

# CHAPTER I

## INTRODUCTION

### 1.1 Introduction

Environmental pollution is becoming more and more serious. The toxic waste disposal of industrial and household effluent has become a problem of growing importance in society. There are different classes of toxic substances, organic and inorganic compounds, which are dangerous to both the environment and human health. Therefore, detoxification of polluted water becomes a significant task in environment protection. However, a traditional technology has its limitation. A number of pollutants can only be degraded very slowly, incompletely or not at all by the conventional procedures. Accordingly, the new methods should be developed. The photocatalysis has been a great deal of attention to be an attractive process for degradation of any water pollutants by ultraviolet light using a titanium dioxide. However  $\text{TiO}_2$  in powder form it has several problems. For instance separation of photodegradation reaction is likely difficult, the suspended particles tend to aggregate at the high concentrations, and the efficiency was limited by turbidity effect.

The heterogeneous photocatalysis of titanium oxide ( $\text{TiO}_2$ ) has become a subject in the recent years as it has a high capability of the complete elimination of the perpetual chemical pollutants in the environment by using solar or artificial light illumination. The unique advantage of  $\text{TiO}_2$  photocatalysis are low operation temperature, inexpensive, nontoxic and relatively to the stage of commercialization (Fujishima *et al.*, 2000; Frank *et al.*, 1977; Fujishima *et al.*, 2006). In the past few years, the colloidal and particulate  $\text{TiO}_2$  had been widely used to photodegradation of the pollutants in both liquid and gaseous phase. But the suspended system encountered three vital technical problems; which are (a) the need for separation of filtration step after the photodegradation reaction, (b) the particles aggregation especially at high concentrations, and (c) the problematic use in continuous flow system (Sopyan *et al.*, 1996; Arabatzis *et al.*, 2003).

To avoid these problems, various methods have been developed to prepare  $\text{TiO}_2$  films on the solid support substrates including sol-gel (Li *et al.*, 2002; Zainal *et*

*al.*, 2007), sputtering (Sirghi *et al.*, 2001; He *et al.*, 2006), chemical vapor deposition (Yoshitake *et al.*, 2002; Bessergenev *et al.*, 2006), and liquid-phase deposition (Masuda *et al.*, 2003; Yu *et al.*, 2006). However, the efficiency of the immobilized system is much lower than that of the corresponding slurries, because of the inevitable reduction of the overall surface active area association to catalyst immobilization (Rachel *et al.*, 2002). Compared with the TiO<sub>2</sub> films mentioned above, TiO<sub>2</sub> nanotube array film is expected to be a promising photocatalysis to overcome such drawbacks due to its great high surface-to-volume ratio and size-dependent properties. Moreover, the TiO<sub>2</sub> nanotube array film possesses a very strong mechanical strength, because it grows directly of the titanium substrate by electrochemical anodic oxidation method, which is verified to be a relatively simple and efficient process for fabricating the nanostructured TiO<sub>2</sub> films such as template synthesis, hydrothermal reaction, spray pyrolysis (Wang *et al.*, 2004; Hoyer, 1996; Chen *et al.*, 2005).

In the previous anodization studies (Gong *et al.*, 2001; Mor *et al.*, 2003; Macak *et al.*, 2005 a; Macak *et al.*, 2005 b; Cai *et al.*, 2005; Paulose *et al.*, 2006; Taverira *et al.*, 2006) have used either constant potential (potentiostatic) or constant current (galvanostatic) nanotube growth modes. On the other hand, the interplay of electrochemical and chemical processes inherent in the anodic film growth suggests that pulsing the potential between carefully chosen limits and varying the duty cycle (i.e., voltage 'on' and 'off' durations) can exert an important influence on the film morphology and nanotube formation. The pulse anodization approach offers a new, hitherto unavailable dimension in fine control and tuning of anodic layer growth and nanotube self-assembly on targeted metal substrates. From a practical process economics perspective, pulse anodization also offers savings in energy consumption relative to the continuous process counterpart.

The efficient utilization of solar energy is one of the major goals of modern science and engineering. However, the widespread technological use of titania is impaired by its wide band gap (3.2 eV), which requires ultraviolet (UV) irradiation, for photocatalysis activation. Because UV light accounts for only a small fraction (8%) of the sun's energy compared to visible light (45%), any shift in the optical response of titania from UV towards full spectrum light will have a positive impact on the photocatalysis and photoelectrochemical utility of the material. Historically, doping of the titania has been the approach taken for band-gap of material. When

employing dopant to change the optical response of a material it is desirable to maintain the integrity of the host material crystal structure while changing its electronic structure (Rajeshwar, 1985 ; Rajeshwar, 2007) The main objective of this research is to investigate TiO<sub>2</sub> nanotube and metal doped TiO<sub>2</sub> nanotube using anodization technique and its application on hazardous waste removal and solar energy conversion.

For this research study, a highly dense, well-ordered, and uniform titanium nanotube array was prepared on Ti substrate by an electrochemical method. The morphology, structure, and composition of TiO<sub>2</sub> nanotube array film were characterized by scanning electron microscopy (SEM), Raman spectroscopy. photoelectrochemical measurements were characterized by a standard single-compartment, three-electrode electrochemical cell and the photocatalysis activity of the TiO<sub>2</sub> array samples in chromium (VI) aqueous solution were evaluated (as Cr (VI) is a high carcinogenic risk, high solubility, and high mobility (Kimbrough *et al.*, 1999)).

## 1.2 Objectives

The objectives of this study are as follow:

1.2.1 To find optimum condition in synthesizing self-organized TiO<sub>2</sub> nanotube arrays by pulse anodization.

1.2.2 To investigate influence of pulse anodization parameters such as anodization voltage, duration of negative voltage and medium modifier on morphology, photoelectrochemical performances, and photocatalytic removal efficiency.

1.2.3 To investigate influence of metal doped parameters such as metal type, loading, duration of pulse, and media modifiers on the formation of metal doped on TiO<sub>2</sub> nanotube using pulse anodization technique.

## 1.3 Hypotheses

1.3.1 Pulse anodization technique provides better-defined nanotube morphologies than constant voltage growth mode. Nanotube TiO<sub>2</sub> provide higher photocatalytic activity than conventional TiO<sub>2</sub> (non-organized film).

1.3.2 Doping of metal ions to TiO<sub>2</sub> provide better efficiency of photocatalytic activity or extend the absorption of light into visible region compared to the undoped TiO<sub>2</sub> films.

## 1.4 Scope of study

1.4.1 Investigation of titanium nanotube which prepared on Ti substrate by anodization method and metals such as Li, Ni, Mn, V, and Nb were used metal-dopant.

1.4.2 The morphology, structure, and composition of TiO<sub>2</sub> nanotube array film were characterized by scanning electron microscopy (SEM), and Raman spectroscopy.

1.4.3 The photoelectrochemical property of TiO<sub>2</sub> nanotube array were examined by photocurrent spectroscopy and photoaction spectra.

1.4.4 In testing of photocatalysis activity of TiO<sub>2</sub>, synthetic wastewater containing Cr (VI) was employed. The Cr (VI) was used as probe reductions.