

## CHAPTER I

### INTRODUCTION

The increase of worldwide surface temperature is now considered as a global challenge due to the rising atmospheric level of greenhouse gases (GHGs). Carbon dioxide (CO<sub>2</sub>) is the most important greenhouse gases emitted via human activities and industrial processes. Starting from the industrial revolution, large amount of fossil fuel has been burned resulting in a dramatic increase of CO<sub>2</sub> level. Accordingly, carbon capture and storage (CCS) has been invented and applied as the most effective methods for reducing CO<sub>2</sub> emission from large industrial plants (Yang *et al.*, 2008; Wanga *et al.*, 2011; Drage *et al.*, 2012; Rubin *et al.*, 2012; Li *et al.*, 2013). The different CO<sub>2</sub> capture technologies such as absorption, adsorption, cryogenics, and membranes have been applied (Choi *et al.*, 2009). Recently, amine-based processes and wet scrubbing processes are the popular commercial processes for CO<sub>2</sub> capture. However, they have critical drawbacks such as energy penalty, corrosion, and solvent degradation (Rubin *et al.*, 2012). Accordingly, adsorption is proposed to be one of the potential techniques for CO<sub>2</sub> capture due to its low cost, low energy requirement, non-corrosive problems, and good cycle performance (Yang *et al.*, 2008; Mondal *et al.*, 2012). Because of their high porous structure, materials such as activated carbon materials, zeolites, silica, metal organic frameworks can be employed as the adsorbents in adsorption process (Sayari *et al.*, 2011).

The carbon materials which have been most commonly studied for applying in CO<sub>2</sub> capture are activated carbon (AC) and carbon nanotube (CNT) (Sayari *et al.*, 2011). Activated carbon (AC) has been utilized in many industrial applications and it is one of the potential candidates employed for CO<sub>2</sub> adsorbent, since there are several advantages of AC over other CO<sub>2</sub> removal adsorbents including its low cost, wide availability, high hydrophobicity, and light weight (Choi *et al.*, 2009). AC can be made from various types of carbonaceous substances such as wood, coconut shells, pitch coke, and coal via a two-step process, carbonization process followed by activation process (Lee *et al.*, 2006). Lately, carbon nano spheres (CNS) as a new form of carbon based materials has increasingly received research attention and applied in a wide range of applications owing to their attractive characteristics, such

as high thermal stability, high strength, and light weight (Auer *et al.*, 1998). There are different techniques used to synthesize the CNS such as chemical vapor deposition, ultrasonic treatment, templating method, arc discharge, and pyrolysis. Plasma in liquid method, as one of the technologies that can produce carbon materials, has attracted more attention and studied by many researchers because of its advantages such as simple to handle, potential for high yield, and economical method. Recently CNS has been successfully produced via a novel plasma in liquid technique namely solution plasma process (SPP). This technique presented several benefits such as the utilization of graphite electrodes and the addition of feed gas was not necessary as compared to the conventional technique (Kang *et al.*, 2013, 2014).

It has been reported that the CO<sub>2</sub> capture capacity of AC, which primarily depends on physical adsorption, can be enhanced by incorporating nitrogen surface groups into the carbon surface. A higher adsorption of CO<sub>2</sub> was promoted due to the role of nitrogen groups as Lewis base can interact with acidic CO<sub>2</sub> (Lewis acid) (Shafeeyan *et al.*, 2010). A number of researchers have introduced basic nitrogen functional groups onto the carbon surface for increasing CO<sub>2</sub> adsorption (Maroto-Valer *et al.*, 2005; Arenillas *et al.*, 2005a; Gui *et al.*, 2013a). One of the popular ways is to incorporate the nitrogen functionalities into carbon structure. This can be performed by treatment of activated carbon by N-containing reagents or preparing activated carbon from N-containing precursors (Raymundo-Piñero *et al.*, 2002; Huang *et al.*, 2003; Przepiórski *et al.*, 2004; Wang *et al.*, 2013). Many researchers have investigated the treatment of activated carbons under ammonia atmosphere and reported that the ammonia treatment is a suitable method to improve the basicity of carbon surface, resulting in an increase in CO<sub>2</sub> adsorption capacity. It was found that free radicals produced during amination can react with oxygen containing functionalities and active site on the carbon surface to create nitrogen surface groups (Przepiórski *et al.*, 2004; Pevida *et al.*, 2008a; Plaza *et al.*, 2009a).

The activated carbon can be provided the oxygen groups on its surface by oxidizing with various oxidizing agents such as O<sub>3</sub>, HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (Daud, 2010). The wet oxidation by nitric acid (HNO<sub>3</sub>) has been reported as a very effective oxidative method to introduce large amount of oxygen functional groups onto the carbon surface. As reported elsewhere (Jaramillo *et al.*, 2010), the oxidation of

activated carbon with  $\text{HNO}_3$  can introduced the difference oxygen functional groups on the carbon surface and carboxylic acid groups are mostly formed. Moreover, Plaza *et al.* (2013) found that the oxidation is able to improve the  $\text{CO}_2$  adsorption of AC due to electron donating of oxygen atoms formed on carbon surface and can react with  $\text{CO}_2$  molecules via electrostatic interactions.

In this work, commercial coconut-based activated carbon (AC), benzene-derived carbon nano spheres (CB), and pyridine-derived carbon nano spheres (CP) were applied as the  $\text{CO}_2$  adsorbents. To prepare activated carbon nano spheres, the CB and CP carbon were carbonized and then activated with  $\text{CO}_2$ . In order to investigate the effect of different surface treatment approaches on  $\text{CO}_2$  capture capacity, AC, ACB, and ACP were chemically modified using  $\text{HNO}_3$  oxidation, amination without  $\text{HNO}_3$  pre-oxidation and amination with  $\text{HNO}_3$  pre-oxidation.