotubes anodized in electrolytes (a), (b), and (c). We can see that the removal efficiencies with nanotubes from electrolytes (b) and (c) are close to each other, and a little higher than that for nanotubes from elec-

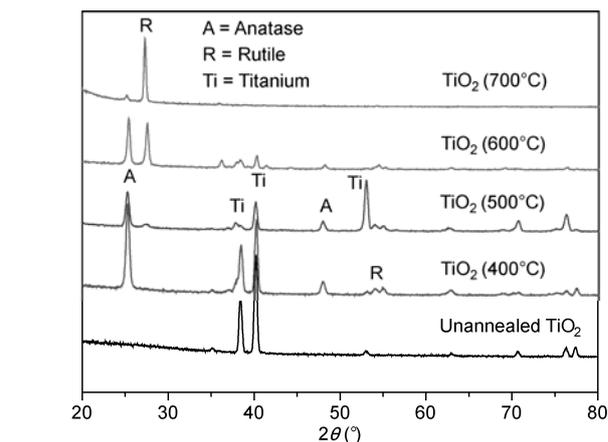
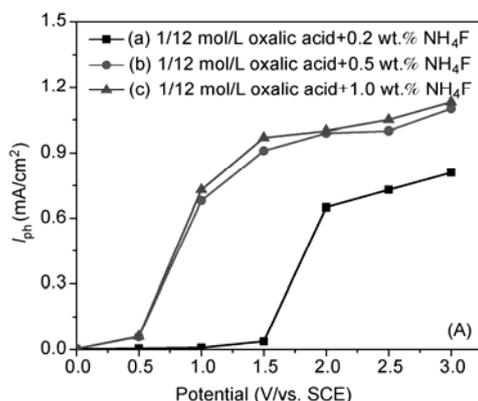


Figure 2 XRD patterns of TiO₂ nanotubes anodized in 1/12 mol/L oxalic acid + 0.5 wt.% NH₄F and annealed at different temperature.

trolyte (a). These results are in good agreement with the photocurrent results, and the higher efficiencies may be attributed to longer tube lengths [19,20]. When the tube length increases, more photons are absorbed and the photocurrent increases. This strong enhancement of the photoresponse can be ascribed to an increased light penetration depth and better scattering within a regular pore structure. Furthermore, the photogenerated charge carriers in the TiO₂ nanotube structure may be separated more efficiently than in a TiO₂ nanofilm, perhaps as a result of the short diffusion distance in the tube wall and the high contact area between the photocatalyst and the electrolyte [21–23].

The photocatalytic efficiencies of MC-LR removal under UV irradiation using TiO₂ nanotubes annealed at different temperature were also investigated, and the results are shown in Figure 4. The MC-LR removal efficiencies within 30 min using TiO₂ nanotubes annealed at 400, 500, 600, and 700°C are 95.3%, 97.2%, 96.7%, and 95.5%, respectively. It is generally considered that anatase can cause the creation of more surface oxygen vacancies to trap electrons and thus has higher photocatalytic activity than does rutile [24]. However, it has also been reported that there is a synergetic effect between anatase and rutile in appropriate proportions,

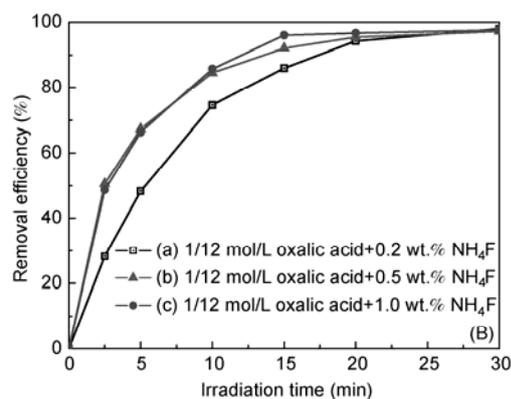


Figure 3 Photocurrent magnitude (A) and photocatalytic degradation of microcystin-LR (B) under UV irradiation using TiO₂ nanotubes anodized in different electrolytes and annealed at 500°C.

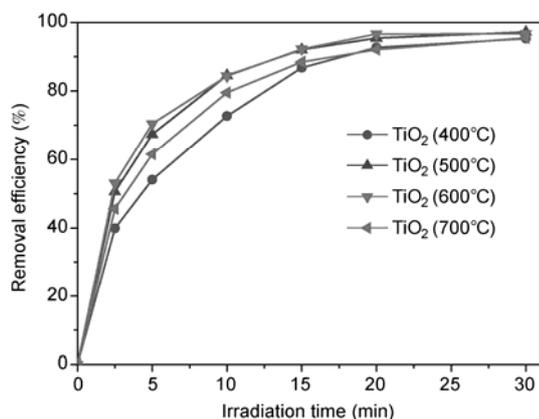


Figure 4 Photocatalytic degradation of microcystin-LR under UV irradiation using TiO_2 nanotubes anodized in 1/12 mol/L oxalic acid + 0.5 wt.% NH_4F and annealed at different temperature.

and the mixture has a higher photocatalytic activity than the single phase [25,26]. This can be explained by the fact that the band-gap energy of rutile TiO_2 (3.0 eV) is lower than that of anatase TiO_2 (3.2 eV), therefore it is easier for the matched electronic structures between the rutile and anatase phases to be activated to conduct the separation of photo-generated electrons and holes [25,27]. Nevertheless, a higher rutile content is not necessarily better. Consequently, the ratio of the two phases in the mixture has an important influence on the photocatalytic activity of TiO_2 .

In the above experiments, the pH values of the MC-LR solutions were not adjusted. In fact, the solution pH has an important effect on the characteristics of the surface electric charges of the catalysts. Experiments on the degradation of MC-LR solutions with pH values ranging from 3.5 to 10.0 were therefore also carried out, and the results are shown in Figure 5. It is clear that MC-LR removal efficiencies are in the order $\text{pH } 3.5 > 8.0 > 10.0$. The surface hydroxyl radicals of TiO_2 can react and produce proton transfer, giving amphoteric and electriferous properties. The point of zero-charge (PZC) of TiO_2 is approximately 6.4. Under the conditions $\text{pH} < \text{PZC}$, TiOH_2^+ dominates the surface of TiO_2

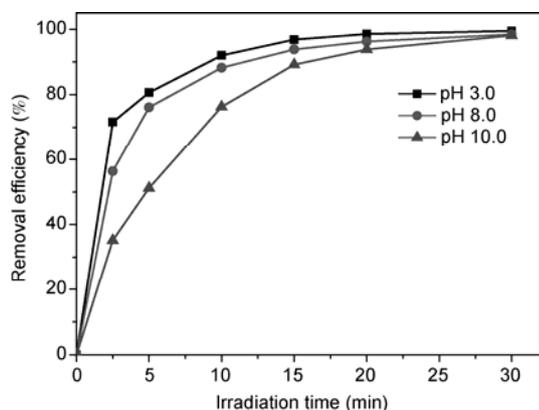
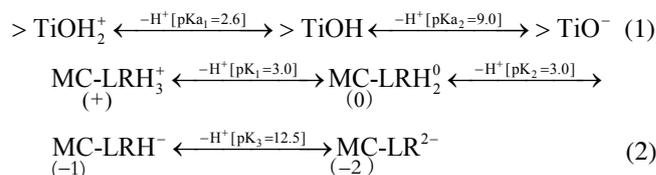


Figure 5 Photocatalytic degradation of MC-LR with different pH values using TiO_2 nanotubes anodized in 1/12 mol/L oxalic acid + 0.5 wt.% NH_4F and annealed at 500°C.

and can adsorb molecules with negative charges, whereas TiO^- is prevalent and can adsorb molecules with positive charges when $\text{pH} > \text{PZC}$ [28,29]. This process favors the photocatalytic reaction, as shown in reaction (1).



As shown in reaction (2), MC-LR can form MC-LRH^- at a solution pH of 3.5, indicating that molecules can be adsorbed by TiOH_2^+ and enhance the photocatalytic efficiency. When the pH is 10.0, large amounts of MC-LR^{2-} have negative charges, the same as TiO^- , which is a further disadvantage in terms of adsorption. In addition, the redox potentials of the conduction and valence bands of TiO_2 are influenced by the solution pH. An increase in pH can cause a decrease in the oxidative ability of TiO_2 [30].

Figure 6 presents the MC-LR photocatalytic removal efficiencies for different initial concentrations, using TiO_2 nanotubes annealed at 500°C. The removal efficiency increased when the initial concentration increased from 1 to 20 mg/L. It is generally considered that the photoreaction fits the Langmuir-Hinshelwood kinetics equation, with the rate being proportional to the coverage θ [26]:

$$r = k\theta = kKC / (1 + KC),$$

where k is the true rate and K is the adsorption constant. When the initial concentration is very low, the term KC in the denominator can be neglected, and then the rate is proportional to the initial concentration C_0 . As a result, at a certain concentration, the reaction rate increases with increasing initial solution concentration. However, the reaction rate is no longer related to the concentration for a high initial concentration. When the initial concentration is increased to 50 mg/L, large amounts of intermediates produced by MC-LR degradation tend to cover the TiO_2 surface and have a negative effect on the absorption of photonic energy. This retards the formation of $\bullet\text{OH}$ and

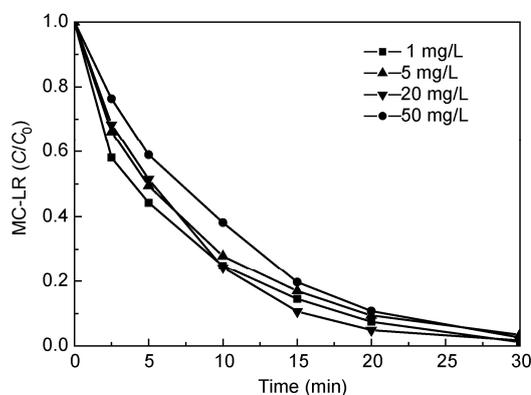


Figure 6 Photocatalytic degradation of MC-LR with different initial concentrations using TiO_2 nanotubes. TiO_2 nanotubes were anodized in 1/12 mol/L oxalic acid + 0.5 wt.% NH_4F and annealed at 500°C.

decreases the removal efficiency.

Figure 7(a) shows the degradation efficiencies of MC-LR under irradiation with sunlight. There is almost no degradation of MC-LR in the absence of a TiO₂ catalyst. A control experiment was also performed using a TiO₂ nanofilm prepared using metal organic chemical vapor deposition [31]. We can see that the MC-LR removal efficiency reaches as high as 96% within 7 h using TiO₂ nanotubes, and 66% using the TiO₂ nanofilm. There are two reasons for this, namely the difference between the band-gap energies and the specific surface areas of the nanotubes and the film [7]. The higher band-gap energy of the TiO₂ nanotubes means that stronger oxidized photocarriers can be generated under irradiation. Furthermore, the larger specific surface area of the TiO₂ nanotubes enables adsorption of larger amounts of organic matter for degradation [7]. Figure 7(b) also shows that MC-LR is totally degraded after 1 d, whereas the removal efficiency without a photocatalyst is as low as 47.7% within 20 d. This period is in accord with the report that the half-life of MC-LR decomposition is around 10 d on exposure to UV light [32]. It is exciting to find that there is a significant difference between the MC-LR removal efficiencies under natural sunlight irradiation with and without TiO₂ nanotubes. Consequently, we can draw the conclusion

that TiO₂ nanotubes possess excellent photocatalytic activity.

The reusability of the TiO₂ nanotubes was investigated by repeating the photocatalytic degradation of MC-LR under irradiation with sunlight for 7 h five times. The TiO₂ nanotube photocatalyst was cleaned by ultrasonication after each experiment. As shown in Figure 8(a), it is obvious that the morphology of the catalyst surface was not as clear as it was before use. Moreover, the surface suffered from some disintegration of morphological integrity. The tube boundaries were not distinct, and some tubes even disappeared and formed holes. This might be attributed to the ultrasonic cleaning to remove adsorbed organic matter. However, it is encouraging to find that after five repeated experiments, the degradation efficiencies were remarkably stable, and during the last run were still around 75% (Figure 8(b)). The TiO₂ nanotube photocatalyst therefore possesses remarkable stability. This photocatalyst is promising for treating refractory MC-contaminated water.

3 Conclusion

In conclusion, we demonstrated the fabrication of TiO₂ nanotubes of diameter 50–80 nm by anodization with

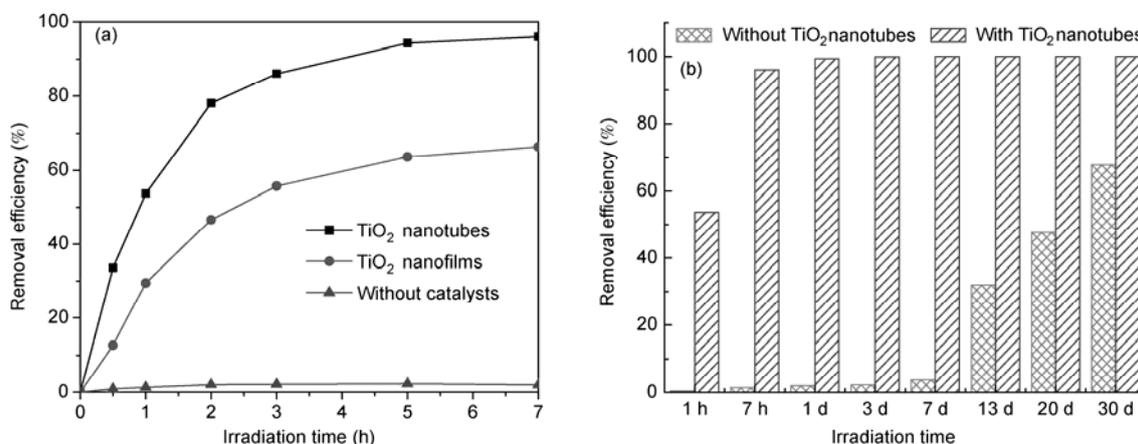


Figure 7 Degradation efficiencies of microcystin-LR under irradiation of sunlight within (a) 7 h using TiO₂ nanotubes and nanofilms, (b) 30 d using TiO₂ nanotubes.

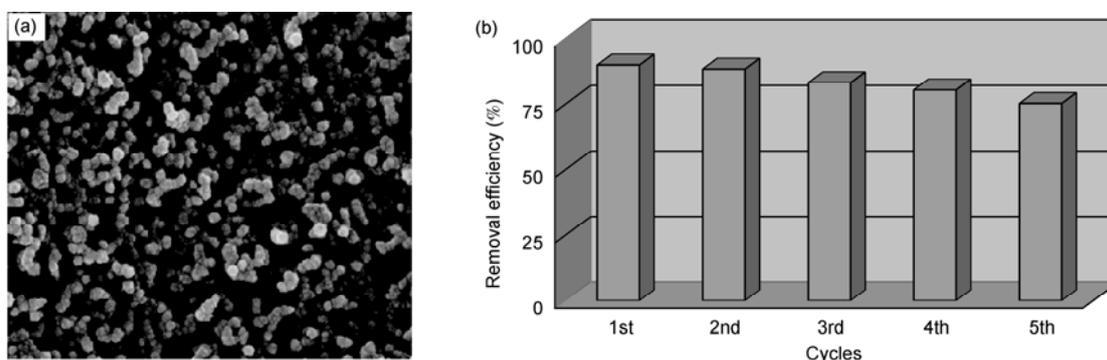


Figure 8 (a) SEM of TiO₂ nanotubes after 5 repeated experiments and (b) degradation efficiencies of microcystin-LR on TiO₂ nanotubes for 5 experimental runs were anodized in 1/12 mol/L oxalic acid + 0.5 wt.% NH₄F and annealed at 500°C.

$C_2H_2O_4 \cdot 2H_2O$ containing NH_4F . The photocatalytic degradation of MC-LR using TiO_2 nanotubes annealed under different temperatures confirmed that a mixture of anatase and rutile had higher photocatalytic activity than the single phase. In addition, the pH can change the properties of the surface electric charges and the redox potentials of the conduction and valence bands of TiO_2 , and can therefore affect its adsorption capacity.

Under irradiation with natural sunlight, MC-LR was totally degraded after 1 d using TiO_2 nanotubes. In contrast, the removal efficiency without TiO_2 nanotubes was only 47.7% within 20 d, indicating the excellent photocatalytic activity of the TiO_2 nanotubes. The TiO_2 nanotube photocatalyst has remarkable stability and the removal efficiencies were around 75% during five experimental runs. This type of photocatalyst is promising for the treatment of MC-contaminated water.

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