CHAPTER I
INTRODUCTION

The pollutant of textile wastewater was seriously considered as one of the sources of water pollutant, especially dye solution. These textile dyes consist of a large group of organic compounds that are toxic to both aquatic life and human beings. Statistics estimated that about million tons of different dyes are produced annually worldwide. Azo-dyes like acid orange 7 represents up to 70% of the dyes available on the world market today. Moreover, approximately 15% of the textile dyes are produced in the industrial effluents during manufacturing or processing operation (Stoyanowa *et al.*, 2014). For removal of dye pollutants, several physical techniques such as adsorption on carbon, ultrafiltration, reverse osmosis, coagulation by chemical, etc., have been used in the past to remove the dye pollutants. However, these methods produced secondary pollutants, which require further treatment, thus increasing the cost of the process. Photocatalysis is one of the best techniques for the degradation of dyes to harmless products (H_2O and CO_2) in waste water (Jaiswal *et al.*, 2012).

TiO_2 has been widely used as a photocatalyst for the decomposition of environmental pollutants because it is cheap, nontoxic, and chemically stable. TiO_2 is capable of decomposing a wide variety of pollutants and toxic materials. The limitation of TiO_2 semiconductor is the need of UV illumination. To increase the TiO_2 photocatalyst activity, the concept of reduction and oxidation energy storage has been investigated. Oxidation energy as reported by coupling n-type TiO_2 with p-type $Ni(OH)_2$. Takahashi and Tatsuma (2005) also revealed that the oxidation energy storage ability of TiO_2-$Ni(OH)_2$ bilayer can be used for the chemical oxidation of various species. Lian *et al.* (2011) reported the behavior of oxidation energy storage by a porous nanostructure TiO_2-$Ni(OH)_2$. The porous nanostructure improved the performance of oxidation energy storage as a result from the change form $Ni(OH)_2$ to NiOOH under UV irradiation. A photocatalyst with reductive energy storage ability was easily developed by dopingTiO_2, an-type semiconductor, with a redox-active n-type such as WO_3, MoO_3 or $H_3PW_{12}O_{40}$. The result showed that the photocatalytic activity was retained without illumination because of the reductive energy storage

ability (Takahashi and Tatsuma, 2005). The oxidation energy storage is more difficult than the reduction energy storage because of a immobiled charge (h^+) in TiO_2. Consequently, the oxidative energy storage has been challenging in recent years.

Zhao *et al.* (2014) also studied a p-n junction catalyst, $CuFe_2O_4/Bi_4Ti_3O_{12}$. The experimental results suggested that the photocatalaytic performance of $CuFe_2O_4/Bi_4Ti_3O_{12}$ was better than the single catalyst. In addition, the photocatalytic activity of $TiO_2$was improved by a metal dopant such as V, Fe, Cr, and Cu. The contact between the n-type TiO_2 and the p-type doped TiO_2 introduces the p-n junction that drives electron and hole. Shifu *et al.* (2008) reported that the p-type semiconductor ZnO and n-type semiconductor TiO_2 can form p-n junction. At the junction, the ZnO region has a negative charge, while TiO_2 has a positive charge. Under the UV illumination, the photogenerated e^-/h^+ pairs were separated by the inner electric field that the electron was moved to the TiO_2 region, and the hole was shifted and trapped on the ZnO region. The separation of e^-/h^+ pairs was efficiently generated leading to the enhancement of photocatalytic acticity. V_2O_5 doped TiO_2 improved the photocatalyst activity by reducing the bandgap of TiO_2 from 3.0 - 3.2 eV to 2.5 - 2.7 eV, leading to a promising visible light-driven photocatalyst. The p-n junction between TiO_2 and V_2O_5 separated charge carriers and also diminished the recombination rate of e^-/h^+ to enhance the photocatalytic activity of TiO_2 (Chang and Liu, 2011).

It is now important to understand how this novel p-n junction approach can reserve energy. Hence, the main goal of this research was to prepare a p-n junction catalyst TiO_2, a n-type semiconductor, with ZnO and V_2O_5, a p-type semiconductors, by sol-gel technique. Moreover, the ZnO and V_2O_5 doped TiO_2 bilayer films were investigated as the oxidation energy storage for photocatalytic of acid orange 7 (AO7) degradation with and without UV illumination.