

# Synthesis and visible-light-derived photocatalysis of titania nanosphere stacking layers prepared by chemical vapor deposition

謝建德\* (Chien-Te Hsieh)  
元智大學化學工程與材  
料科學系

陳郁佳(Yu-Chia Chen)  
元智大學化學工程與材  
料科學系

韓道昀(Tao-Yun Han)  
國立聯合大學土木與防  
災工程學系

國科會計畫編號：國科會計畫編號：NSC101-2628-E-155-001-MY3

## Abstract

In this study, visible-light-derived photocatalytic activity of metal-doped titanium dioxide nanosphere (TS) stacking layers, prepared from chemical vapor deposition (CVD), was investigated. The as-grown TS spheres, having an average diameter of 100–300 nm. The crystalline structures of the TS samples were of anatase-type. With increasing dopant density, the optical band gap of the nanospheres became narrower, e.g., the smallest band gap of Co-doped TS was 2.61 eV. Both Ni- and Co-doped TS catalysts showed a photocatalytic capability in decomposing organic dyes under visible irradiation. In comparison, Co-doped TiO<sub>2</sub> catalyst not only display the adsorption capacity, but also the photocatalytic activity higher than the N-doped TiO<sub>2</sub> catalyst. This result can be attributed to the fact that the narrower band gap easily generates electron-hole pairs over the TS catalysts under visible irradiation, thus, leading to the higher photocatalytic activity.

本研究利用化學氣相沉積法(CVD)製備金屬摻雜之二氧化鈦奈米球體(TS)薄膜,探討可見光下之觸媒催化活性。經CVD製備之TS奈米球,其粒徑約為100-300奈米,由X光繞射分析為銳鈦礦晶型結構。隨金屬摻雜濃度提升,TS薄膜能隙價帶變窄,由鈷所摻雜之TS薄膜可達最小能隙約2.61 eV。光催化測試結果顯示經鈷與鎳摻雜之TS薄膜皆具分解有機染料之催化能力,兩者比較可知鈷摻雜之TS薄膜不僅具有優異的染料吸附能力,亦具良好可見光催化性能。以上結果可歸因於鈷摻雜之TS薄膜具較窄之能隙價帶,可於可見光下產生電子電洞對引發較優異之光催化性能。

**Keywords:** photocatalysis, titania nanospheres, chemical vapor deposition, metallic doping

## INTRODUCTION

It is generally recognized that anatase-type  $\text{TiO}_2$  photocatalyst has attracted a great deal of interest owing to its redox capability under ultraviolet (UV) irradiation, i.e., usually under a wavelength of  $< 385$  nm. However, UV light in the solar light spectrum only contributes to less than 3–4% of the energy, while visible light contributes to 45% of the energy from solar radiation.<sup>1</sup> This implies that only 3–4% of solar light can be applied according to the band gap of anatase-type  $\text{TiO}_2$  of 3.0–3.2 eV.<sup>2</sup> Accordingly, this study aims to advance an integrated approach that could incorporate  $\text{TiO}_2$  growth with metallic doping, demonstrating the following advantages: simplicity, cost-effectiveness, and convenience.

This study attempted to develop a CVD approach for synthesizing Co- and Ni-doped TS stacking layers in one stage. Two kinds of metal-containing Ti sols (i.e., Co and Ni ionic solutions) with appropriate atomic ratios of dopant to titanium served as a precursor. Both Co and Ni dopants were expected to narrow the band gap of  $\text{TiO}_2$  spheres that can effectively facilitate visible-light photocatalysis of organic compounds. The photocatalysis of a basic dye (basic violet 10 (BV10)) on Co- and Ni-doped TS layers was investigated. The removal efficiency of the basic dye was considered to be an indicator for evaluating the photocatalytic ability of the catalysts. In addition, the efforts to explore the adsorption/photocatalysis rate constants and the equilibrium capacities were also devoted.

## EXPERIMENTAL

### Synthesis of metal-doped TS layer

A similar procedure for TS stacking layers has already been reported.<sup>3</sup> In brief, the precursor solution used in the present work contained titanium isopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , reagent grade) and metal nitrates ( $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$ , reagent grade), without any further purification. The concentrations of metal nitrates used in this study were 0.01 M. The growth of Co-/Ni-doped  $\text{TiO}_2$  layers was established on a home-made CVD apparatus, as illustrated in Fig. 1. First, the cleaned substrates were placed in appropriate positions in the CVD reactor. A mixture precursor was then heated to  $450^\circ\text{C}$  at a heating rate of  $3^\circ\text{C min}^{-1}$ . The CVD process was carried out under a steady  $\text{N}_2$  flow for the period of 1 h. To inspect the effect of dopant concentration, Ti-containing precursors with different molar ratios ( $\text{M}:\text{Ti}= 1$  and 3%, where  $\text{M}=\text{Ni}$  and  $\text{Co}$ ) were adopted to synthesize various  $\text{TiO}_2$  stacking layers on glass substrates. The as-synthesized TS stacking layers were designated as Ni-1-TS, Ni-3-TS, Co-1-TS, and Co-3-TS,

respectively, according to the preparation of different M/Ti molar ratios.

### **Liquid-phase adsorption and photocatalysis**

Analytical-grade basic dye, BV10 (molecular formula:  $C_{28}H_{31}ClN_2O_3$ ; molecular weight: 478.5; supplier: Sigma Chemical Co.) served as the target organic pollutant for adsorption and photocatalysis experiments. First, an adsorption experiment of BV10 in complete darkness was performed before photocatalysis under visible irradiation. The purpose of this setup was to clarify the effects of adsorption and photocatalysis. Subsequently, we added a certain amount of  $TiO_2$  spheres (*ca.* 0.02 g) and the prepared BV10 solution (100 mL) into a glass-stoppered flask. The adsorption temperature duration was 40°C and 6 h, respectively. Following dark adsorption, photodegradation of BV10 on titanium samples was carried out to study the photocatalytic reactivity under visible illumination. Based on the Beer–Lambert law, the dye concentration was found to be linearly proportional to the absorbance of the measured spectrum within the concentration range of around 30 mg L<sup>-1</sup>. The BV10-adsorbed titania slurries were also illuminated at 40°C, employing a fluorescent lamp. To ensure no UV-light illumination, the irradiation from the fluorescent lamp was filtered through a UV-cut filter (Newport FSQ-GG 400) that allowed the visible light of > 400 nm to pass through it. The incident intensity of illumination from the visible light was set at 40 Lux.

## **RESULTS AND DISCUSSION**

### **Textural characteristics of TS layers**

Fig. 2 shows the cross-sectional (2(a)) and top (2(b)) views of FE-SEM images of Ni-doped TS, prepared from the CVD process using a mixed precursor of  $Ti(OC_3H_7)_4 + Ni(NO_3)_2$ . The spherical shape of Ni-doped  $TiO_2$  particles is similar to our pervious study,<sup>4</sup> i.e., the as-prepared layer consisting of a large number of titania particles on a glass substrate. It can be observed that the TS have an average diameter of 100–300 nm, and that the layer-by-layer sphere stack generates a primary surface roughness. This morphology is also observed in Co-doped TS, as depicted in Fig. 2(c) and 2(d), respectively.

### **Adsorption and visible-light photocatalysis on TS layers**

Several studies have proposed a possible photocatalytic mechanism to describe the decomposition of various organic molecules on  $TiO_2$  and ZnO catalysts.<sup>5–10</sup> In our case, the mechanism for removing BV10 molecules from

liquid phase consists of (i) liquid-phase adsorption of BV10 and (ii) photocatalysis of adsorbed BV10 under visible illumination. The dark adsorption and visible-light-derived photocatalytic kinetics as the functions of time are shown in Fig. 5. It can be seen that an equilibrium state of BV10 adsorption was reached within 5 h. The equilibrium-adsorption capacities of all the TS samples exhibited the following order: Co-3-TS ( $22.5 \text{ mg g}^{-1}$ ) > Co-1-TS ( $11.5 \text{ mg g}^{-1}$ ) > Ni-3-TS ( $10.2 \text{ mg g}^{-1}$ ) > Ni-1-TS ( $8.2 \text{ mg g}^{-1}$ ) > TS ( $5.0 \text{ mg g}^{-1}$ ) > P25 ( $2.0 \text{ mg g}^{-1}$ ). This demonstrates that the TS catalysts exhibit different numbers of active sites for BV10 adsorption in liquid phase, i.e., surface heterogeneity.

Both adsorption and photocatalysis kinetics were observed to take an identical period of 5 h until they reached an equilibrium state. The removal capability from photocatalysis after 5 h of visible illumination exhibited the following order: Co-3-TNT ( $21.0 \text{ mg g}^{-1}$ ) > Co-1-TNT ( $15.2 \text{ mg g}^{-1}$ ) > Ni-3-TNT ( $4.1 \text{ mg g}^{-1}$ ) > Ni-1-TNT ( $3.2 \text{ mg g}^{-1}$ ). Accordingly, we observed the following two correlations: (i) an inverse relationship between photocatalytic capacity and optical band gap and (ii) an increasing adsorption capacity with photocatalytic activity.

## CONCLUSIONS

This study investigated the visible-light-derived photocatalytic activity of BV10 on metal-doped TS catalysts, prepared by an in situ metallic doping CVD technique. The approach was capable of producing TS stacking layer on glass substrate. A large number of TS with an average diameter of 100–300 nm created a layer-by-layer sphere stack layer. In comparison, Co-3-TS catalyst not only offered the highest adsorption capacity, but also the best photocatalytic activity. Accordingly, this study reported a one-step efficient approach to synthesize metal-doped TS catalysts to photocatalyze BV10 molecules in aqueous solution.

## REFERENCES

- 1 Anpo M, *Pure Appl Chem* **72**:1787–1792 (2000).
- 2 Mor GK, Shankar K, Paulose M, Varghese OK and Grimes CA, *Nano Lett*

- 5:191–195 (2005).
- 3 Hsieh CT, Fan WS, Lin JY and Chen WY, *Sep Purif Technol* **67**:312–318 (2009).
  - 4 Hsieh CT, Lai MH and Cheng YS, *J Colloid Interface Sci* **340**:237–242 (2009).
  - 5 Matos J, Laine J and Herrmann JM, *J Catal* **200**:10–20 (2001).
  - 6 Matos J, Laine J and Herrmann JM, *Appl Catal B* **18**:281–291 (1998).
  - 7 Zou L, Luo Y, Hooper M and Hu E, *Chem Eng Process* **45**:959–964 (2006).
  - 8 Barton DG, Shtein M, Wilson RD, Soled SL and Iglesia E, *J Phys Chem B* **103**:630–640 (1999).
  - 9 Kaneco S, Katsumata H, Suzuki T and Ohta K, *Chem Eng J* **125**:59–66 (2006).
  - 10 Yu Y, Yu JC, Chan CY, Che YK, Zhao JC, Ding L, Ge WK and Wong PK, *Appl Catal B* **61**:1–11 (2005).

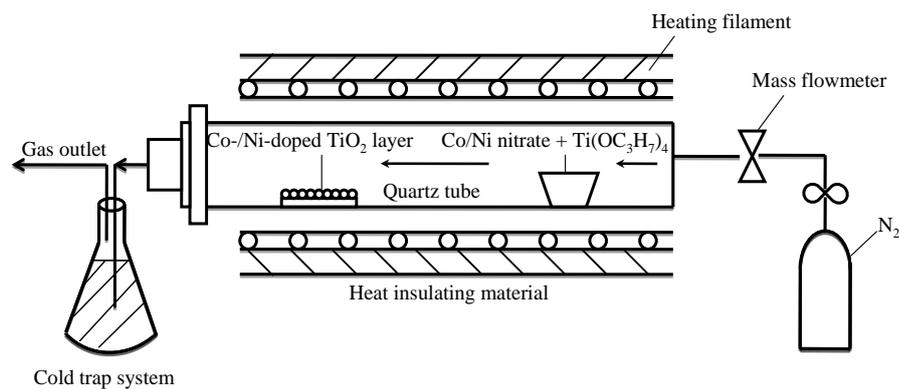


Figure 1. Schematic diagram of the CVD reactor for growing metal-doped TiO<sub>2</sub> sphere stacking layers.

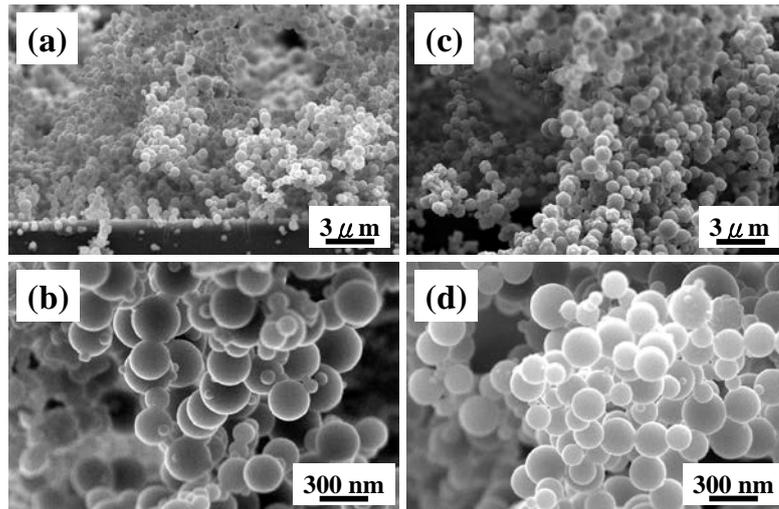


Figure 2. FE-SEM images of Ni-doped TiO<sub>2</sub> spheres: (a) side and (b) top views. FE-SEM images of Co-doped TiO<sub>2</sub> spheres: (c) side and (d) top views.

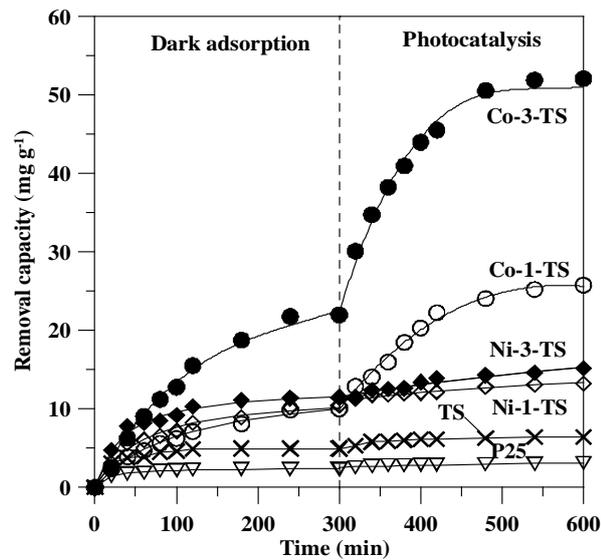


Figure 5. Liquid-phase adsorption of BV10 followed by visible-light photocatalytic kinetics of Ni- and Co-doped TiO<sub>2</sub> nanospheres at 40°C.

The kinetic data of BV10 on commercial P25 was also plotted to compare with that of as-grown TiO<sub>2</sub> spheres.