CHAPTER 1
INTRODUCTION

1.1 Rationale

Formaldehyde (HCHO), which is a volatile organic compounds (VOCs), has been described as a cause of indoor air pollution. HCHO involves various nonspecific symptoms such as headache and fatigue. Nonspecific symptoms that occur to occupants who live in nonindustrial buildings, was called as "sick building syndrome" (Bernstein et al., 2008). The major sources of HCHO air pollution can be divided into two paths, primary and secondary sources. The primary sources of HCHO are from indoor construction materials such as particleboard (PB), fiberboard, and plywood. Normally, HCHO concentrations in residential building are higher than office buildings because of the relatively large ratio of pressed wood products to air volume in homes. The secondary sources of HCHO are from the occupant's activities for example the burning of forests, agricultural land and household waste, the use of kerosene lamps, industries and vehicles emissions (Norback et al., 1990 and Bruce et al., 2000). According to World Health Organization (WHO) guidelines for indoor air quality: selected pollutants 2010 (regional office for Europe), the HCHO concentrations has corrected and reported. The results showed that indoor HCHO concentration was 8.1–600 $\mu g\ m^{-3}$ depending on the age of the building, temperature, relative humidity, air exchange rate and season (World Health Organization (WHO), 2010).

The concentrations of HCHO in vehicles and buildings have also been studied. Hanoune (2009) demonstrated the feasibility of HCHO quantification inside a moving vehicle by using infrared diode laser spectrometer. It was noted that HCHO concentration inside vehicles was about 15.5 ppbV. The combustion process of an alternative fuels such as ethanol-blended fuels and biodiesel blends also emit HCHO to an environment. However, biodiesel blends seem to reduce the emissions of HCHO in comparison with that of ethanol-blended fuel (Pang et al., 2008 and Peng et al., 2008).

Temperature is an important factor in increasing HCHO concentration. HCHO concentration inside vehicles at 65 °C was above 1000 ppbV (Schupp et al., 2005). Lee et al. (2000) studied the indoor and outdoor air quality investigation at school in Hong Kong.

The annual average of HCHO concentration in classrooms was about 55 μg m^{-3}. This value is below the Hong Kong Interim Indoor Air Quality Guidelines (HKIAQ). However, this report suggested that air pollutants that were produced by outdoor sources can effect to indoor air quality. Although, the ventilation systems have installed in a building in order to distribute adequate amounts of air and remove pollutants. However, it does not mean that air-conditioned rooms have completely prevented for outdoor air pollutants. Kim et al. (2005) investigated the effect of various temperatures on HCHO emission from laminate, plywood, medium density fiberboard (MDF) and furniture materials. Normally, those materials always make of phenol-formaldehyde (PF) resin.

The Japanese standard method with a desiccator's (LIS A 1460) was used to determine the HCHO emissions from many materials. In this method, the quantity of HCHO can be obtained in the term of the concentration of HCHO absorbed in distilled water or deionized water. It was note that the HCHO emission of laminate was about 1.44 ppm and plywood flooring was about 0.63 ppm. HCHO emission of MDF and PB was observed about 4.73 ppm. At room temperature, the concentrations of HCHO emitted from laminate and plywood flooring were still about 4 ppm at 28 days. JIS A 1460 recommended that the HCHO emission level of materials under 0.3 ppm is not effect to the occupants and it is not cause of sick building syndrome.

The relation between temperature and remaining equilibrium concentration of HCHO can be explained. At low temperature, almost all HCHO can easily adsorbed in water but at high temperature most of the HCHO will expose to the air. Therefore, HCHO exposure in buildings including vehicles will affect to indoor air quality. It was noted that most of carbonyl compounds concentrations are all as low as ppbV level for in indoor and outdoor air quality (Feng et al., 2004). Gilbert and white (1984, U.S. Patent 4,443,354) invented the sorbent material for reducing HCHO emission. This technique used carbon granular sorbent which was treated with impregnating agents such as sulfamic acid, sodium salt and sodium sulfamate. The results show that the service life of carbon granular sorbent increases with increasing the amount of sodium sulfamate concentration.

Hyman (1990, U.S. Patent 4,892,719) presented the invention of an efficient method of removing indoor pollutants using the reaction of polymeric substance which contains

carboxylic groups (–COOH) or sulfonic acid groups ($–SO_3H$). Both carboxylic and sulfonic acid groups can remove basic gases, such as ammonia or amines, and basic groups, such as amines can remove acidic gases such as hydrogen halides, hydrogen sulfide and formaldehyde. The catalytic process for formaldehyde oxidation was described by Erik et al. (1996, U.S. Patent 5,585,083). The catalysts (metal oxide) can convert HCHO to carbon dioxide (CO_2) and water (H_2O). Therefore, it does not constitute a waste problem. The photocatalytic method has been applied for indoor air purification (Bynug, 2007; Yong et al., 2009 and Rolf, 2010). Jo et al. (2001) suggested that TiO_2 photocatalytic technologies are suitable for VOCs degradation in low ppb concentrations commonly associated with in-vehicle air quality issues because of high degradation efficiency. However, it has been reported that the photocatalytic activity of TiO_2 is limited because of its large band gap (3.2 eV) and low adsorption property (Wellia et al., 2011). Thus, several materials have been used to synthesized co-adsorbents for TiO_2 such as clays (Kibanova et al., 2012), zeolites (Ichiura et al., 2003) and carbon-based adsorbent materials (Leary and Westwood, 2011) in order to improve the photocatalytic activity of TiO_2. Doping with metal ion, nonmetal and sensitizer have been used as a technique in order to reduce band gap energy of TiO_2 (Wonyong et al., 1994; Ohno et al., 2004 and Xei et al., 2010).

1.2 Literature review

1.2.1 Graphene (GR) and Graphene–TiO_2 (GR–TiO_2) photocatalyst

Graphene consists of two-dimensional carbon atoms that bond in a hexagonal lattice. The structure of graphene gives outstanding properties such as large specific surface area, thermal properties and easy functionalization. Therefore, graphene-base materials have attracted and studied for its application in many fields such as electronic and catalytic materials. Zhang et al. (2010b) studied the photocatalytic activities of P25 (TiO_2), graphene–TiO_2 (GR–P25) and carbon nanotubes–TiO_2 (CNTs–P25) and methylene blue (MB) solution was used as indicator for determining the photocatalytic activities. The results show that under UV light irradiation, GR–P25 exhibited larger photocatalytic activity than that of CNTs–P25 and P25. Briefly, under UV light irradiation, MB was degraded by GR–P25 around 90% and 85% for CNTs–P25. However, P25 exhibited poor photocatalytic activity about 65% because it was limited by its large band gap. According to the reduced graphene oxide–TiO_2 nanocomposite with high photocatalytic activity for the degradation of rhodamine B report, Wang et al. (2011c) synthesized reduced graphene

oxide–TiO_2 (RGO–TiO_2) nanocomposites using graphene oxide (GO) and commercial P25 as starting materials of TiO_2. It was obvious that the photocatalytic activity of RGO–TiO_2 depended on the weight ratio of graphene oxide to TiO_2. Under UV irradiation, the order of degradation efficiency of rhodamine B in the presence of photocatalysts can be arranged as following under UV light: (1:20) RGO–TiO_2 > (1:40) RGO–TiO_2 > (1:10) RGO–TiO_2 > (1:100) RGO–TiO_2 > P25 > (1:3) RGO–TiO_2.

Natural graphite can be used as an inexpensive material for synthetic graphene, including graphite oxide. Graphite oxide is obtained by oxidation graphite. Oxygen atoms that exist in graphite oxide and reduced graphite oxide lead excellent supporters to anchor TiO_2. Hummer's method is a trusty method for preparation graphene oxide. The mixture of concentrated sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$) and potassium permanganate ($KMnO_4$) were used as a oxidizing reagent for synthesis graphene oxide at relatively low temperature around 100 °C (Dreyer et al., 2009).

X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FTIR), Ultraviolet–visible (UV–vis) absorption spectroscopy are normally used to analyze GR and GR–TiO_2. The XRD spectra patterns of GR–TiO_2 are similar to that of TiO_2 and the wrinkled two dimensional structure of grapgene oxide can be clealy observed by using TEM (Low and Boonamnuayvitaya, 2013b). The FTIR spectra of TiO_2 show the broad absorption peak at low frequency around 1000 cm^{-1}. This absorption peak was attributed to vibration of Ti–O–Ti bonds. In the case of GR–TiO_2, GR–TiO_2 shows a broad absorption peak at low frequency higher than that of TiO_2 because of the combination of Ti–O–Ti vibration and Ti–O–C vibration of GR–TiO_2 (Zhang et al., 2010a).

It was noted that the absorption edge of GR–TiO_2 shifts to longer wavelength around 430 nm. This result indicated that the band gap of GR–TiO_2 was narrowed more than that of pristine TiO_2 because of the formation of Ti–O–C bond. Zhang et al. (2010b) reported that the amount of graphene that was added to TiO_2 could affect the light absorption of GR–TiO_2 photocatalyst. The band gap energy of GR–TiO_2 at the different amount of graphene was calculated by using the Kubelka–Munk function. The results of this method shows that band gap energy of GR–TiO_2 and TiO_2 samples are 2.83, 3.02, 2.96, 3.17, 3.16, 3.19, 3.15, and 3.36 eV corresponding to GR(30%)–TiO_2, GR(10%)–TiO_2, GR(5%)–TiO_2,

GR(2%) TiO_2, GR(1%)–TiO_2, GR(0.5%)–TiO_2, GR(0.2%)–TiO_2, and bare TiO_2, respectively. In addition, graphene can receive excited electrons from the valence ban of TiO_2. This phenomenon plays a vital role in order to suppress charge recombination.

P25 is the most popular TiO_2 standard material for preparing GR–TiO_2 composite. Liu et al. (2008a) prepared TiO_2 hydrosols from titanium sulfate ($TiOSO_4$) and metatitanic acid (H_2TiO_3) by using chemical precipitation–peptization method. The photocatalytic activity of TiO_2 and P25 were examined via degradation of formaldehyde. The results showed that TiO_2 catalyst that were synthesized from $TiOSO_4$ and H_2TiO_3 exhibited higher photocatalytic reaction rate than that of P25 around 1.6 times because TiO_2 hydrosols had smaller particle sizes, large surface areas and better transparency than that of P25. In the sol-gel method, the conversion of amorphous TiO_2 into anatase phase requires calcination at high temperature (500–600 °C). In the hydrothermal precipitation-peptization method, TiO_2 suspension was obtained in the solution by adding ammonium hydroxide (NH_4OH) and nitric acid (HNO_3) solutions and heating at a temperature of 65 °C in the acidic condition at pH 1–2. Since high temperature and acidity not only damage substrates, but also change the properties of color and transparency of the catalyst films (Liu et al., 2008a and Ge et al., 2006a).

There have been some reports related with this matter. The refluxed PTA solution leads a practical solution in order to solve the problems that come from sol-gel and TiO_2 hydrosol methods, since PTA performs in neutral pH value and amorphous TiO_2 can be converted into anatase phase by refluxing PTA solution at relatively low temperature (Boonamnuayvitaya and Photong, 2009). Moreover, Gao et al. (2003) synthesized anatase TiO_2 by using aqueous peroxotitante solution produced by dissolving metatitanic acid (H_2TiO_3) in a mixture of hydrogen peroxide (H_2O_2) and NH_4OH. Sasirekha et al. (2009) used an H_2O_2 as an oxidizing agent in order to prepare titanium peroxide solution and heat titanium peroxide solution at a temperature of 97 °C for 8 h.

1.2.2 Peroxo titanic acid (PTA) solution

Low-temperature synthesis of photocatalytic TiO_2 film from aqueous precursor by using PTA is of great interest because it can overcome some of disadvantages of sol-gel method. The advantages of refluxed PTA method are: low material cost, neutral pH, stability of

TiO_2 sol and lower calcination temperature (Sasirekha et al., 2009). Ichinose et al. (2001) synthesized peroxotitanium acid solution and peroxo-modified anatase sol derived from peroxotitanium hydrate. In this report, peroxotitanium hydrate was prepared and precipitated by adding NH_4OH solution to peroxotitanium complex solution, and peroxotitanium complex solution obtained by mixing titanium tetrachloride ($TiCl_4$) aqueous solution and excess H_2O_2, 30%. Arrowhead-like TiO_2 with fine anatase crystals size about 20 nm can be observed and TiO_2 crystals increased in size with increased heating time. Ge et al. (2006b) prepared PTA solution using titanyl sulfate ($TiOSO_4$) as starting a material. Anatase TiO_2 was obtained after refluxing PTA solution at 100 °C for 10 h. The chemical structure of PTA and TiO_2 can be determined by using FTIR. The crystallinity of the TiO_2 was analyzed by using XRD and the morphology of TiO_2 nanoparticles were observed by TEM.

TiO_2 (PTA) exhibits peaks at 400–750, 900, 1400 and 1620 cm^{-1}, as well as a broad band at 3000–3600 cm^{-1}. The broad band at 3000–3600 cm^{-1} is attributed to the stretching vibration of OH groups of the adsorbed water and the titanium hydroxide. The peaks at 1400 and 1620 cm^{-1} are due to the stretching vibration of the N–H bonds in NH_4^+. The adsorption peak at 900 cm^{-1} is attributed to the peroxo groups. The peaks at 430 and 500 cm^{-1} are likely due to the vibration of the Ti–O–Ti bonds in the TiO_2 lattices (Ge et al., 2006b and Boonamnuayvitaya and Photong, 2009). Sasirekha et al. (2009) suggested that the color of the PTA solution changes form yellow to while because of the decomposition of peroxide chain. This assumption was supported by the decrease in an intensity of FTIR adsorption peak of peroxo at 900 cm^{-1}. However, the chemical structures of PTA have differently proposed depending on the particular processes. Basically, at pH > 10 a colorless solution of PTA was obtained and either $[Ti(O_2)_2(OH)_2]^{2-}$ or $[Ti(O)(O_2)(OH)_2]^{2-}$ was proposed to be an major spices in the solution. When the pH was greater than 10, the color of PTA solution was yellow green (Gao et al., 2003). The monomer of PTA complex can further deprotonation to form dinuclear complex species such as $[Ti_2O_5(OH)_3(H_2O)]^-$, $[Ti_2O_5(OH)_4]^{2-}$, $[Ti_2O_5(OH)_4]^{2-}$, $[Ti_2O_5(OH)_5]^{3-}$ and $[Ti_2O_5(OH)_6]^{4-}$ (Seok et al., 2010).

TiO_2 (PTA) shows five distinctive anatase TiO_2 at 25.3°, 37.9°, 48.0°, 54.6° and 62.8° corresponding to anatase (101), (103, 004 and 112), (200), (105 and 211) and (204) crystal

plane (JCPDS 21–1272), respectively. The crystalline size of TiO_2 was calculated by using Scherrer's Equation (1.1).

$$D = k\lambda/\beta\cos\theta \quad (1.1)$$

where D is the crystallite sizes of TiO_2, λ is the radiation wavelength (0.154 nm), β is the full width at half maximum at $2\theta = 25.3°$ for anatase and k is a constant of 0.94 (Sasirekha et al., 2009). The weight fraction of anatase phase in the samples that contain both anatase and rutile phases can be estimated by the following empirical relationship.

$$AF = 100 \times I_A / (I_{A(101)} + 1.26I_{R(110)}) \quad (1.2)$$

where $I_{A(101)}$ and $I_{R(110)}$ are the peak intensities of the anatase (101) and rutile (110) planes, respectively (Liu et al., 2008b).

The crystal size of TiO_2 from TEM may be different from the crystal size calculated by Scherrer's equation because the accuracy of the equation is affected by many factors, such as diffraction line wide, defects and instrument broadening effect. Table 1.1 shows the comparison crystal size of TiO_2 by heating at different time and temperature. TiO_2 crystal increases in size with increasing heating time and some spherical shape observed may be due to the agglomeration of particles with prolonged heating time. The decrease in particle size could be attributed to the released oxygen from H_2O_2 in TiO_2 particles by heating (Sasirekha et al., 2009).

The photocatalytic activity of TiO_2 can be measured in term of degradation efficiency of methylene blue (MB) (Houas et al., 2001), methyl orange (Bao et al., 2004) and HCHO (Boonamnuayvitaya and Photong, 2009 and Huang et al., 2007). Under UV irradiation, the degradation mechanism of HCHO using TiO_2 can be briefly explained. When HCHO was adsorbed and further reacts with $^{\bullet}O_2^-$ and $^{\bullet}OH$ on TiO_2 surface. Formic acid, defined as an intermediate, is oxidized to CO_2 and H_2O (Liu et al., 2008a).

Table 1.1 TiO_2 preparation condition and crystal size of TiO_2 by heating PTA solution.

Researcher	Heating time (h)	Temperature (°C)	Crystal size (nm)
Ge et al. (2006b)	2	100	5.0
	6	100	33.0
	10	100	40.0
Sasirekha et al. (2009)	2	88	2.0
		95	3.2
	4	88	9.0
		95	12.0
	8	88	12.7
		95	14.0
	12	88	11.6
		95	12.3

The repeatability of the photocatalyst is very important for the practical use of photocatalyst for ambient air purification. It was observed that the degradation efficiency of TiO_2 was still higher than 70% after the TiO_2 film was used seven times (Boonamnuayvitaya and Photong, 2009).

1.2.3 Doping

The applications of TiO_2 photocatalyst is limited by its large band gap. Therefore, the extendable photoexcitation to the visible light region or the reduced band gap energy of the TiO_2 photocatalyst by doping was introduced. Furthermore, TiO_2 absorbs only 5% energy of the solar spectrum (Sonawane et al., 2004 and Xei et al., 2010). Therefore, the shift of the absorption edge of TiO_2 to visible light is the effective way to increase the photooxidation. There are two main methods that are used to improve photocatalytic efficiency of TiO_2: doping and sensitization.

Doping with metal ions can enhance photocatalytic activity of TiO_2 because metal ion acts as charge separation for electron-hole pairs and generate a new band gap energy structure by creating other lower energy levels (upper the valence or lower the conduction band of TiO_2). Iron (Fe) is widely used for TiO_2 doping. Iron can effectively enhance photo activity of TiO_2 because iron has stable half-filled electron configuration. The increase in

photocatalytic activity with Fe^{3+} doping is due to shift in optical absorption of the catalyst toward visible region (Seok et al., 2010). In the case of TiO_2, thin film doping with Fe^{3+}, the band gap energy of Fe^{3+}–TiO_2 was reduced to 2.83 eV. However, the increase in concentration of Fe^{3+} can decrease anatase crystallinity (Wang et al., 2009).

Devi et al. (2010) reported the enhanced photocatalytic activity of transition metal ions Mn^{2+}, Ni^{2+} and Zn^{2+} doped polycrystalline titania for the degradation of aniline blue under UV/solar light irradiation. In this report, it was noted that Mn^{2+}–TiO_2 has higher photocatalytic activity than Ni^{2+}–TiO_2 and Zn^{2+}–TiO_2 because Mn^{2+} has $3d^5$ electronic valence configurations. The other metal ion that can act as charge trapping is Ag ion. Ag ion can be turned to Ag atom when Ag ion gains electron from TiO_2 (Sahoo et al., 2005 and 2006). In the case of Fe^{3+} doping, the energy level of Fe^{2+}/Fe^3 is close to Ti^{3+}/Ti^{4+} level. Therefore, the trapped electron in Fe^{2+} can migrate to a neighboring surficial Ti^{4+} leading to interfacial transfer process (Wonyong et al., 1994). The photocatalytic activities of TiO_2 can increase by doping with nonmetallic species, such as N, C, S, P and halogen atoms (Lettmann et al., 2001; Ohno et al., 2004; Wu et al., 2007; Lin et al., 2007 and Luo et al., 2004).

Nonmetallic species can enhance TiO_2 absorption in the visible light region by creating new band gap energy level. Park et al. (2009) claimed that carbon doping can increase photocatalytic activity because it leads to lower band gap. In the case of titanium alkoxide precursor, carbons species from precursor could be incorporated into the TiO_2 lattice by calcination at low temperature around 200–250 °C. Wu et al. (2010) synthesized Fe/C–TiO_2 via solvothermal method. It was noted that Fe/C–TiO_2 photocatalyst showed high specific surface areas, small crystallite size. Under visible light irradiation, Fe/C–TiO_2 photocatalyst showed larger degradation efficiency of acid orange 7 (AO7) in comparison with that of TiO_2, Fe/TiO_2 and C/TiO_2.

Surface modifications, sensitization by adding metal nanoparticles, other semiconductors and organic sensitizers are used to improve the photocatalytic activity of TiO_2 but organic sensitizers are unstable and/or are toxic substances. The combination of narrow semiconductor (CdS (2.5 eV) and Ag_2S (1.0 eV)) and TiO_2 is an interesting way to increase the efficiency of photocatalytic activity by extending the photoresponse of catalyst

to visible light region. Linsebigler et al. (1995) introduced the model of photoexcitation in composites semiconductor-semiconductor photocatalyst that can be used to explain the increase in photocatalytic activity of CdS–TiO_2. CdS–TiO_2 shows a broad absorption band at 550–750 nm. It was noted that electron in valence band of CdS were excited to the conduction band of CdS and then transferred to the conduction band of TiO_2. This phenomenon called suppresses charge recombination leading to the increase in the photocatalytic activity of CdS–TiO_2. Xei et al. (2010) synthesized Ag_2S–TiO_2 using PTA as a starting material for preparing TiO_2 and silver acetate ($C_2H_3AgO_2$, AgAc) was used as a source of silver for Ag_2S preparation. The results showed that Ag_2S–TiO_2 exhibits good absorption in visible light region and performed large photocatalytic activity than that of TiO_2. Furthermore, when the Ag/Ti molar ratio increases, the visible light absorption of the Ag_2S–TiO_2 becomes stronger.

In this research work, the photooxidation process using TiO_2 was applied for indoor and car interior HCHO removal. Graphene, Fe^{3+} and Ag_2S were used to improve the photocatalytic activity of TiO_2. GR–TiO_2, GR/Fe^{3+}–TiO_2 and GR/Ag_2S–TiO_2 photocatalysts were synthesized and the photodegradation efficiency of prepared photocatalysts were examined by using MB and HCHO as indicators under UV and visible light irradiation.

1.3 Research objectives and scope of research work

The objectives of this study were to compare the photocatalytic activities of GR–TiO_2, GR/Fe^{3+}–TiO_2 and GR/Ag_2S–TiO_2 films, which were synthesized by using refluxed PTA solution. After the best photocatalyst for HCHO removal was found, the selected photocatalyst was further studied for indoor and car interior HCHO removal under real environmental conditions. The scope of this study is divided into three parts.

1. Synthesize GR–TiO_2, GR/Fe^{3+}–TiO_2 and GR/Ag_2S–TiO_2 photocatalysts
2. Examine the photocatalytic activities of prepared photocatalysts
3. Study the use of photocatalyst film (coated on glass substrate) for car interior HCHO removal under real environmental conditions (outdoor sunshade) using a glass chamber to simulate car interior environmental conditions.