

逢甲大學學生報告 ePaper

報告題名：

^[1] 二氧化鈦納米管陣列：

管長度對百草枯的光催化降解的影響

TiO₂ Nanotube arrays:

Influence of tube length on the photocatalytic degradation of Paraquat

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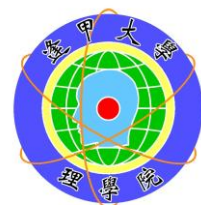
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中文摘要

(1) 目的：

高序性的 TiO_2 奈米管因光催化去除有機污染物而備受關注。而管形態在光催化作用中具有良好的效果。但是尚未有研究來解釋最佳光催化活性與管長度的關係。而本篇觀察陽極生長過程中管形態的變化情形，並對光催化活性進行分析。

(2) 過程及方法：

我們透過陽極氧化法製作奈米管陣列並且觀察在陽極生長過程中管的形態演變的狀況，並透過 SEM、XRD 等儀器來分析相應的光催化活性與管長度之間的關係。

(3) 結果：

TiO_2 奈米管陣列的光催化活性大多數取決於陽極氧化時間。小內徑的短管光催化活性較差，是因為污染物擴散困難，而長管具有薄壁，因此光在更長距離被吸收，並且污染物必須進一步擴散以到達由電子電洞對產生的氧化物質才可以產生反應，而最佳管長度由這兩個結果之間折衷給出。

關鍵字： 二氧化鈦奈米管陣列、光觸媒、光催化降解、陽極氧化法

Abstract

Highly ordered TiO₂ nanotubes have attracted a lot of attention for the photocatalytic removal of organic pollutants. A few studies demonstrated that the tube morphology plays a key role on the photocatalytic activity. However, no studies have been performed to explain the optimal photocatalytic activity observed for a precise tube length. Here we studied how the morphology of the tubes evolves during anodic growth and we evaluated the corresponding photocatalytic activity. In our conditions, the optimal activity was found for 7 μm long tubes. The SEM study reveals that short tubes have a small pore opening thus hindering pollutant diffusion into the tubes. On the other hand, tubes longer than 7 μm have thinner walls due to etching by the fluoride ions. Consequently the volume of TiO₂ decreases strongly in the upper part of the tubes as the tube length increase and light should travel a longer pathway before absorption and production of electron-hole pairs. Hence the organic species have to diffuse further and the photocatalytic activity decreases.



Keyword : TiO₂ nanotube arrays, photocatalyst, anodic oxidation

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一、文獻回顧

1. 摘要

高序性的 TiO_2 奈米管因光催化去除有機污染物而備受關注。而管形態在光催化作用中具有良好的效果。但是尚未有研究來解釋最佳光催化活性與管長度的關係。而本篇觀察陽極生長過程中管形態的變化情形，並對光催化活性進行分析。根據實驗結果， $7\mu\text{m}$ 的奈米管有最佳的光催化性能。透過 SEM 分析，短管具有較小的孔，這會阻礙污染物擴散到管中。而由於氟離子的蝕刻，超過 $7\mu\text{m}$ 的奈米管管壁會更薄。奈米管隨著長度的增加，其上半部 TiO_2 的含量會下降，這樣在產生電子電洞對之前，光線所需的路徑會拉長。使得有機物要降解必須擴散的更遠才行，也導致光催化的活性下降。

2. 介紹

近期水污染和大氣污染的問題備受關注，光觸媒可利用光催化反應使污染物降解成無毒無害的二次產物淨化水及空氣，受到廣泛之重視。而二氧化鈦 (TiO_2) 是研究最多的半導體之一，因為它具有無毒、使用壽命長、高化學穩定性和光催化效率。本文利用百草枯 (1,1-二甲基-4,4-聯吡啶二氯化物) 進行光催化降解，已知這個除草劑會被這些氧化自由基降解。

光催化降解是先產生單吡啶酮和二吡啶酮，然後在完全礦化後產生二氧化碳，水， NH_4^+ ， NO_2^- ，還有 NO_3^- 。在過程中有不少阻礙而降低此光催化過程，例如：電子電洞的再結合， TiO_2 表面積太小無法有效吸收污染物及光能，二氧化鈦僅在紫外光區具有活性，因此導致光催化效率還未令人滿意。而奈米管比起其他奈米材料，多了內徑的面積，吸收光線和反應之面積會大幅提升，若是將其製備為奈米管陣列可使電子傳輸方向一致且順暢，應可大大的增加污染物的降解效率。所以我們製作奈米管陣列並且觀察在陽極生長過程中管的形態演變的狀況，來判斷相應的光催化活性與管長度之間的關係。

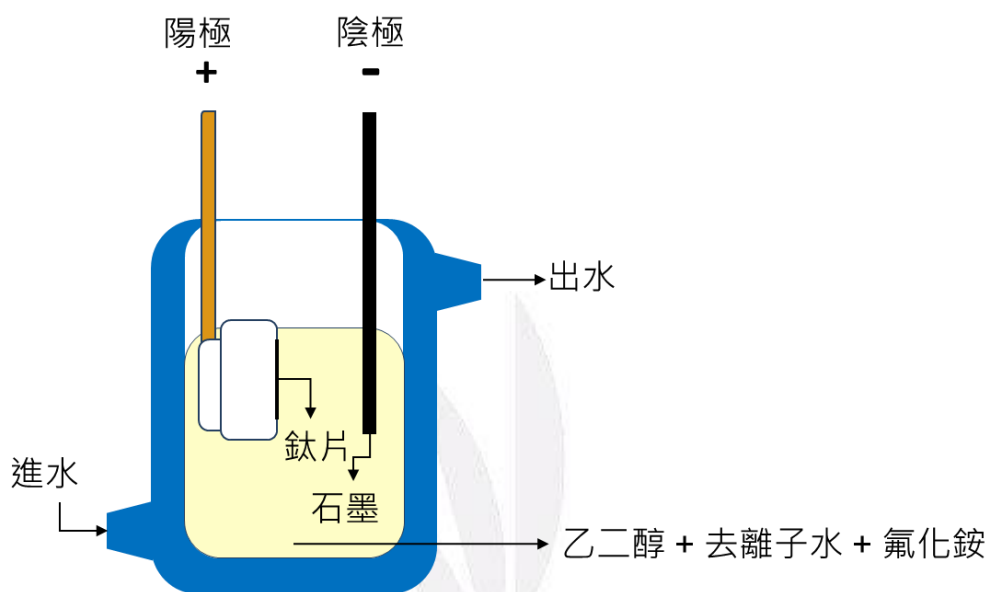
3. 實驗步驟

3.1 前處理和溶液製備

將鈦片裁成 1.5 公分×1.5 公分的大小後，以脫脂和酸洗的方式進行試片的前處理。試片浸入丙酮、無水乙醇、蒸餾水中超音波震盪 5 min，清洗試片表面的油漬和髒汙，再放入酸性溶液中去除表面雜質，酸性溶液為體積比 1:3 之硝酸、鹽酸，約處理 30 s 待試片與溶液不再有劇烈反應後，以去離子水清洗試片並吹乾，完成前處理。

隨後將鈦片連接至直流電源供應器之陽極，陰極接上石墨片，置

入電解槽中，電解液為氟化銨 (0.3 wt%) 和去離子水 (2 v%) 的乙二醇 ($\text{HOCH}_2\text{-CH}_2\text{OH}$) 溶液，在固定電壓 60 V 下，反應溫度維持於 20°C ，開始進行陽極氧化反應，反應裝置如下圖。



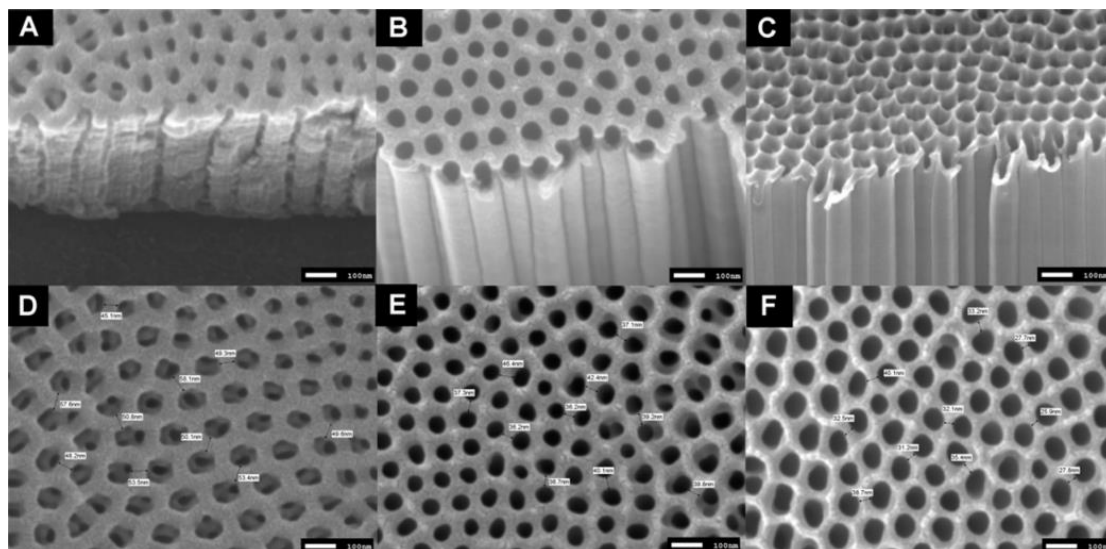
陽極氧化處理裝置示意圖

3.2 製備不同尺寸 TiO_2 奈米陣列

反應後之鈦片 (30 min)，以超音波震盪方式將氧化層剝離，並將樣品轉移到 5 wt% H_3PO_4 的乙二醇溶液中浸沒 1 小時。結束後再次於原氧化層的位置及原溶夜中相同電壓下進行二次陽極氧化。最終以陽極氧化時間為 5-120 分鐘製備出不同尺寸的 TiO_2 奈米管。最後將樣品浸泡在乙醇中 1 h，然後在 450°C 下煅燒 2 h ($5^\circ\text{C}/\text{min}$)。

4. 結果與討論

4.1 樣品的表徵



各種管長的側視圖及俯視圖：

1.5 μm (A, D), 7 μm (B, E) 和 10 μm (C, F)

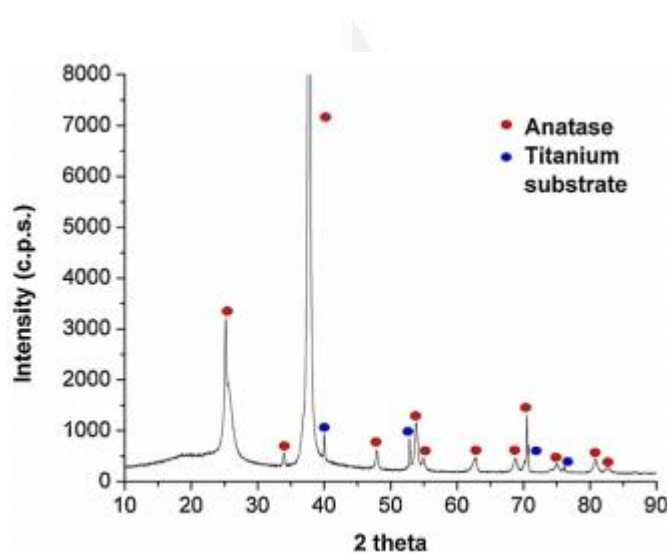
上圖顯示了各種長度的管形態，其中短管 (A) 具有非常小而且不規則的孔。隨著長度的增加，孔隙和通道開口變得更加的明顯 (B、C)。我們可以看到 7 μm 的孔洞是相當明顯的 (B)，而隨著管長度的增加，因為氟離子的化學蝕刻，(C) 上面的 TiO₂ 的量大大的減少。預計這些形態特徵對光催化性能有很大影響。

Sample ID	Tube length L (μm)	Volume of TiO ₂ V (nm ³)
NT-1	1.5	9.9×10^6
NT-2	4.5	8.9×10^6
NT-3	7	7.9×10^7
NT-4	10	6.6×10^6
NT-5	13	5.5×10^6
NT-6	25	4.2×10^6

在前 1.5 μm 的各樣品中 TiO₂ 的體積

從上表我們可以看出，隨著管長度的增加，前 $1.5\ \mu\text{m}$ 的 TiO_2 量會減少。因此光必須擴散到更遠的距離才能被完全吸收。

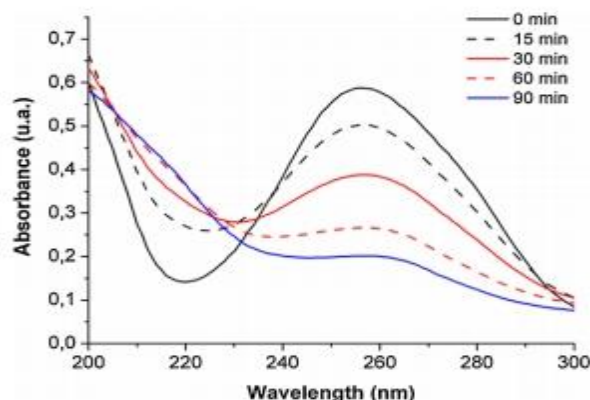
如果我們假設光在前 $1.5\ \mu\text{m}$ 完全被吸收，需要 $9.9 \times 10^6\ \text{nm}^3$ 的 TiO_2 。而對於較長的管，例如 $13\ \mu\text{m}$ 的奈米管 ($5.5 \times 10^6\ \text{nm}^3$)，對於相同量的 TiO_2 ，光應該最多會在 $3\ \mu\text{m}$ 深的地方被吸收，然後才產生電子電洞對，而污染物將擴散至更遠的距離。



TiO_2 納米管的 XRD 衍射圖

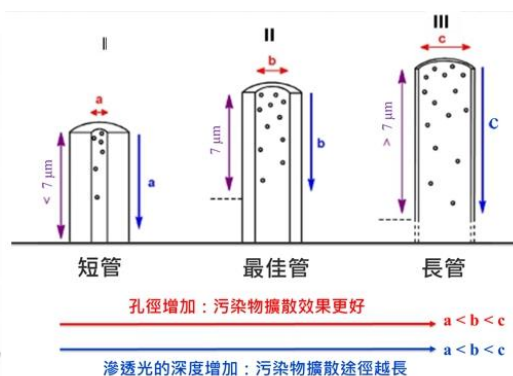
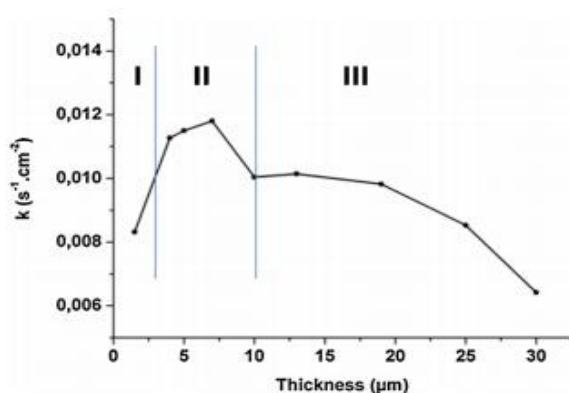
上圖顯示樣品的 XRD 圖，我們可以發現 TiO_2 納米管在 450°C 下的結晶可以獲得高含量的銳鈦礦。而並未發現金紅石峰。與金紅石相比，銳鈦礦顯示出更好的光催化能力，因為銳鈦礦晶格中的電子遷移率更高。

4.2 光催化效率



TiO₂ 納米管的光催化活性

我們要檢測 TiO₂ 納米管的光催化活性，首先將納米管在黑暗中浸泡在百草枯溶液中 30 min 以達到吸附平衡。然後將燈打開 ($t = 0$ min) 並發生光催化降解。在圖中我們可以看到，在光催化降解之後進行紫外光、可見光譜分析，可以看到在 257 nm 有著最大值，對應於百草枯的最大吸收峰。我們可以發現，由於二次產物的形成，200-235 nm 區域的吸收增加，而隨著降解時間的增加，二次產物逐漸變少。



管長與動力學常數的相關性

由圖中我們可知約 5-7 μm 長度的管為最佳值。為了準確的確定最佳值的搜索。我們利用了一個相對簡單的模型來合理化最佳的光催化活性。當管子很短時，擁有更厚的管壁，而在光的照射下會產生許多電子電動對。所以管長度必須足夠長才可以允許整個 UV 光被吸收。另一方面，短管具有相對小的內徑，阻礙污染物擴散。當管子更長時，光線被完全吸收並且污染物降解。而當管子更長時，管壁更薄，光線被完全吸收並且污染物降解。當管長長於 7 μm 時，我們可以發現光催化活性的降低。這說明了壁中的 TiO_2 體積正在減少，因此光在較長的路徑上被吸收。所以污染物應該在會在更深的距離上擴散。

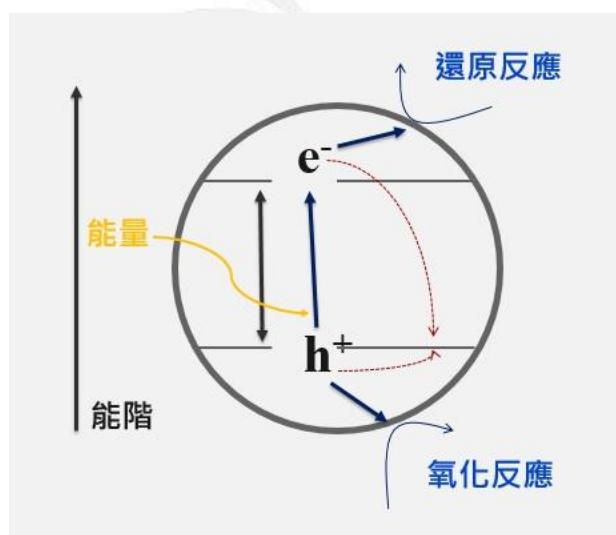
5. 結論

1. TiO_2 奈米管陣列的光催化活性大多數取決於陽極氧化時間。
2. 小內徑的短管光催化活性較差，是因為污染物擴散困難。
3. 長管具有薄壁，因此光被更長距離吸收，並且污染物必須進一步擴散以到達由電子電洞對產生的氧化物質。
4. 最佳管長度由這兩個結果之間折衷給出。

6. 相關資料

6.1 TiO₂ 光催化的缺點以及原理^[2]

光觸媒的原理很簡單，就是利用光能轉變成化學反應所需要的能量。光照射 TiO₂ 後，它的能量被 TiO₂ 吸收，電子會從價帶躍遷至導帶而留下電洞，產生電子電洞對，電子和電洞分離並遷移至光觸媒的表面進行氧化還原反應，汙染物降解並形成副產物，而由於電子與電洞間有庫倫作用力，因此可再結合並產生光或熱。在過程中有不少阻礙而降低此光催化過程，例如：電子和電洞的再結合、TiO₂ 表面積太小無法有效吸收汙染物及光能、二氧化鈦僅在紫外光區具有活性，因此導致光催化效率還未令人滿意。



TiO₂ 汙染物降解的光催化機制圖

二、問題與討論 Q&A

Q1: 是否能再詳細說明光觸媒的原理?

A: 光觸媒被光照射以後，材料中的電子會跳出來，並產生電子電洞對。而當電子與空氣中的氧分子相遇時，即生成反應性很強的超氧分子；當電洞與空氣中的水氣相遇時，會搶奪水中氫氧基的電子，而失去電子的氫氧基立刻變成不安定的氫氧自由基。一旦氫氧自由基遇到附在物體表面上的有機物時，又會藉由搶奪對方電子的方式使自己趨於穩定。如此一來，有機物即被氧化，變成水和二氧化碳，消散在空氣中。

Q2: 為何要使用陽極氧化法來製備二氧化鈦奈米管?

A: 陽極氧化法比起水熱法和溶膠凝膠法，更能夠讓奈米管有序的生長在鈦金屬基板上，獲得排列較為整齊之奈米管，得以使結構更為穩固，而陽極氧化法的實驗過程也較其他方法簡單快速，且能夠較容易控制所需要的管長，實驗的效率較好。

Q3: 在實驗步驟中 v% 所代表的意義是什麼?

A: v% 代表的是體積百分濃度

三、專題討論簡報報告內容

二氧化鈦納米管陣列： 管長度對百草枯光催化降解的影響

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日期：2019.04.15

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結論

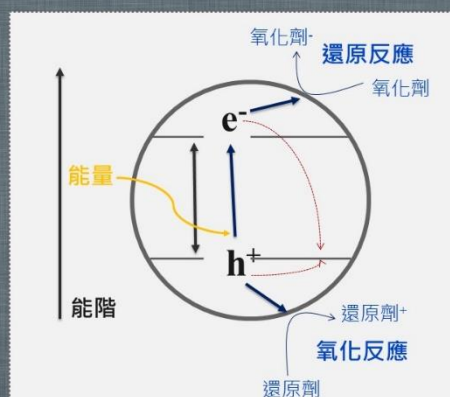
一、摘要與介紹

- 近期水污染和大氣污染的問題備受關注，**光觸媒**可利用**光催化反應**使**污染物降解**成無毒無害的二次產物淨化水及空氣，受到廣泛之重視。
- **二氧化鈦** (TiO_2) 是研究最多的半導體之一，因為它具有**無毒**、**使用壽命長**、**高化學穩定性**和**光催化效率**。
- 光催化去除有機污染物包括用**紫外光**照射半導體，通常是 TiO_2 ，以產生**電子電洞對**。在分離後，電洞與水或吸附的 OH^- 反應，電子與溶解的雙氧反應，分別產生**羥基**和**超氧自由基**。這些化合物是高度氧化的物質，它們與有機污染物反應，導致完全**礦化**。

摘要與介紹

- 在這次實驗中我們使用百草枯（1,1-二甲基-4,4-聯吡啶二氯化物）進行光催化降解，已知這個除草劑會被這些氧化自由基降解。光催化降解是先產生單吡啶酮和二吡啶酮，然後在完全礦化後產生二氧化碳，水， NH_4^+ ， NO_2^- ，還有 NO_3^- 。

而右圖為二氧化鈦之光催化降解污染物的機制圖

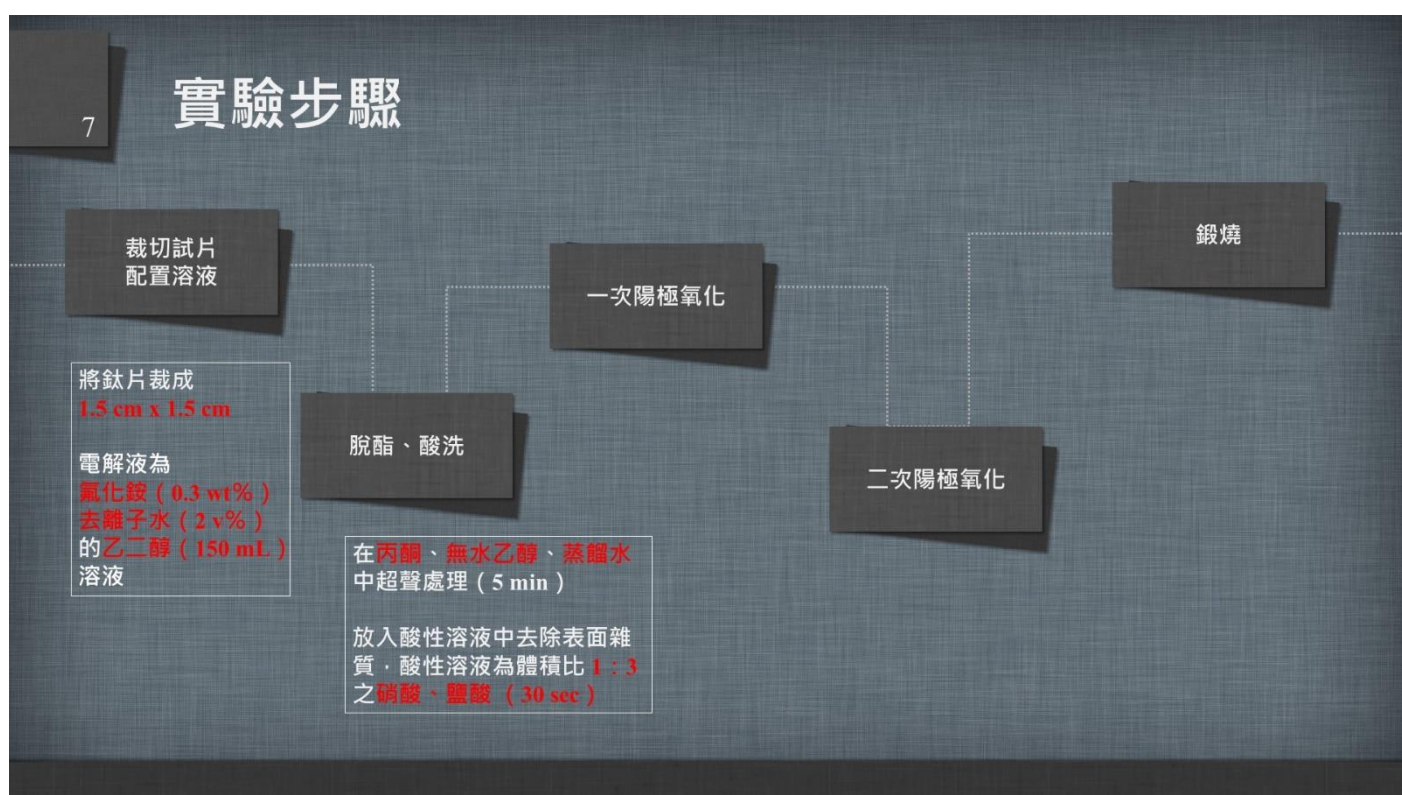


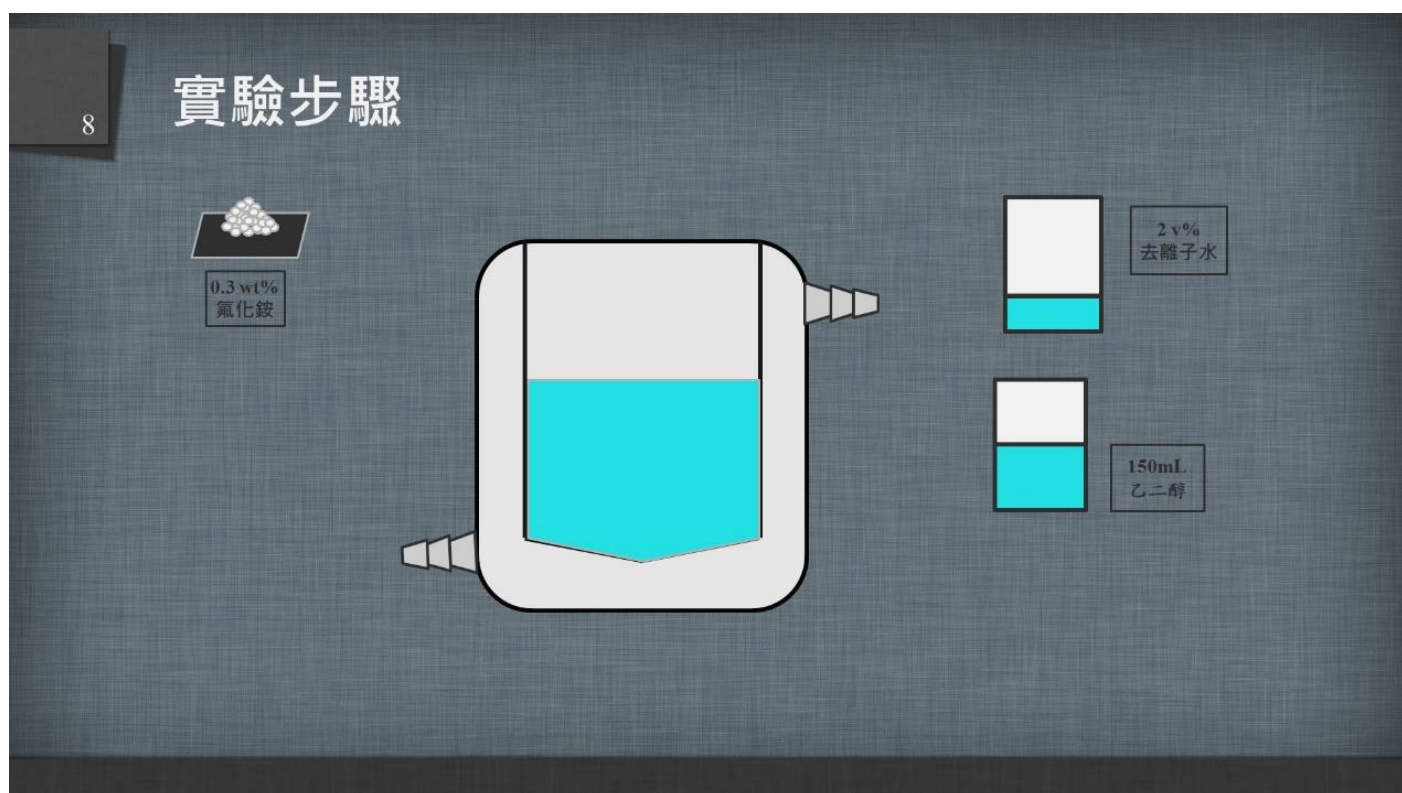
摘要與介紹

- 在過程中有不少阻礙而降低此光催化過程，例如：電子電洞對**再結合率高**，二氧化鈦**表面積太小**無法有效吸收污染物及光能，二氧化鈦**僅在紫外光區具有活性**，因此導致光催化效率還未令人滿意。
- 奈米管比起奈米線和奈米柱，多了內徑的面積，吸收光線和反應之面積會大幅提升，若是將其製備為奈米管陣列可使電子傳輸方向一致且順暢，應可大大的增加污染物的降解效率。
- 透過觀察在陽極生長過程中管的形態演變的狀況，來判斷相應的光催化活性。



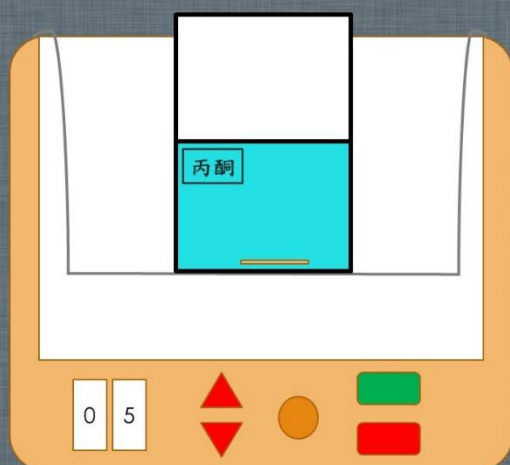
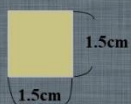
二 實驗步驟



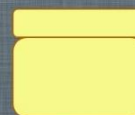


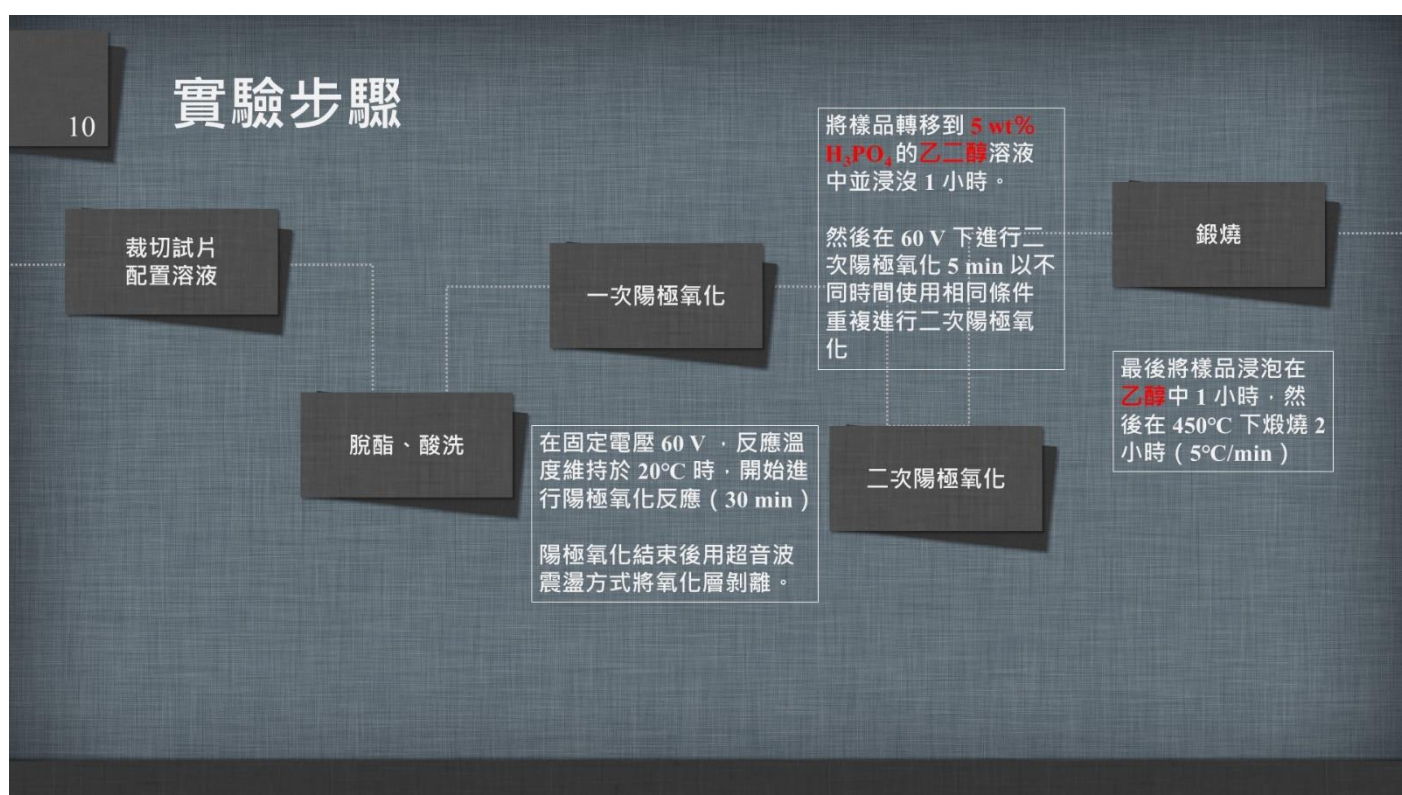
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實驗步驟



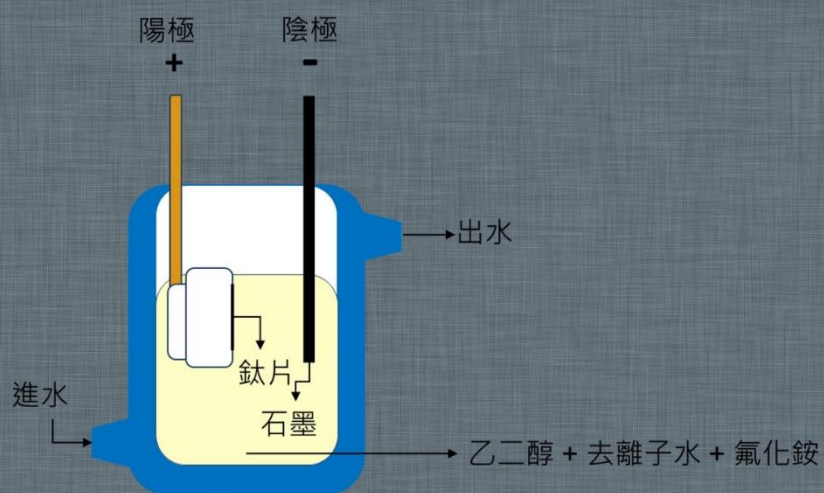
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實驗步驟





三

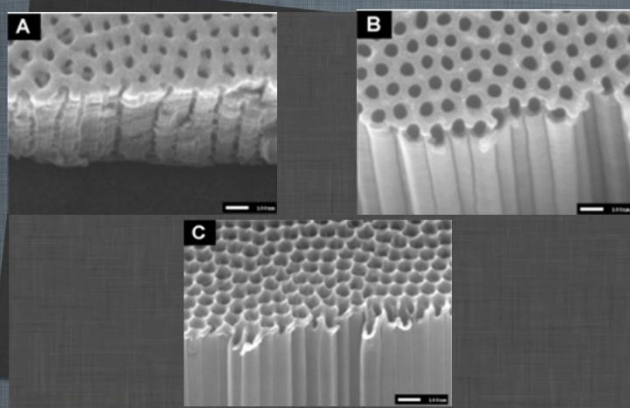
結果與討論

13

結果與討論

各種管長的側視圖：

1.5 μm (A) , 7 μm (B) 和 10 μm (C)



左圖顯示了各種長度的管形態。短管 (A) 具有非常小且無序的孔。隨著長度的增加，孔隙和通道開口變得更加的明顯 (B、C)。而隨著管長度的增加，由於氟離子的化學蝕刻，頂部的 TiO₂ 的量大大減少。預計這些形態特徵對光催化性能有很大影響。

結果與討論

管長度的值與相應的平均壁厚和孔徑

樣品	陽極氧化時間 (min)	管長 (μm)	管壁厚度 (nm)	內徑 (nm)
NT-1	5	1.5	27.7	49
NT-2	15	4.5	23.4	57
NT-3	30	7	19.5	64
NT-4	45	10	16.2	72
NT-5	50	13	13.4	78
NT-6	120	25	10.3	85

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結果與討論

在前 1.5 μm 的各樣品中 TiO_2 的體積

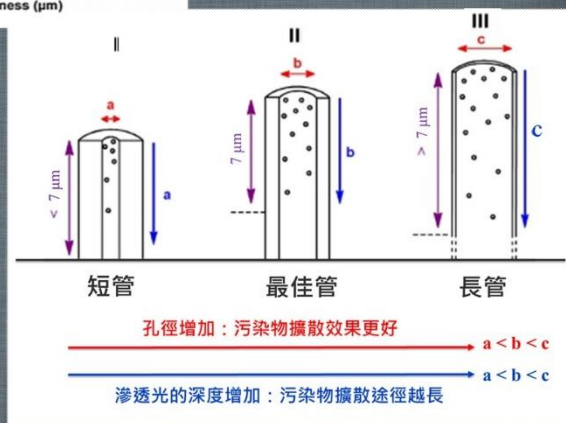
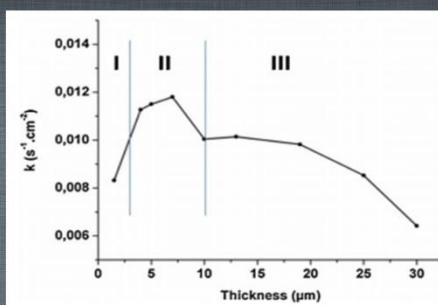
樣品	管長 (μm)	二氧化鈦的體積 (nm^3)
NT-1	1.5	9.9×10^6
NT-2	4.5	8.9×10^6
NT-3	7	7.9×10^6
NT-4	10	6.6×10^6
NT-5	13	5.5×10^6
NT-6	25	4.2×10^6

根據左表，我們可以看出，隨著管長度的增加，前 1.5 μm 的 TiO_2 量減少。因此，光應該在更長的距離上完全吸收。

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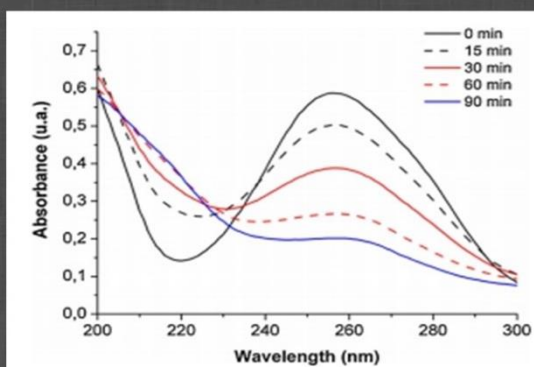
結果與討論

在光的照射下，產生許多電子電洞對。但是，管長度必須足夠長才可以讓整個 UV 光被吸收。另一方面，短管具有相對小的內徑以及更厚的管壁，阻礙污染物擴散。而當管子更長時，管壁更薄，光線被完全吸收並且污染物降解。當管長長於 $7\ \mu\text{m}$ 時，我們可以發現光催化活性的降低。這說明了壁中的 TiO_2 體積正在減少，因此光在較長的路徑上被吸收。所以污染物應該在會在更深的距離上擴散。



結果與討論

二氧化鈦納米管的光催化活性



我們要檢測 TiO_2 納米管的光催化活性，首先將納米管在黑暗中浸泡在百草枯溶液中 30 min 以達到吸附平衡。然後打開燈 ($t = 0 \text{ min}$) 並發生光催化降解。正如我們在圖中可以看到的那樣，光催化降解之後是 257 nm 的紫外光可見光譜，對應於百草枯的最大吸收峰。




四 結論

結論

- TiO_2 納米管陣列的光催化活性很大程度上取決於陽極氧化時間。
- 具有小內徑的短管表現出差的光催化活性，因為污染物擴散是困難的。
- 長管具有薄壁，因此光被更長距離吸收，並且污染物必須進一步擴散以到達由電子電洞對產生的氧化物質。
- 最佳管長度由這兩個現象之間的折衷給出。


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TiO₂ Nanotube arrays: Influence of tube length on the photocatalytic degradation of Paraquat

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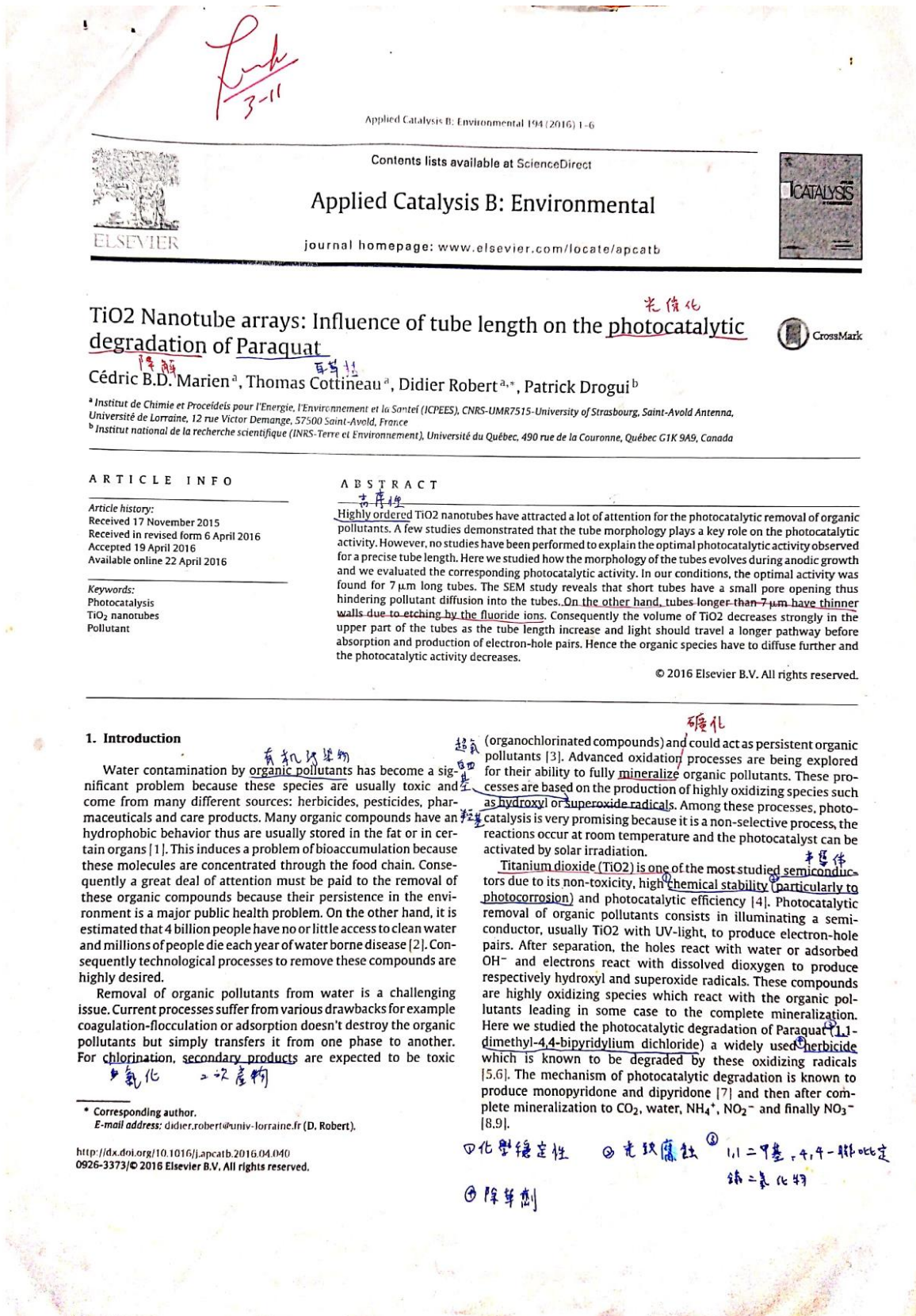
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That's all!

Thank you! 😊
Any questions?

四、參考文獻



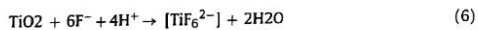
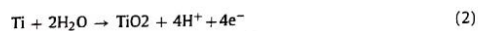
①懸浮液
②多孔性
③聚苯氧基管
④聚乙二醇
⑤絡合劑氧化鋅

Photocatalysis has been widely used with suspension of TiO₂ nanoparticles. However, the recovery of the catalyst involves expansive separation processes. The immobilization of TiO₂ on a substrate is attractive due to its simplicity of recovery. However for a same amount of TiO₂, a suspension offers a higher active surface area than a thin film due to the close packing in thin films. To overcome this problem, nanostructured thin films with high active surface area are desired for photocatalysis.

Controlling the porosity is usually performed thanks to the template-assisted method which involves a pore-directing agent to control the porosity: polystyrene spheres [10], polyethylene glycol [11] or anodic aluminium-oxide [12]. However the removal of the template can lead to fragile thin films with poor mechanical stability. Moreover the template-assisted growth is time consuming and often involves several steps.

Electrochemical methods have been recently reported for the fabrication of various TiO₂ nanostructures: nanotubes [13], fishbone [14], mesosponge [15] or nanochannels [16]. The anodic growth consists in oxidizing a titanium foil in an adequate media to produce a porous TiO₂ coating on the surface. This approach is fast, facile and allows a precise control of the porosity. Moreover anodic TiO₂ nanostructures are produced on a conductive electrode which is ready-to-use for the photoelectrocatalytic removal of organic compounds [17]. Despite these advantages, only the tubular structure can be obtained at ambient temperature where a hot phosphate-glycerol electrolyte (temperature >150 °C) is required to produce other structures (fishbone, mesosponge and nanochannels). Consequently anodically grown TiO₂ nanotubes have a great potential for photocatalysis due to their large internal surface area and their facile fabrication.

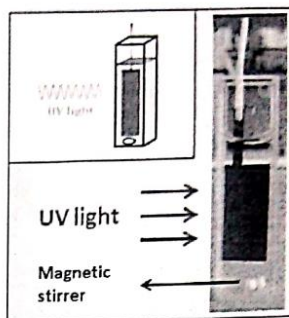
The anodic growth of TiO₂ nanotubes consists in applying a DC voltage on a Ti foil immersed in an organic electrolyte, usually ethylene glycol, with water and fluoride ions (third generation nanotubes) [18]. This growth can only be achieved under optimized conditions where equilibrium is reached between oxide formation (Eqs. (1)–(4)) and oxide dissolution (Eqs. (5) and (6)):



The oxide dissolution produces a water soluble complex (TiF₆²⁻). At the same time, hydrogen evolves at the counter electrode, usually platinum:



The tube morphology has a significant influence on the photocatalytic performances of the TiO₂ nanotubes for water depollution. Smith et al. [19] demonstrated that nanotubes with large diameters have a better photocatalytic activity because the photocatalyst surface is more available. Many reports also focus on the optimal tube length for photocatalytic degradation experiments: 6 μm [20], 16 μm [13], 17 μm [21] and 18 μm [22]. In these papers, the growth conditions are different thus the tube morphology (internal diameter and wall thickness) is expected to be different for a same tube length. Besides UV light is absorbed in the first 1–2 μm [23] thus the top morphology should play a key role. Mazzarolo et al. [24] investigated the influence of the top morphology on the photocatalytic activity. They revealed that tubes with a well defined open mouth have an enhanced photocatalytic activity compared to grassy tubes and tubes with an initiation layer. In this paper,



Scheme 1. Photocatalytic setup: quartz cuvette with a TiO₂/Ti sample and a small magnetic stirrer at the bottom.

we studied the influence of the top tube morphology for various lengths and we correlated this to the photocatalytic activity in the case of the degradation of Paraquat in water. The aim is to provide a basic understanding of the underlying mechanism.

2. Experimental methods

2.1. Electrochemical growth of TiO₂ nanotubes

Titanium foils (thickness: 125 μm) were purchased from Mateck (Germany). Samples were cut in 2 × 1.5 cm² pieces and welded on the backside with a thin titanium contact (0.4 × 2 cm²). Surface impurities were removed by immersion in regia aqua (HCl/HNO₃-3/1 in volume) and then degreased by successive immersions, under ultrasonication in acetone, anhydrous ethanol and distilled water (5 min each). The samples were then dried with compressed air. Electrochemical anodisation was performed with a three-step process. First samples were preanodised at 60 V during 30 min at 20 °C in ethylene glycol with NH₄F (0.3 wt%) and H₂O (2 v%). The nanotube layer was then peeled-off by ultrasonication. The samples were then anodized in the same electrolyte with the same conditions during various durations. After anodisation, the samples were immediately transferred in a 5 wt% H₃PO₄ in ethylene glycol and immersed during 1 h. The post anodisation was then performed during 5 min at 60 V to produce an oxide layer that improves the nanotubes adhesion. Samples were finally immersed in ethanol during 1 h before calcination in air at 450 °C during 2 h (5 °C/min).

2.2. Samples characterization

SEM analysis were performed with a JEOL-JSM-7600F at the Coatings Research Institute (CoRI, Belgium). For thickness measurements, samples were wrapped in an epoxy resin. The surface of the epoxy was then polished to reveal the edge of the electrode perpendicular to the surface. Samples were platinized before analysis to avoid the charging effect. XRD allowed to examine the crystallinity thanks to a Shimadzu instrument (MiniFlex II) using the Cu K-alpha radiation.

2.3. Evaluation of the photocatalytic activity

Photocatalytic tests (Scheme 1) were performed with a quartz cuvette filled with 3 ml of Paraquat dichloride (10 ppm, Aldrich) at pH = 7 and a magnetic stirrer (3 mm). The concentration of Paraquat was followed at 257 nm thanks to Beer-Lambert law. Two UV lamps (8 W each) were used at 3 cm from the cuvette

and the irradiance was measured with a HD 9021 instrument from Delta Ohm: 13 W/m² (UV-A: 315–400 nm) and 50 mW/m² (UV-B: 280–315 nm). The samples were cut to fit in the cuvette (2 × 0.8 cm²) and the exposed surface was precisely measured with the Imagej software.

3. Results and discussion

3.1. Characterization of TiO₂-NT samples

Fig. 1 shows the tube morphology for various lengths. Short tubes (fig. 1A) represent the initiation layer with very small and disordered pores (thin channels). As the length increases, the pores and the channels are opening (fig. 1B and C). In our conditions, the opening is well-defined for 7 μm long tubes (fig. 1B). As the tube length increases the amount of TiO₂ on the top is highly reduced due to chemical etching by the fluoride ions. These morphological features are expected to have a strong influence on the photocatalytic properties [24].

Fig. 1C shows very thin top tubes whereas they look thicker on Fig. 1D, because the 2D top view flattens the picture. Top views (Fig. 1) clearly demonstrate the wall thinning and the pore opening. Based on Scheme 2, we can estimate the pore size with the Imagej software.

The wall thickness can be evaluated by dividing by 2 the distance between neighboring pores 2W. All the data are given in Table 1:

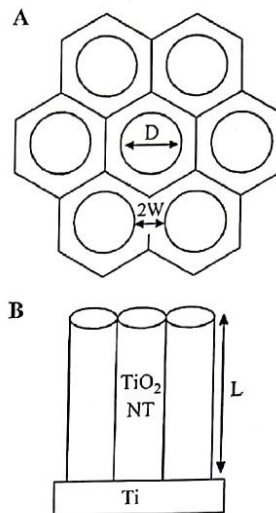
Table 1 allows to evaluate the amount of TiO₂ in the upper part of the tubes. Assuming straight tubes instead of the classical v-shape, we can calculate the volume V of TiO₂ in the tube wall with the following formula:

$$V = \pi L r_{\text{ext}}^2 - \pi L r_{\text{int}}^2$$

Since the external diameter is constant (2 r_{ext} = 2W + D = 104 nm) and the internal diameter is D the volume of TiO₂ is:

$$V = \pi L (52^2 - (D/2)^2)$$

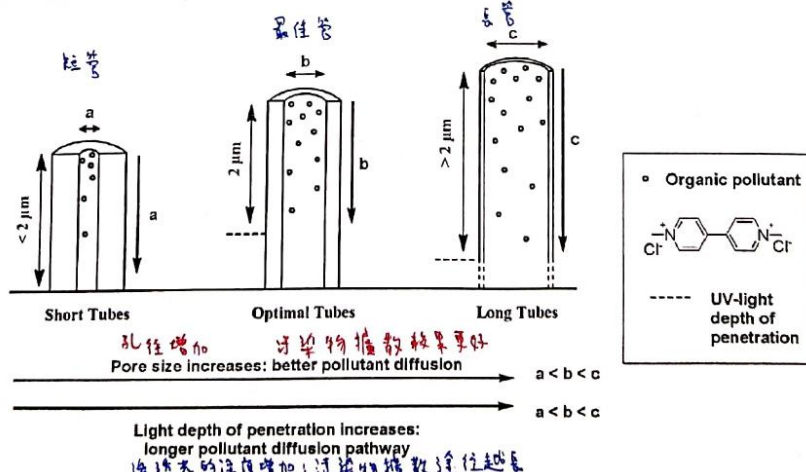
This relationship demonstrates that the amount of TiO₂ decreases as the inner diameter become more open. According to Choi et al. [25] the light depth penetration in a compact thin film of TiO₂ nanoparticles is limited to ~1.3 μm for wavelengths >300 nm.



Scheme 2. Morphological features of TiO₂ nanotubes: (A) top-view and (B) side-view.

However the porosity of a nanotube array, is expected to be higher than a compact thin film of nanoparticles thus light should penetrate deeper in the tubes. Consequently we can assume that light is entirely absorbed in the first 1.5 μm region. Table 2 compares the volume of TiO₂ converting light into electron-hole pairs:

Based on Table 2, we can see that the amount of TiO₂ in the first 1.5 μm decreases as the tube length increases. Consequently light should be entirely absorbed on a longer distance. If we assume that light is entirely absorbed in the first 1.5 μm, 9.9 × 10⁶ nm³ of TiO₂ are required. For longer tubes, for example 13 μm (5.5 × 10⁶ nm³), for a same amount of TiO₂, light should be absorbed on almost 3 μm.



Scheme 3. Interpretation of the optimal photocatalytic activity for various top tube morphologies: short tubes (left), optimal tubes (center) and long tubes (right).

Table 1
Values of tube length with the corresponding average wall thickness and pore size (evaluated with SEM top-view).

Sample ID	Anodization time (min)	Tube Length L (μm)	Wall thickness W (nm)	Internal diameter D (nm)
NT-1	5	1.5	27.7	49
NT-2	15	4.5	23.4	57
NT-3	30	7	19.5	64
NT-4	45	10	16.2	72
NT-5	50	13	13.4	78
NT-6	120	25	10.3	85

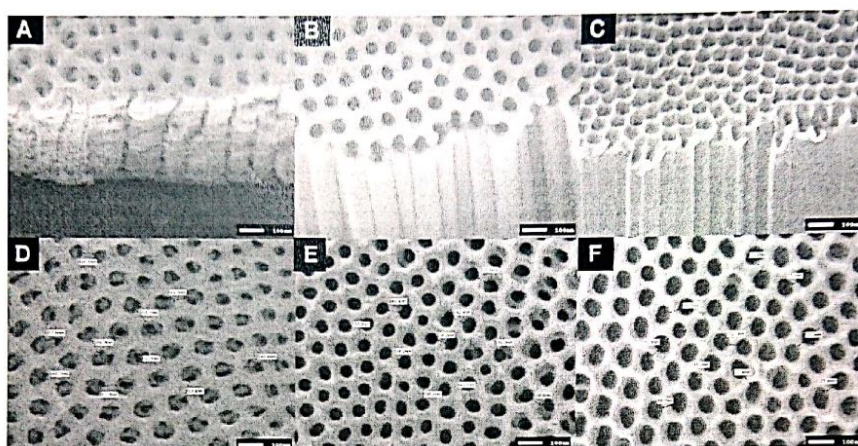


Fig. 1. SEM analysis – Side and Top view for various tube length: 1.5 μm (A, D), 7 μm (B, E) and 10 μm (C, F).

Table 2
Volume of TiO₂ for various samples in the first 1.5 μm.

Sample ID	Tube length L (μm)	Volume of TiO ₂ V (nm ³)
NT-1	1.5	9.9 × 10 ⁶
NT-2	4.5	8.9 × 10 ⁷
NT-3	7	7.9 × 10 ⁷
NT-4	10	6.6 × 10 ⁸
NT-5	13	5.5 × 10 ⁸
NT-6	25	4.2 × 10 ⁹

Consequently **electron-hole** pairs would be generated further and the pollutant would travel a longer distance (**diffusion controlled**).
 Fig. 2 shows the XRD pattern of a sample. The crystallization of TiO₂ nanotubes at 450 °C allows to obtain a high anatase content. No rutile peaks were found. The anatase phase shows better photocatalytic properties due to higher electron mobility in the lattice of anatase compared to rutile [26].

3.2. Photocatalytic efficiencies

The photocatalytic activity of the TiO₂ nanotubes was evaluated with the degradation of Paraquat. The concentration was followed by UV-vis spectroscopy. The nanotubes were first immersed in the Paraquat solution in the dark during 30 min to reach the **adsorption equilibrium**. Then the light was turned on (t = 0 min) and the photocatalytic degradation occurred. **As we can see on Fig. 3, the photocatalytic degradation was followed by UV-vis spectroscopy at 257 nm corresponding to the maximum absorption peak of paraquat.**

As we can see it on Fig. 3, paraquat's removal is followed by an increase of the absorption in the region 200–235 nm due to the

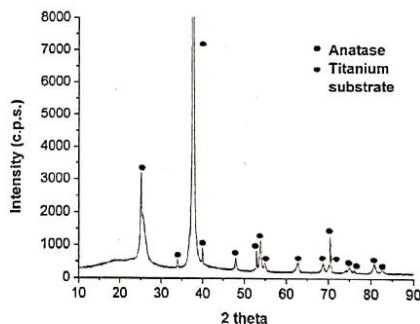


Fig. 2. XRD diffractogram for TiO₂ nanotubes.

formation of secondary products. For sufficiently long periods of degradation, the secondary products are not observed anymore.

Fig. 4 is a compilation of different degradation kinetics of paraquat for various tube lengths. We can see that the optimum is for 7 μm long tubes in our conditions. Moreover, short tubes (4.5 and 7 μm) have a better photocatalytic activity than other tubes.

These degradations follow a pseudo-first order law:

$$\ln(C/C_0) = -k \times t$$

where C is the concentration (0 for initial), k the kinetic constant (s⁻¹) and the time t. Consequently we obtain the following graph (fig. 5):

• 吸光度

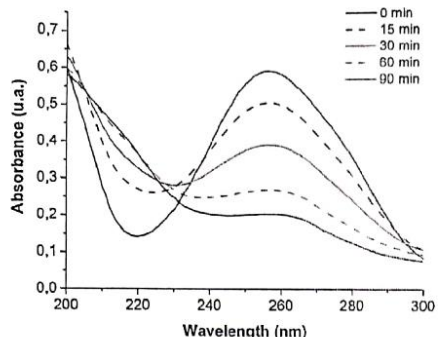


Fig. 3. Photocatalytic degradation of paraquat followed by UV-vis spectroscopy.

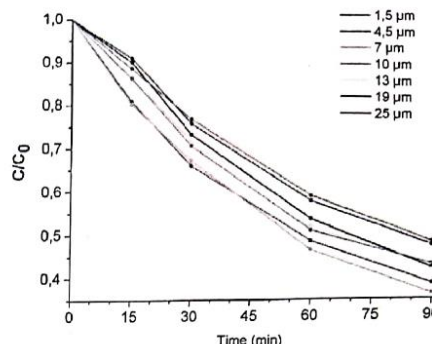


Fig. 4. Degradation of Paraquat for various tube lengths.

Fig. 5 shows an optimum for tubes around 5–7 μm of length. This optimum should be correlated to the top tube morphology. Indeed the top-tube morphology presents a well defined open-mouth with relatively thick walls. This morphology is expected to exhibit a better photocatalytic activity as confirmed by Mazzarolo et al. [24]. According to the literature many different values were reported but the experimental conditions of growth are always different (concentration, temperature, applied potential). Consequently we believe that the presence of a well-defined open mouth depends on the synthetic conditions and the search of the optimum should be accurately determined. We developed a relatively simple model to rationalize the optimal photocatalytic activity (Scheme 3). When the tubes are short, the wall thickness is large thus the amount of TiO₂ is important in the first micrometers. Consequently under illumination many electron-hole pairs are created. However the tube length must be sufficiently long to allow the entire UV light to be absorbed. On the other hand short tubes exhibit a relatively small inner diameter hindering pollutant diffusion (limiting step). When the tubes are longer, the light is entirely absorbed and the pollutant is degraded. When the tubes are longer than 7 μm, in our case, we observed a decrease in the photocatalytic activity. We believe that the volume of TiO₂ in the walls is decreasing thus light is absorbed on a longer pathway. Consequently, the pollutant should diffuse on a longer distance and the photocatalytic removal is controlled by diffusion.

①濃度
②溫度
③施加電位

a shorter distance, pollutant has to travel a short distance) and easy-access inside the tubes (large internal diameter improves pollutant diffusion). This interpretation is presented in Scheme 3.

This interpretation explains why different optimal photocatalytic activities were reported in the literature (6 μm, 16 μm, 17 μm and 18 μm). Indeed depending on the synthetic route, the well-defined open-mouth appears for different lengths. Consequently the variation of parameters such as pH, composition of the electrolyte, applied potential or temperature should strongly affect the optimal tube length for photocatalytic degradation of organic compounds.

④變化 ⑤參數 ⑥電解質成分

4. Conclusion

The photocatalytic activity of TiO₂ nanotubes arrays strongly depends on the anodisation time. Short tubes with a small internal diameter exhibit poor photocatalytic activity because pollutant diffusion is ineffective. Long tubes have thin walls thus light is absorbed on a longer distance and pollutant has to diffuse further to reach the oxidizing species produced by the electron-hole pairs. The optimal tube length is given by a compromise between these two phenomena.

Acknowledgements

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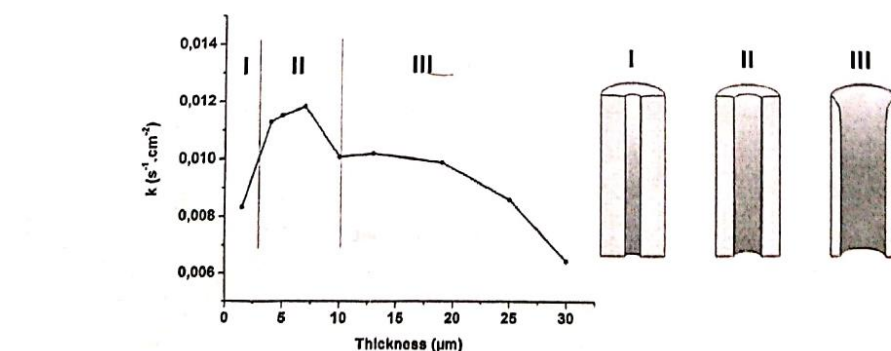
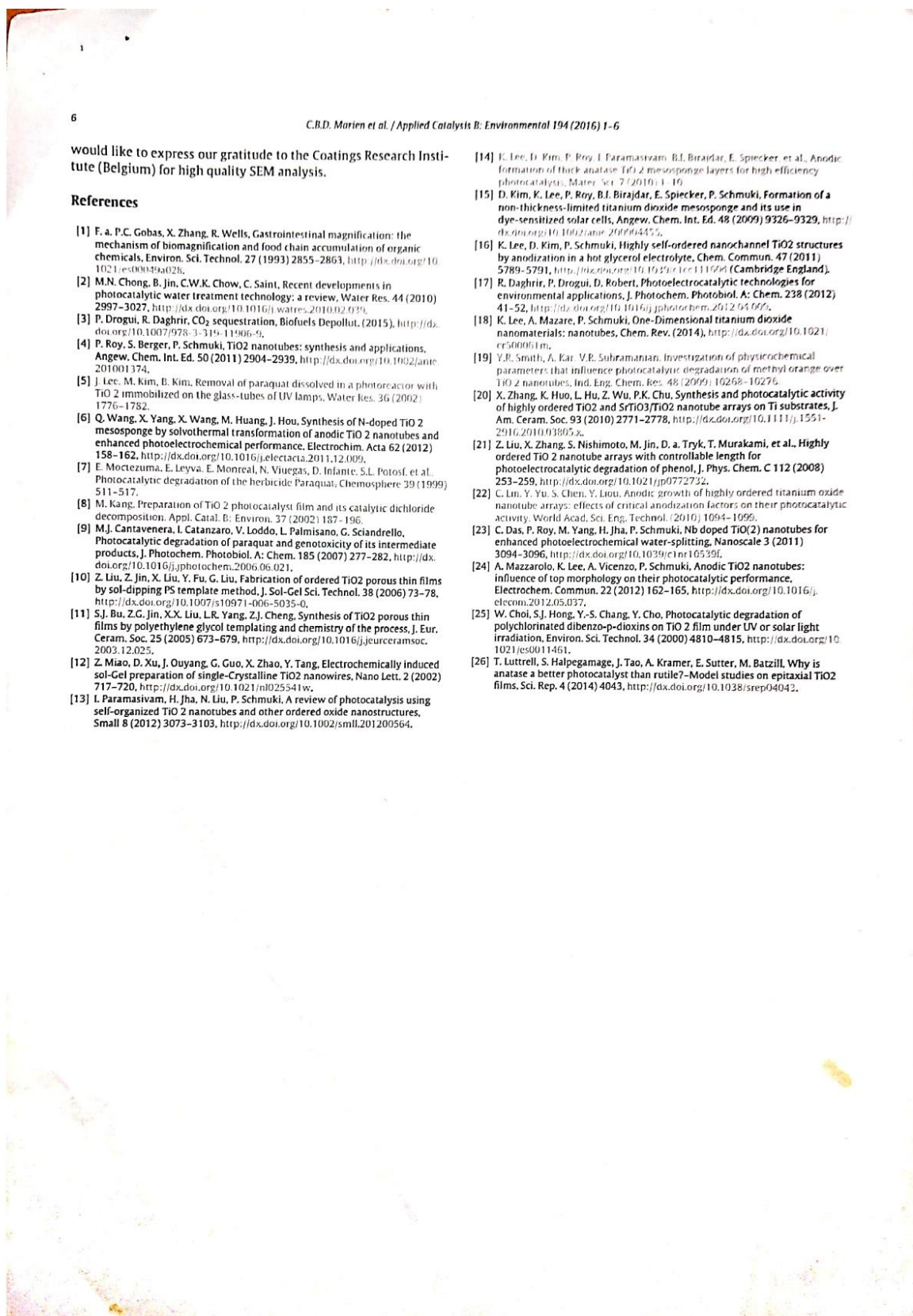


Fig. 5. Correlation between tube length and kinetic constant.



would like to express our gratitude to the Coatings Research Institute (Belgium) for high quality SEM analysis.

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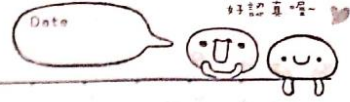
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五、課堂筆記

<專題討論>



key word
key concept
key statement

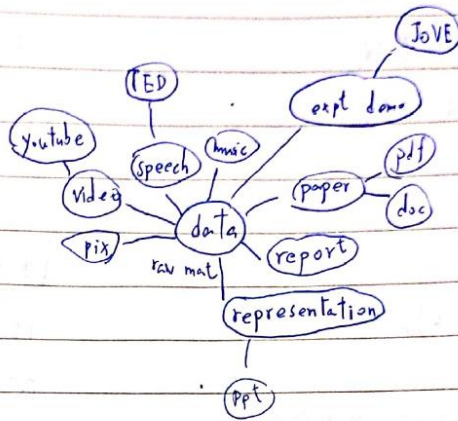
mindmap

結構

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- 投影片準備不超過 30 張



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條列 · 正黑 · 圖 · 加粗 · 重點

IBM 主張「Think」:

Think Big

Think Different

Think Simple

Icon, Symbol, Cartoon, animation

animation + 專有名詞

A + B = 45g > 300 kg (唯溫度不空)

有單位使用英文

目錄不要講

千: k 小寫 M = 10⁶ m = 10³ μ = 10⁶

專有名詞 · 縮語 須附上原文 · 自碼

THEME	
靜電紡織法	生物可降解聚合物
簡單、產量高、成本效益高	PHB (生物可降解聚酯)
高分子選擇種類多	咪唑
NGP、奈米石墨紙	恆溫與非恆溫結晶行為
PVDF: 聚偏二氟	Avrami, Ozawa, Moynihan
引極性	[TFSI] ⁻ → [CF ₃ SO ₂] ⁻ NI ⁺ 離子液體
超級電容	生物可降解聚合物
電雙層電容器	PLLA (聚左旋乳酸)
擬電容器	PEA (聚己二酸二乙酯)
MnO ₂ /NWs - AuNPs: 阻抗較低	塑化劑
表面積較大、電荷儲存能力增加	DMA (動態機械分析儀)
阻抗分析	恆溫與非恆溫分析
渦輪發動機	氧化石墨烯
熱阻層	GO膜 → 氧化石墨烯 → 可提高 SERS 訊號
電子束物理氣相沉積法	旋塗法: 高速成膜, 均勻薄膜
交流電鍍	碳訊號: d band, g band
電漿噴塗	石墨化: 使碳的結晶性、結構更趨近於
TGO → 熱生成氧化物	石墨的過程
Al₂O₃ 氣體感測	生物活性玻璃
甲醛感測	BAG
檢測甲醛: 分光光度法	HCA: 硫酸羧基 磷灰石
酶分析法, AHMT法	

Date



錫銻氧化物

ITO

奈米銀線：導電性、透光性佳

氬氣電漿

CBD 化學沉積法

超氧自由基

錫銻氧化物-二氧化鈦

超級電容

孔隙多 → 利於電解質擴散

時間 ↑, 奈米線 ↑ → 溶解再結晶

充放電曲線圖

兩電層、擬電容

光催化產生 H₂

ALD 沉積

食人魚溶液

光催化效能

↑ 300nm 最佳性能

V% → 體積百分濃度

熱歷史 → 高分子材料在加工、儲存等條件

下產生的結晶、應力變化

食人魚溶液：濃硫酸、過氧化氫 3:1 混合

石墨化：使碳的結構、結晶更趨近於石墨的過程

水熱法、溶膠凝膠法、陽極氧化法

電化學視窗：電位差

恆溫與非恆溫的差別：一個偏向理論一個偏向實際

「專題討論」自我評量表 (請將此表裝訂在書面報告的最後一頁)

1. 本學期中我從自己的「專題討論」課程學到什麼？我從班上其他同學身上真正學到什麼特別之處？(請具體描述)

在這學期的專題討論中，我學會了許多東西，首先最明顯的就是製作 PPT 的方法。透過老師每一堂課的指正，什麼該加什麼不該加，怎樣可以使 PPT 重點更加的明確，老師還曾經說過「一個好的 PPT 其實看封面就可以知道」老師教會了許多我們不知道地技巧。還有就是在蒐集資料的部分老師也提供了許多很好的方法，並不只是侷限在我們所常用的 Google 或者是維基百科上。而在班上同學身上我發現了許多我自己欠缺的東西，首先在他們緊張的時候其實他們不會表現的特別明顯，還有就是對時間良好的掌控能力，上台時說話的技巧等這些都是我該學習的地方。

2. 我個人在「專題討論」表達力方面，有哪些尚須值得改進加強的地方呢？(請具體描述)

對我而言，我覺得我有相當多的地方需要改善，首先就是對演講內容的熟悉，我看很多同學一上台就可以侃侃而談，非常的有自信而且熟練，而我雖然也讀了很多次但是上台後我還是非常的緊張，有時候內容還會有所錯漏，後來一問才知道原他們在上課前 3 個小時就來教室模擬報告了，提早來熟悉環境，我想這對我應該也有所幫助。還有就是面對同學的提問時，因為準備不足而無法回答同學的問題，再來就是肢體擺動的部分，因為緊張而不自覺地看向 PPT，並且身體不自覺地擺動，這個問題對我而言也是一個需要改善的地方。

3. 我對「專題討論」課程提出一些創新性建議，敘述如下：

其實因為這堂課的報告內容沒有限制，所以有時候面對一些自己不熟的題目會使人更加的感興趣，同樣的，如果課程題目不熟而內容卻又艱澀難懂，這樣會導致讓人沒有想聽下去的慾望，而且到最後問問題的時候，找不到可以問的問題，因為會完全聽不懂，所以我希望能夠在當初選擇的時候就限制 paper 的難度。還有就是希望可以在第一組正式報告之前，可以進行一些 PPT 教學，這樣才不會導致到了正式報告的時候 PPT 還是沒有達到標準。

4. 我這學期中上課出席率(100%)是95%。
5. 我共花費336小時準備報告資料，共收集研讀5篇中文英文相關資料。
6. 我自評對「專題討論」的個人學習滿意程度為 75分 (以滿分為 100 分評量)
7. 我自評對「專題討論」授課老師教學滿意度為 90分 (以滿分為 100 分評量)
8. 我的「專題討論」的「書面報告(小論文)」經過圖書館 Turn It In 軟體的比對結果所出現的相似度比率為2% (後面請附上 Turn It In 比對結果的列印資料)



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參考文獻

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