

# 行政院國家科學委員會補助國內專家學者出席國際學術會議報告

96年07月10日

附件三

報告人姓名	黃武章	服務機構 及職稱	國立屏東科技大學環境工程與科學系副教授
時間 會議地點	96年7月1-6日 新加坡	本會核定 補助文號	<b>NSC 95-2221-E-020-023-</b>
會議 名稱	(中文) 2007 第四屆高等技術材料國際會議 (英文) The 4 <sup>th</sup> International Conference on Materials for Advanced Technologies 2007		
發表 論文 題目	(中文) 以日光照射增進二氧化鈦粉末於聚苯乙烯材質中的分散 (英文) Dispersion Enhancement of TiO <sub>2</sub> Powder in Polystyrene Matrix by Visible Light Irradiation		
報告內容應包括下列各項： <ul style="list-style-type: none"> <li>一、參加會議經過</li> <li>二、與會心得</li> <li>三、考察參觀活動(無次活動)</li> <li>四、建議</li> <li>五、攜回資料名稱及內容</li> <li>六、其他</li> </ul> <p style="text-align: center;">詳見以下附文</p>			

## 一. 目的

本會議為二年一次的國際性會議，主要由新加坡材料學會(MRS)與國立新加坡大學，南洋理工大學及材料工程研究院聯合舉辦。於 2006 年 7 月 1 ~ 6 日在新加坡的 Suntech Singapore International Convention and Exhibition Centre 舉行，自 1991 年起已經舉辦過三次。本次研討會的議題共有 18 個，分別為：

Symposium A: Advanced functional bio-materials

Symposium B: Developing nano-bio interface

Symposium C: Bio functional materials

Symposium D: Semiconductor photonics

Symposium E: Nano-devices and nano-fabrication

Symposium F: Micro-structured and nano-structured optical fibers

Symposium G: Sensing probe microscopy in material research

Symposium H: MEMS technology and devices

Symposium J: Materials for advanced sensors and detectors

Symposium K: Nano-structured and bulk materials for electrochemical power sources

Symposium L: Catalytic materials and technologies for a sustainable economy

Symposium M: New routes to inorganic materials, films and nano-crystals

Symposium O: Frontiers in computational materials science

Symposium P: Electromagnetic materials

Symposium Q: Advanced structural and functional materials for protection

Symposium R: Polymer and molecular electronics

Symposium S: Education in nano-science nano-engineering

可知其涵範圍相當廣，幾乎將目前先進科技包容在內。此次會議共有來自 44 個國家研究人員計 2032 位與會。除了新加坡當地出席人數 611 位排名第一外，臺灣此番前往人數有 144 位則名列第二；中國大陸則只有 65 人與會。值得關注的是印度有 107 人出席也是相當多的。晚生由於在本校從事環境科學研究，對於光解觸媒的研究有一些新鮮的發現，想藉此機會向國際學者們請教與釋疑。並了解目前國際間的研究動向以供國內相關單位參考。下一次會議舉辦時間為 2009 年的 6 月 28 至 7 月 3 日。

## 二. 會議過程

"2007 第四屆高等技術材料國際會議" 的日期為 7 月 1~6 日，晚生因有校內期末考關係故延至於 7 月 2 日方抵達星國。會議全程於新達城購物中心的國際會議中心進行相關議程。大會主辦此番共邀請了 9 位重量級大師進行大會演講：其中三位是 Nobel Laureates: Prof. C., Cohen-Tannoudji (France), Prof. B. Sharpless (USA), Prof. H. R. Horvitz (USA)，與發現奈米碳管的 Prof. S. Iijma (Japan)。

因為個人興趣與研究領域關係，晚生選了 Prof. Horvitz 與 Prof. Iijma 的演講。講題分別為”Cell Suicide: Programming Cell Death in Development and Disease”及”Nano-Carbon Meaterial: Their Fundamentals and Various Applications Including Nano-Biotechnology”，因目前晚生亦從事 CNT 的環境應用與廢棄物的生物毒性研究，感覺受益良多。

本次會議的論文發表計有 1200 篇分為 Oral 與 Poster。晚生所作的“以日光照射增進二氧化鈦粉末於聚苯乙烯材質中的分散(Dispersion Enhancement of TiO<sub>2</sub> Powder in Polystyrene Matrix by Visible Light Irradiation)”，安排於 3 日下上 14:00~16:00 於 3F 之壁報會場中展示。所發表的文章主要在於報告省能源製造均勻分散 TiO<sub>2</sub>/PS 高分子膜的方法。筆者之論文引起 3 位學者的駐足與深入討論，幸且詳列其人名國籍與意見:

第一位是 Prof. Alex Oelov，目前任教於 U. of Cambridge, 明年 2 月前往 U. of Suny Stony Brook。他一直覺得光用日光照就可以增加分散度很有趣，還一直追問晚生知不知道作用機制。

第二位是最後勇奪 Symposium L 最嘉論文獎的 Mr. Petre Hanys，來自日本 Tokyo U. 的塞爾維亞交換學生才到日本研就四個月就出來 show...。他較關心的是這種材料應用在何處。

第三位是 Prof. Michael H.-C. Jin，來自美國 U. of Texas at Arlington，他也是問晚生如何判定分散增加與其作用機制。

### 三. 心得與建議

筆者是第四次出席國際會議，對於主辦單位能邀請如此多位的國際級講者感到佩服。因此看到了不少位專精於觸媒的國際學者或其學生，這些學者平易近人的溫和是此行另一個收穫。此番造訪星國是第二次，感覺最大不同在於其捷運的路線多兩條，還有路上行人講華語的人與皮膚較深的印度人多很多，原來這與最近大陸學生占外國學生大半有關。

### 五. 攜回之重要文件

1. “2007 高等技術材料國際會議論文集”一本(共計 252 頁/附光碟).

# **Dispersion Enhancement of TiO<sub>2</sub> Powder in Polystyrene Matrix by Visible Light Irradiation**

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## A. ABSTRACT

Polystyrene (PS) is a hard, brittle, and highly transparent polymer with low moisture absorption, and it is the ease of incorporation of colorants and fills. Recently, the photocatalytic process of  $\text{TiO}_2$  has been recognized to be a very efficient technique for the degradation of organic pollutants, toxics, herbicides or dissolve carbons in water and wastewater. One of the key techniques regarded to practical applications is how to prepare a  $\text{TiO}_2$  well dispersed film with a high catalyzing efficiency. Because of that the maximum absorption peak of  $\text{TiO}_2$  is mainly at 300~400 nm, which only occupies a small fraction in natural sunlight or indoor visible light. In the past years people have effort on shifting this excitation energy by doping transition metals or nonmetals into  $\text{TiO}_2$  crystal. All of these processes need a drying and sintering treatment to obtain a uniform solid  $\text{TiO}_2$  film. However, blending of  $\text{TiO}_2$  powder with polymers, steel or cement is another cost and energy-saving methods. In this presentation, the authors have found that the dispersion of  $\text{TiO}_2$  particles in PS matrix could be improved by visible light irradiation without any PS degradation, and  $\text{TiO}_2$ /PS films are prepared through a simple solution blending.

## INTRODUCTION

Harnessing the photocatalytic effect of titanium dioxide ( $\text{TiO}_2$ ) has been recognized recently as a very efficient method for degrading organic pollutants, toxins, herbicides, or other dissolved carbon-based materials in water and wastewater [1]. A key challenge for the practical application of  $\text{TiO}_2$  is mixing it homogeneously with other materials. The maximum absorption energy of  $\text{TiO}_2$  is located at wavelengths in the range 300–400 nm, which occupies only small fraction of the spectrum of natural sunlight or indoor visible light. If this excitation energy can be shifted into visible light region, then it is more convenience for practical application of  $\text{TiO}_2$  catalyst [2].

The aim of this study is to increase the physical dispersion and photocatalytic properties of  $\text{TiO}_2$  in a PS matrix through a simple pretreatment. Because PS possesses many benzene rings on the side groups, we think that the pi electrons on benzene rings could be excited to pi\* energy levels and energy-transferred to  $\text{TiO}_2$  particles to form  $[\text{PS}^+][\text{TiO}_2^-]$  pairs. The formation of  $[\text{PS}^+][\text{TiO}_2^-]$  pairs would provide a strong driving force to separate the aggregated  $\text{TiO}_2$  particles.

## EXPERIMENTAL

Commercial TiO<sub>2</sub> and PS powder, which were purchased from Ismihara Sangyo Company (Japan) and Formosa Plastic Company (Taiwan), respectively. TiO<sub>2</sub> and PS were used without further purification.

### **Preparation of Synthesized TiO<sub>2</sub>/PS Polymer Films**

TiO<sub>2</sub> powder (0.01, 0.05, 0.1, 0.5, or 1.0 g) was added to a solution of PS (10 g) in toluene (60 mL). Each mixture was painted onto a glass disc several times and then air-dried in a hood for 3 days. The freshly synthesized TiO<sub>2</sub>/PS polymer film has an area of 86.5 cm<sup>2</sup> and a thickness of several micrometers.

### **UV Irradiation of Synthesized TiO<sub>2</sub>/PS Polymer Films**

These TiO<sub>2</sub>/PS polymer films were then cut into small pieces (1 cm<sup>2</sup>) to explore the effects of irradiation with UV or visible light. Irradiation times were set as 0, 3, 6, 9, and 12 hr. The distance between the TiO<sub>2</sub>/PS polymer film and the light source was set as 30 cm, and the measured light intensity was 2.249 W/m<sup>2</sup> for visible light and 0.412 W/m<sup>2</sup> for UV light. The film irradiated with UV light for 12 hr was used for the following photodegradation experiment.

## RESULTS

The aim of this study was to increase the physical dispersion and photocatalytic properties of TiO<sub>2</sub> in a PS matrix through a simple pretreatment. In the experiments of UV spectrum of TiO<sub>2</sub> solid film, a thin solid film TiO<sub>2</sub> was prepared using hand compressor. Figure 1 displays a map of the size distribution of the commercial TiO<sub>2</sub> powder with and without physical grinding; the particle sizes within the TiO<sub>2</sub> powder ranged from 10 to 1000 nm. The particle sizes of the TiO<sub>2</sub> powder before grinding exhibited a bimodal distribution with peak maximum at 4.24 and 17.18 μm; while the ground TiO<sub>2</sub> powder displayed a single distribution.

### **Optical Properties of Synthesized TiO<sub>2</sub>/PS films**

Figure 2 presents the UV spectra of two pure TiO<sub>2</sub> solid films and two TiO<sub>2</sub>/PS polymeric films, which were prepared using ground and non-ground TiO<sub>2</sub> powders. The absorption peak maximum of the TiO<sub>2</sub> solid film appeared near 258 nm. Several small peaks also appeared between 400 and 610 nm, the so-called “phthalo-dip peaks”, which were firstly observed in the UV spectra of inorganic filler-filled PS and poly(methyl methacrylate) (PMMA). The formation mechanism of “phthalo-dip peak” is unclear [1]. We attribute the appearance of the phthalo-dip peaks in Figure 2 to the scattering of

aggregated  $\text{TiO}_2$  powders. Figure 1 suggests that the particle sizes of these aggregated  $\text{TiO}_2$  powders ranged from 5-25  $\mu\text{m}$ ; therefore, the scattering region is ca. one-tenth of the aggregate size, i.e. 400–615 nm.

Figure 3 displays the UV transmittance of the various films. Results show that PS had the highest transmittance in the region 300–600 nm, and the pure  $\text{TiO}_2$  film had the lowest transmittance in this region but with phthalo-dip peaks. Figure 4(A) presents the UV spectra of the non-ground  $\text{TiO}_2/\text{PS}$  polymer films with respect to their  $\text{TiO}_2$  loadings. Results show that higher  $\text{TiO}_2$  loadings caused a decreased transmittance in the region 300–600 nm. We observe similar behavior in Figure 4(B), which presents the spectra of PS blended with ground  $\text{TiO}_2$  at various loadings. Figure 5 displays the effect of  $\text{TiO}_2$  loadings on the UV spectrum of visible light irradiated films. It is clear that the transmittance in the region 300–600 nm increased to values as high as that of the pure PS film. Because PS film is a total transparency film, when the UV spectra of  $\text{TiO}_2/\text{PS}$  films are similar with that of pure PS film which means that the physical dispersion of  $\text{TiO}_2$  particles is becoming homogeneously. Figure 6 demonstrates the similar behavior in the UV spectrum of the film irradiated with UV light but with a slower incremental rate. The FT-IR spectra of these  $\text{TiO}_2/\text{PS}$  polymer films (data are not shown here) irradiated

with visible and UV light did not show any significant changes after prolonged irradiation. It has been suggested that the increases in transmittance in the region 300–600 nm might have been caused by de-aggregation of TiO<sub>2</sub> powder in the PS matrices.

In summary, when TiO<sub>2</sub> powder was solution-blended with PS, we obtained an extremely inhomogeneous film. Illumination under visible light or UV irradiation led to an increase in the homogeneity of these freshly synthesized films, through the formation of a finer dispersion of TiO<sub>2</sub> particles in the PS matrix.

### **Improving Mechanism of TiO<sub>2</sub> in PS Films with Visible Light Pretreatment**

All above results have indicated that the pretreatment of PS/TiO<sub>2</sub> films can improve the physical dispersion of TiO<sub>2</sub> powder in PS films. The improving mechanism has been proposed: because the maximum absorption peak of pure PS film is at 400-600nm (in Figure 3) and the phthalo-dip peak of TiO<sub>2</sub> powder is also at 400-600 nm (in Figure 2), therefore energy interactions between excited TiO<sub>2</sub> and PS occurs. Benzyl rings of PS would be the electron-donators and TiO<sub>2</sub> could be the electron-acceptors to form [PS<sup>+</sup>][TiO<sub>2</sub><sup>-</sup>] pairs, thus the dispersion of TiO<sub>2</sub> particles in the PS substrate could be improved through this proposed mechanism.

## CONCLUSIONS

The photocatalytic efficiency of TiO<sub>2</sub>/PS films toward KMnO<sub>4</sub> can be improved through pretreatment of the film through irradiation with visible or UV light for 12 h. For the first time the dispersion of TiO<sub>2</sub> powder could be improved in benzene ring-containing polymers by visible light pretreatment.

## REFERENCES

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**Table 1 TiO<sub>2</sub>/PS Films Prepared for the Photodegradation of KMnO<sub>4</sub> Solution**

Run	Solution	Light Source	TiO <sub>2</sub> /PS Film?	Film Pretreatment?
1	10% KMnO <sub>4</sub>	None/Dark	Yes	No
2	10% KMnO <sub>4</sub>	Xe laser	No	No
3	10% KMnO <sub>4</sub>	Sunlight	Yes	No
4	10% KMnO <sub>4</sub>	Xe laser	Yes	No
5*	10% KMnO <sub>4</sub>	Xe laser	Yes	Yes

\* The film used was pretreated by UV irradiation for 12 h.

**Table 2 Removal Efficiency of 10% KMnO<sub>4</sub> Solution Photodegraded by Untreated and Pretreated TiO<sub>2</sub>/PS Films**

Removal (%)	Irradiation Duration (min)					Condition of used film	
	Runs	0	30	60	90		120
1	0%	0%	0%	0%	0%	0%	No changes
2	0%	0%	2%	2%	2%	5%	No changes
3	0%	0%	4%	6%	9%	13%	No changes
4	0%	0%	16%	22%	22%	27%	Dark spots were generated
5	0%	0%	20%	21%	27%	38%	Slightly ablated from glass reactor

(\*Standard derivation of removal percentage is about 3.2%)

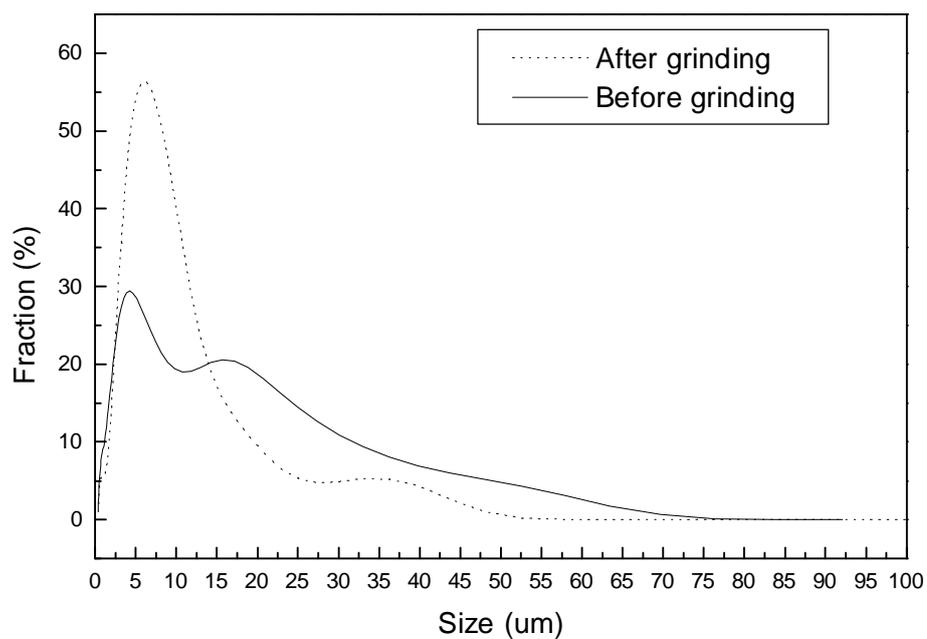


Figure 1 Size distribution of commercialized  $\text{TiO}_2$ , with and without physical grinding.

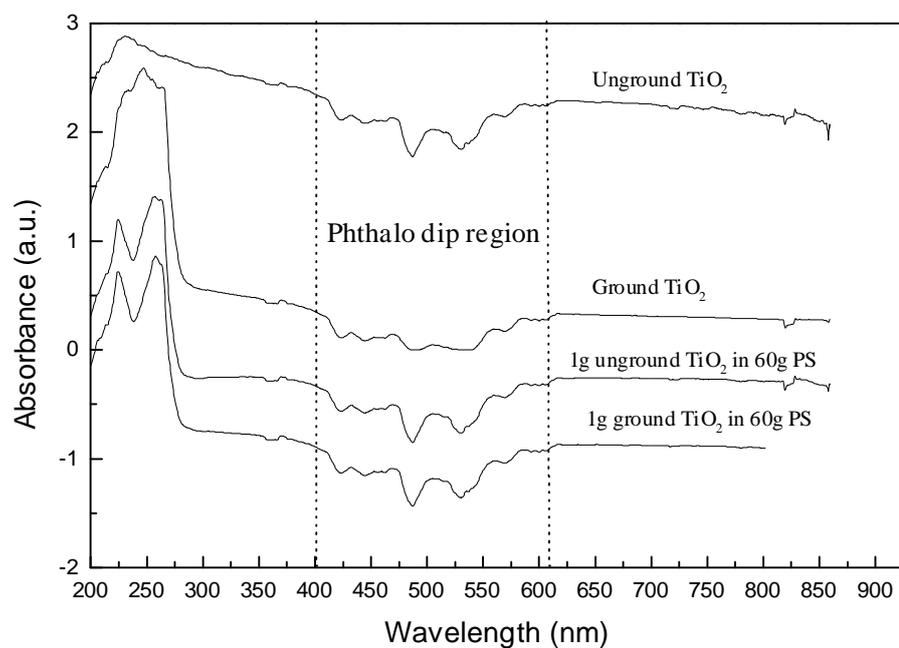


Figure 2 UV absorption spectra of two pure  $\text{TiO}_2$  films and two  $\text{TiO}_2/\text{PS}$  films prepared with ground and unground  $\text{TiO}_2$  powders.

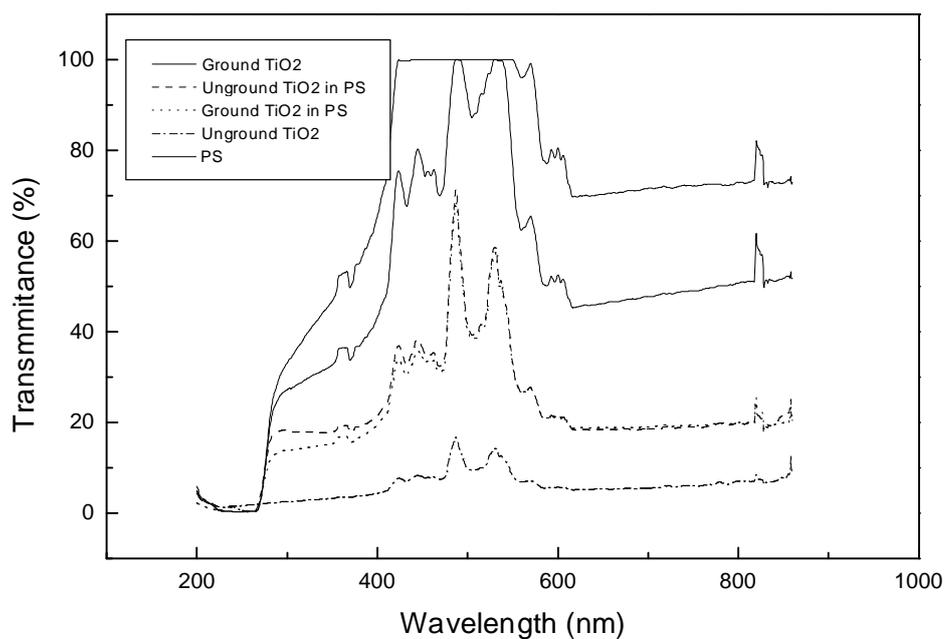


Figure 3 UV spectra of two pure  $\text{TiO}_2$  films and two  $\text{TiO}_2/\text{PS}$  films prepared with ground and unground  $\text{TiO}_2$  powders.

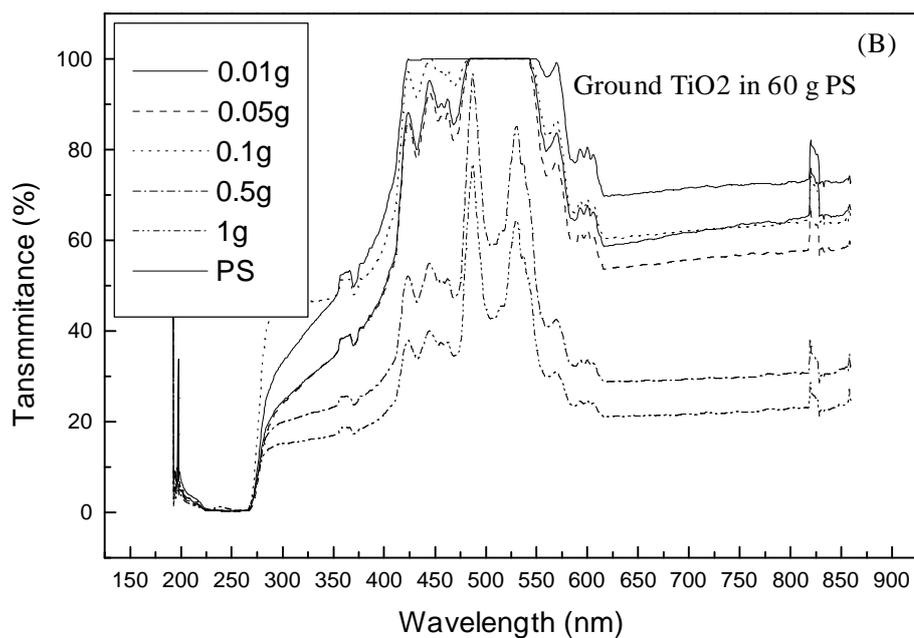


Figure 4 UV spectra of  $\text{TiO}_2/\text{PS}$  films prepared with various loadings of ground  $\text{TiO}_2$ .

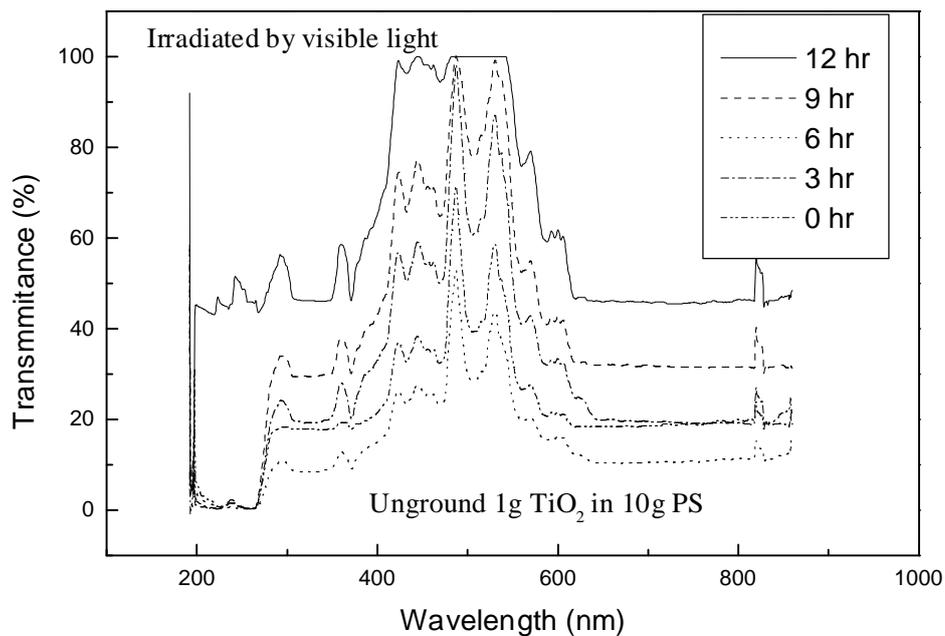


Figure 5 UV spectra of the film prepared from 1 g of  $\text{TiO}_2$  in 10 g of PS and irradiated with visible light.

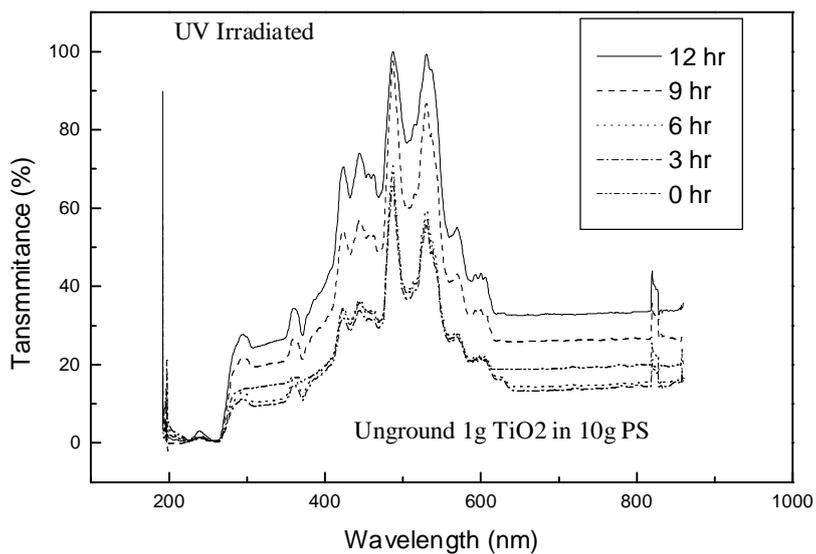


Figure 6 UV spectra of the film prepared from 1 g of  $\text{TiO}_2$  in 10 g of PS film and irradiated with UV light.