CHAPTER I
INTRODUCTION

Recently, the most common problems in many countries of the world are rigorous environmental standards and regulation on volatile organic compounds (VOCs). The VOCs are divided into two groups: non-halogenated hydrocarbons, and halogenated hydrocarbons. Non-halogenated hydrocarbons are volatile hydrocarbons that do not contain a chlorine atom within the molecule. Normally, this group is found in daily life products such as plastics, cleaning solvents, and paints, and it can affect human health through the respiratory system. Examples of non-halogenated hydrocarbons are aliphatic hydrocarbons, aromatic hydrocarbons, alcohol, aldehyde, and ketones. The other type of VOCs is halogenated hydrocarbons which consist of a chlorine atom within the molecule. They are used in dry cleaning, metal cleaning, furniture making, thermoplastics production, degreasing, printing, paper and textile production, and paint removal. They are clear liquids, and vaporize at room temperature (Penza *et al.*, 2003; Kukla *et al.*, 2009; Feng *et al.*, 1999). Examples of halogenated solvents are trichloroethylene, perchloroethylene, methylene chloride, ethylene chloride, carbon tetrachloride, chloroform, and methyl chloroform. The toxicity of these chemical vapors is more severe to human health than non-halogenated hydrocarbons. The solvents pose a major source of environmental problems such as stratospheric ozone depletion, smog formation, acid rain production, and global warming. Health problems caused by exposing humans to these solvents are systemic, immunological, neurological, reproductive, developmental, and genotoxic and carcinogenic in nature; which can lead to death (Whitaker *et al.*, 1965). The severity of the chemicals on human health depends on the concentration and exposure levels. The National Institute of Occupational Safety and Health (NIOSH) defined the limit for personal exposure to the chemical that cause death or immediate or delayed permanent adverse health effects as the immediately dangerous to life or health concentrations (IDLHs) (U.S. Department of Commerce, 2012). For instance, the exposure level of chloroform that leads to death in humans is ~40,000 ppm (Featherstone, 1947). The level of chloroform that leads to human loss of responsiveness, loss of skeleton muscle reflex, and decreased stress response is less than 22,500 ppm (Whitaker *et al.*, 1965; Wikipedia, 2012). The deadly inhalation concentration for methylene chloride, or dichloromethane (DCM), in a study of animals, was ~3,000 ppm (Williams *et al.*, 2000). Hence, effective sensory systems are required to identify the presence of these solvents.

One development of sensing materials has focused on conductive polymers due to their unique properties. They are: light weight, easy to synthesize, possess high sensitivity and short response time, and have good mechanical properties over metal oxides (Bailey *et al.*, 2008; Bai *et al.*, 2007; Albert *et al.*, 2000). Polydiphenylamine (PDPA) is an N-aryl substituted derivative of polyaniline and it shows better mechanical strength, electrochemical, conductivity, and electro chromic properties than polyaniline (Li *et al.*, 2008; Hua *et al.*, 2005; Hua *et al.*, 2003; Chung *et al.*, 2001). Additionally, PDPA has been used as a sensing material for many sensory systems: pH sensors, CO sensors, and glucose biosensors (Santhosh *et al.*, 2009; Santhosh *et al.*, 2007; Rodriguez *et al.*, 2007). Moreover, a highly sensitive sensor system can be improved with increasing material surface area to mass ratio. Conductive polymers have been developed at nanoscale: nanowires (Huang *et al.*, 2010; Wang *et al.*, 2014; Hangarter *et al.*, 2010), nanotubes (Kwon *et al.*, 2012), nanofibers (Nicholas, 2013; Huang *et al.*, 2002), etc for used as a sensing materials. Another important property of a sensor system is selectivity (Askim *et al.*, 2013). Zeolites are of interest as a selective material because they provide optimal sizes and shapes, which can absorb chemical vapor molecules while sustaining a high surface area to mass ratio due to its porous structure (Zhou *et al.*, 2003). Recently, conductive polymer/zeolite composites have been used as a selective material for many toxic gases: e.g., poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate/zeolite ZSM5 as a carbon monoxide sensor (Chanthaanont *et al.*, 2012); poly(3-thiopheacetic acid)/zeolite Y composite as an ammonia sensor (Konkayan *et al.*, 2013); polypyrrole/zeolite 3A as a chemical lacquer thinner sensor (Wannatong *et al.*, 2008), etc. The zeolite properties can be controlled by varying the Si/Al ratio. The dealumination method is a method to remove aluminum from the framework resulting in a higher Si/Al ratio, chemical and thermal stabililty, and zeolite hydrophobicity (Saidina *et al.*, 2002; Holmberg *et al.*, 2004; Kumar *et al.*, 2000; Triantafillidis *et al.*, 2000).

This work is aimed at fabricating the composites between PDPA and zeolite Y with H^+ as a cation (YH) to discriminate between the non-halogenated and halogenated hydrocarbon solvents, based on the electrical conductivity response when exposed to halogenated vapors. The sensitivity of the composites has been developed by increasing both surface area to mass ratio of PDPA and Si/Al ratio of zeolite Y. PDPA has been synthesized in nanoscale via emulsion polymerization. The size and shape of PDPA nanoscale (nPDPA) have been controlled by incorporating different surfactants—anionic, cationic, and nonionic. The surfactant concentration, morphology, particle size, crystallinity, electrical conductivity, optical band gap, and thermal stability of nPDPA are investigated. Zeolite Y has been modified by a dealumination process to increase the Si/Al ratio (DYH). The influences of the Si/Al ratio, acid treatment times, zeolite Y content, and vapor concentration of the halogenated solvents on the electrical conductivity response of the composites are investigated. The physical adsorption of the halogenated solvents on the composites is examined by FT-IR and UV-Vis spectroscopy. It is expected that the composite of nPDPA and DYH can be used as sensor array to discriminate between different halogenated solvents.

Scope of Research Work

Research Work 1: Polydiphenylamine/Zeolite Y Composites and Electrical Conductivity toward Halogenated Hydrocarbons

Study the effect of Si/Al ratios, zeolite contents, and vapor concentrations of halogenated solvents on the electrical conductivity and sensitivity response toward those solvents and study the reaction of adsorbed halogenated solvents on the PDPA, YH, and PDPA/YH composites.

Research Work 2: Development of Polydiphenylamine/Zeolite Y Composites by Dealumination Process as a Sensing Material for Halogenated Solvents

Study the effect of acid treatment times, YH contents, vapor concentrations, and cyclic responses on the electrical conductivity and sensitivity response toward the halogenated solvents and study the reaction of adsorbed halogenated solvents on the PDPA, dealuminated zeolite Y (DYH), and PDPA/DYH composites.

Research Work 3: Synthesis of Polydiphenylamine with Tunable Size and Shape via Emulsion Polymerization

The emulsion polymerization was used to synthesize and to control size and shape of nPDPA by incorporating different surfactants—anionic, cationic, and nonionic. The surfactant concentration, morphology, particle size, crystallinity, electrical conductivity, optical band gap, and thermal stability of nPDPA were investigated and compared with conventional micro scale PDPA (cPDPA).

Research Work 4: Polydiphenylamine/Zeolite Y Composite as a Sensor Array for the Selection of Different Chemical Vapors

nPDPA and DYH[80] were incorporated together to form a compressed composite to be used as a sensor array to discriminate between different halogenated solvents.