CHAPTER 3
METHODOLOGY

3.1 Photocatalyst preparation

3.1.1 Preparation of peroxo titanic acid (PTA) solution and TiO_2 nanoparticles

Materials

Titanyl sulfate ($TiOSO_4$, Sigma-Aldrich), Hydrogen peroxide (H_2O_2, 30%, Merck), Ammonia solution (NH_4OH 30%, Merck). All chemicals were high purity reagents and were used without further purification.

Method

Titanyl sulfate ($TiOSO_4$, 5.0 g) was dissolved in distilled water. The white precipitate ($Ti(OH)_4$) was observed by adding NH_4OH (1 M). After filtering and rinsing with de-ionized water for several times, H_2O_2 (0.98 M) solution was added to the $Ti(OH)_4$ at 1:5 molar ratio of H_2O_2 to titanium under continual stirring until the yellow transparent PTA solution was obtained. The PTA solution was diluted with de-ionized water in 500 ml volumetric flask. The TiO_2 nanoparticles can be obtained by refluxing PTA solution at 100 °C for 10 h.

3.1.2 Preparation of graphene oxide powder

Materials

Sodium nitrate ($NaNO_3$, Rankem), Potassium permanganate ($KMnO_4$, Qrec), Sulfuric acid (H_2SO_4 97%, Merck), Hydrogen peroxide (H_2O_2, 30%, Merck), Natural graphite (fine powder extra pure, Merck). All chemicals were high purity reagents and were used without further purification.

Method

Graphene oxide was synthesized by using Hummer's method. The concentrated H_2SO_4 (32 mL) and $NaNO_3$ (1.0 g) was mixed and stirred in an ice bath. After $NaNO_3$ had completely dissolved, natural graphite (1.0 g) was then added in a mixture. $KMnO_4$ (4.5 g) was slowly put to the above mixture under continual stirring at 30 °C for 1 h. The mixture solution was diluted by adding 250 mL of distilled water and further heated at 98 °C for 1 h. The remaining $KMnO_4$ in the mixture was terminated by adding H_2O_2 (30 %, 10 ml). The dark brown precipitate was separated by centrifugation and washed with distilled water for purification until a neutral pH of 7 is reached. The graphene oxide power was obtained after drying at 35 °C.

3.1.3 Preparation of graphene–TiO_2 (GR–TiO_2 (PTA)) photocatalyst

Materials

TiO_2 (PTA, refluxed 10 h) nanoparticles (Section 3.1.1), Graphene oxide powder (from 3.1.2), Ethanol (C_2H_5OH, Merck). All chemicals were high purity reagents and were used without further purification.

Method

Graphene oxide was added at the weight ratio of graphene oxide to TiO_2 at 1:100, 1:50, 1:20 and 1:10 to the TiO_2 (PTA refluxed at 100 °C for 10 h) colloidal suspension (50 mg l^{-1}) in ethanol (70%). Next, graphene oxide–TiO_2 were irradiated with two 8 W UVA lamps for 48 h (Williams et al., 2008). The GR–TiO_2 powders were obtained after drying in hot air oven at 50 °C for 6. The series of GR–TiO_2 (PTA) is given in the notations of GR–TiO_2 (PTA, 1:x) where x stands for the weight ratio of graphene oxide.

3.1.4 Preparation of GR/Fe^{3+}–TiO_2 (PTA) photocatalyst

Materials

TiO_2 (PTA, refluxed 10 h) sol (Section 3.1.1), Graphene oxide powder (Section 3.1.2), Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck), Ethanol (C_2H_5OH, Merck). All chemicals were high purity reagents and were used without further purification.

Method

GR–TiO_2 (PTA, 1:50), which showed the highest photocatalytic activity compared to that of GR–TiO_2 (PTA, 1:100, 1:20 and 1:10, see Chapter 4), was synthesized. Graphene oxide was added at the weight ratio of graphene oxide to TiO_2 at1:50 in ethanol (70%), Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) was then added to the graphene oxide–TiO_2 at 0.06, 0.12 and 0.18 wt% Fe^{3+}. Next, the graphene oxide/Fe^{3+}–TiO_2 sol was irradiated with two 8 W UVA lamps for 24 h (Williams et al., 2008).

3.1.5 Preparation of Fe^{3+}–TiO_2 photocatalyst

Materials

TiO_2 (PTA, refluxed 10 h) sol (Section 3.1.1) and Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck). All chemicals were high purity reagents and were used without further purification.

Method

Fe^{3+}–TiO_2 photocatalyst was synthesized by adding $Fe(NO_3)_3 \cdot 9H_2O$ to TiO_2 (PTA refluxed at 100 °C for 10 h) sol at 0.12 %wt Fe^{3+}.

* Fe^{3+}–TiO_2 (0.12 %wt Fe^{3+}) was prepared in order to study its photocatalytic activity in comparison with that of GR/Fe^{3+}–TiO_2 (0.12 %wt Fe^{3+}, see Chapter 5)

3.1.6 Preparation of Silver sulfate (Ag_2S) sensitizer

Materials

Thiourea ($CS(NH_2)_2$, Ajax Finechem), Silver acetate ($C_2H_3AgO_2$, AgAc, Sigma-Aldrich). All chemicals were high purity reagents and were used without further purification.

Method

Silver sulfide (Ag_2S) was successfully synthesized using the reaction between silver acetate and thiourea. Thiourea ($CS(NH_2)_2$, 0.38 g) was dissolved in 50 mL of distilled water and further heated at 60 °C. Next, silver acetate solution prepared from silver acetate power ($C_2H_3AgO_2$, 0.42 g) was slowly added to warm thiourea solution. The clear transparent of thiourea solution was continuously turned to dark color solution because of the formation of Ag_2S. The observed Ag_2S was heated in water bath for 6 h.

3.1.7 Preparation of Ag_2S–TiO_2 (PTA) photocatalyst

Materials

TiO_2 (refluxed PTA) sol (Section 3.1.1) and Ag_2S nanoparticles (Section 3.1.6). All chemicals were used without further purification.

Method

Hydrothermal method was applied to synthesize Ag_2S–TiO_2 photocatalyst. The synthesized Ag_2S and TiO_2 (refluxed PTA solution) was mixed with Ag_2S at 2.9, 5.6 and 8.2 wt% Ag_2S under ultrasonication for 30 min and then heated in water bath at 65 °C for 3 h.

3.1.8 Preparation of GR/Ag_2S–TiO_2 (PTA) photocatalyst

Materials

Ag_2S–TiO_2 photocatalyst and graphene oxide powder. All chemicals were used without further purification.

Method

Hydrothermal method and UV–assisted photocatalytic reduction of graphene were applied to synthesize GR/Ag_2S–TiO_2 photocatalyst. Graphene oxide was mixed with Ag_2S–TiO_2 under ultrasonication for 30 min. Graphene oxide/Ag_2S–TiO_2 was further heated in water bath at 65 °C for 3 h. Ethanol was added to graphene oxide/Ag_2S–TiO_2. Graphene oxide was reduced to graphene by using UV–assisted photocatalytic reduction of graphene (Williams et al., 2008).

3.1.9 Preparation photocatalyst films using methyltrimethoxysilane (MTMOS) as a binder

Materials

Methyltrimethoxysilane (MTMOS, Merck), Hydrochloric acid solution (0.055 M), Ammonia solution (NH_4OH 3 M), Methanol (CH_3OH, Merck), TiO_2, GR–TiO_2, GR/Fe^{3+}–TiO_2, Fe^{3+}–TiO_2, GR/Ag_2S–TiO_2 and Ag_2S–TiO_2. All chemicals were high purity reagents and were used without further purification.

Method

The silica binder was synthesized via the condensation reaction of MTMOS using HCl and NH_4OH as a catalyst. Methanol (10.00 ml) and MTMOS (1.00 mL) was added to TiO_2, GR–TiO_2, GR/Fe^{3+}–TiO_2, Fe^{3+}–TiO_2, GR/Ag_2S–TiO_2 or Ag_2S–TiO_2 sol (25.00 mL). MTMOS was hydrolyzed by adding HCl (0.055 M, 0.5 mL). After the solution was vigorously stirred at 65 °C for 20 min, The TiO_2, GR–TiO_2, GR–Fe^{3+}/TiO_2, GR/Ag_2S–TiO_2 or Ag_2S–TiO_2 with silica binder was obtained by adding NH_4OH solution (3 M, 0.25 mL) under continual stirring at 65 °C for 10 min.

3.2 Characterizations

The crystalline structure of the TiO_2 photocatalyst was determined by X-ray diffractometer (Bruker, D8–Discover). Nickel-filtered Cu K_α radiation (λ = 0.15418 nm) was used with a generator voltage of 40 kV and a current of 40 mA, scanned at a speed of 0.1°/s and step size of 0.02° at an angular range of 20–80°. The crystalline sizes of anatase were calculated via Scherrer's equation:

$$D = k\lambda/B \cos \theta_B \tag{3.1}$$

where D is the crystallite particle size, λ is the wavelength of CuKα irradiation (0.15406 nm), k is a constant of 0.9, B is the full width at half maximum, and θ_B is Bragg's angle of the anatase (101) plane.

The functional groups of catalysts were determined by Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer, Spectrum One). The nitrogen adsorption/desorption isotherms were measured at a liquid nitrogen temperature of 77 K using a high precision surface area and pore size analyzer (Belsorp, Belsorp-mini). The specific surface area and total pore volume were calculated by the Brunauer–Emmett–Teller (BET) method. The morphology and selected area electron diffraction pattern (SAED) of catalysts was observed using a transmission electron microscope (TEM, JEOL, JEM–2100). The absorption edge wavelength of catalysts was recorded by UV-vis spectrometer (UV1900 UV/VIS, Hitachi). Photocurrent tests were measured by using automated potentiostat (ACM Instrument, Gill AC). The conventional three-electrode cell configuration with a standard Ag/AgCl as a reference electrode, inert Platinum (Pt) sheet as a counter electrode and a working electrode was immersed in the 0.1 M Na_2SO_4 solution. A 8 W black light blue (BLB, λ = 365 nm, Philips) or 8 W fluorescent lamp ($\lambda > 420$ nm, Osram) was used as the source of the UV and visible light, respectively. The band gap energy of photocatalyst can be estimated by using the Kubelka–Munk function as shown in Equation (3.2).

$$(\alpha h\nu)^{1/2} = A_i(h\nu - E_g) \quad (3.2)$$

where α is the absorption coefficient (cm^{-1}). $h\nu$ is the photon energy (eV) and A_i is a constant value. The absorption can be converted to adsorption coefficient by using Equation (3.3).

$$\alpha = ((2.303 \times 10^3)\, A\rho)/lc \quad (3.3)$$

where A is the absorption of the sample. ρ is a constant value of 3.98 g cm^{-1} (density of TiO_2 photocatalyst). l is the length of cell (1 cm) and c is the concentration of TiO_2 photocatalyst. (Karthick et al., 2011).

3.3 Photocatalytic activity test

The photocatalytic activities of prepared photocatalysts were measured in terms of the degradation efficiency (%) of MB or HCHO by the following equation:

$$\text{Degradation efficiency (\%)} = (C_0 - C_i)/C_0 \times 100 \quad (3.4)$$

where C_0 is the initial concentration of MB or HCHO and C_i is the concentration of MB or HCHO after UV or visible light irradiation.

3.3.1 Photocatalytic activity test of photocatalysts using MB as an indicator (Chapter 4)

Photocatalytic activities of photocatalysts were evaluated by degradation of MB aqueous solution. An irradiation box with dimensions of 410 mm × 350 mm ×123 mm was equipped with UV or visible light lamps: two 8 W black light blue (BLB, λ = 365 nm, Philips) or 8 W fluorescent lamps (λ > 420 nm, Osram), respectively. The light sources were placed parallel to one another at an equal distance of 20 mm from the photoreaction vessel as shown in Figure 3.1.

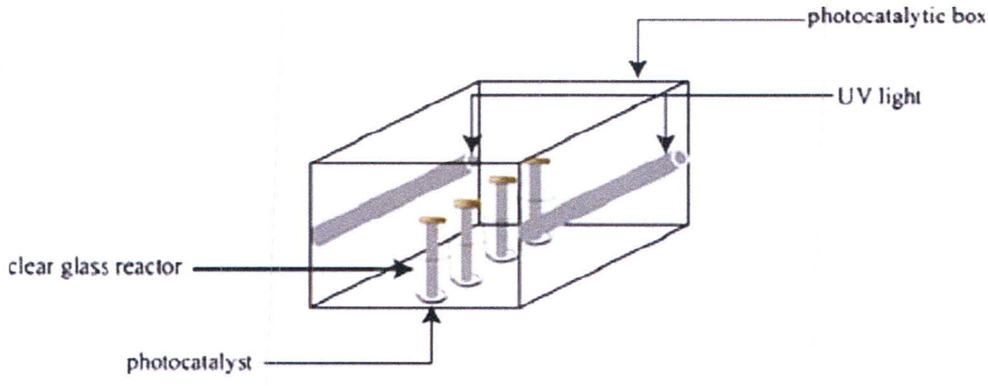

Figure 3.1 Schematic diagram of irradiation box (Kaewtip et al., 2012b).

The experiment was conducted in two steps. In the first step, the catalyst suspension comprising catalyst powder (1 mg) dispersed in 40 mL of 4.5 ppm MB solution was kept in the dark for 3 h in order to ascertain the adsorption–desorption equilibrium. In the second step, under ambient conditions and stirring, the beakers were exposed to UV or visible light for 15, 30, 45, 60, 90, and 150 min respectively. Then, 3.0 ml of sample was taken out after a determined period of time and centrifuged at 5250 rpm for 10 min. The concentration of MB in the sample was determined by UV-vis spectrophotometer (U1900 UV/VIS, Hitachi) at a visible wavelength line of 659 nm.

3.3.2 Photocatalytic activity test of photocatalysts using HCHO as an indicator (Chapters 5 and 6)

The obtained TiO_2 (PTA), GR–TiO_2 (PTA, 1:50), GR/Fe^{3+}–TiO_2 (0.06, 0.12 and 0.18 wt% Fe^{3+}) Fe^{3+}–TiO_2, GR/Ag_2S–TiO_2 (2.9, 5.6 and 8.2 wt% Ag_2S) and Ag_2S–TiO_2 photocatalyst was mixed with SiO_2 binder and further coated on a glass plate (1 cm × 5 cm) using a laboratory-constructed dip-coating instrument with a pulling rate of 25 cm min^{-1}. The photocatalyst film was further air-dried at 70 °C for 10 min. Formaldehyde was also used an indicator to evaluate the photocatalytic activity of catalyst. Glass plate with photocatalyst was inserted in a 60 ml glass vial and gaseous formaldehyde was then added at an initial formaldehyde concentration of about 3000 ppmV. The vial was kept in the dark condition until the adsorption–desorption equilibrium is reach and then irradiated with

UV or visible light using an irradiation box. The concentration of formaldehyde was measured using a gas chromatograph flame ionization detector (Shimadzu, GC–FID 2014).

3.3.3 Study of the practical use of photocatalyst (Chapter 7)

The experiments were be conducted using a cubic glass chamber reactor with the dimensions of 45 cm × 45cm × 45 cm. The components of glass reactor are follows: (1) lid, (2) Septum port, (3) Fan hold, (4) Fan and (5) hygrometer and thermometer as shown in Figure 3.2.

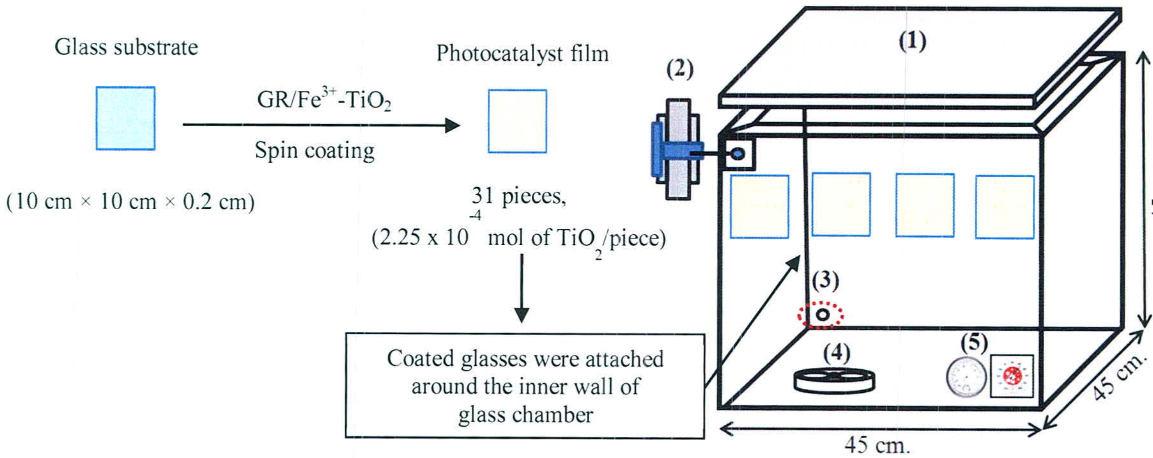

Figure 3.2 Procedure of preparation GR/Fe^{3+}–TiO_2 photocatalyst film and schematic diagram and components of glass chamber reactor (Kaewtip et al., 2012a).

GR/Fe^{3+}–TiO_2 photocatalyst (with silica binder) prepared using the described procedure in section 3.1.9, was coated on glass substrate (10 cm × 10 cm × 0.2 cm) using home-made spin coating machine (60 KTYZ, Synchronous motor 14 W) with spin speed of 110 rpm. The photocatalyst glass was dried in hot air oven at 70 °C for 1 h. The glasses coated with GR/Fe^{3+}–TiO_2 photocatalyst films (31 pieces) were attached around inner wall of glass reactor. The intensity of visible light and UV was measured using light meter Lutron (LX–100) and UV light meter Lutron (UVA–UVB, 290–390 nm, UV–340A), respectively. In this study, gaseous HCOH was prepared by heating paraformaldehyde vial (60 ml) at 155 °C for 2 h. Injection and sampling of HCHO gas in the glass chamber were conducted through the septum port by means of a syringe. The humid air was pumped and passed to a glass reactor with the volumetric flow rate of 1.5 L min^{-1} before the experiment. All experiments using visible light irradiation were carried out at room temperature. The glass reactor was kept under dark condition until the adsorption–desorption is reached and then irradiated with visible light. Table 3.1 shows the studied parameter and controlled parameter for the study of effect of environmental parameters on GR/Fe^{3+}–TiO_2 photocatalyst.

Table 3.1 Studied and controlled parameters for the study of the effect of environmental parameters on GR/Fe^{3+}–TiO_2 photocatalyst.

Studied parameter	Controlled parameter	
HCHO (ppmV)	Relative humidity (%RH)	Visible light intensity (W m^{-2})
750 1500 2000	30	0.23–0.25
Relative humidity (%RH)	HCHO (ppmV)	Visible light intensity (W m^{-2})
30 60 70–80	1500	0.23–0.25
Visible light intensity (W m^{-2})	HCHO (ppmV)	Relative humidity (%RH)
0.23–0.25 0.60–0.62 1.24–1.27	1500	30

For the study of the practical use of GR/Fe^{3+}–TiO_2 photocatalyst, the initial concentration HCHO was fixed around 670±90 ppmV. The glass reactor was also kept under dark conditions until the adsorption–desorption was reached and then irradiated with outdoor visible light. The decrease in the concentration of HCHO was determined by using a gas chromatograph flame ionization detector (Shimadzu, GC–FID 2014).