CHAPTER III
EXPERIMENTAL

3.1 Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$) was purchased from UNIVAR Co. Triethanolamine (TEA, $N(CH_2CH_2OH)_3$) was supplied by QRëC Co. Ethylene glycol (EG, $HOCH_2CH_2OH$) and ethanol (CH_3CH_2OH) were purchased from J.T. Baker Inc. Glacial acetic acid (CH_3COOH) and acetonitrile (CH_3CN) were purchased from RCI Labscan Co.Ltd. Titanium butoxide ($Ti(OCH_2CH_2CH_2CH_3)_4$) was obtained from Sigma-Aldrich Co. NaOH was purchased from Univar Co. And tetrapropylammonium bromide ($(CH_3CH_2CH_2)_4N(Br)$) was purchased from Fluka Co. All chemicals were used as received.

3.2 Facile Route to Synthesize Bismuth Titanate

3.2.1 Bismuth Glycolate Synthesis

Bismuth nitrate pentahydrate was dissolved in EG in a 250 mL round-bottom flask and magnetically stirred until a clear solution was obtained. Triethanolamine was then added. The mixture was heated at 100 °C under nitrogen atmosphere for 2 h to obtain white precipitate. The precipitate was washed three times with acetronitrile, dried overnight in vacuum desiccators at room temperature and kept in vacuum desiccators for further characterization.

3.2.2 Bismuth Titanate Preparation

Bismuth glycolate (0.45 g) and titanium butoxide (0.35 g), used as bismuth and titanium sources respectively, were mixed in acetic acid and ethanol mixture(2.5 mL). The mixture was stirred at room temperature for 1, 3 or 6 h to obtain gel. The gel was then dried at 80°C for 6 h to obtain white powder, followed by calcination at temperatures in a range of 300–700°C.The optimal calcination temperature obtained was used to study an optimal calcination time.

3.3 Flower-Like Bismuth Oxide

Bismuth nitrate pentahydrate was mixed with and without TEA in 100 mL of EG. The mixture was carried out in a 250-ml three-necked round-bottom flask and placed in the oil bath. Then, it was stirred vigorously and heated under nitrogen atmosphere at various temperatures (100, 150, and 200 °C) to obtain precipitate. The precipitated powder was removed and washed with acetonitrile several times to remove all $Bi(NO_3)_3.5H_2O$, TEA, and EG. The powder was then dried in vacuum desiccators at room temperature before calcinations at temperatures ranging from 300–500°C for 1 h using a heating rate of 0.5 °C/min to achieve bismuth oxide.

3.4 Catalyst Preparation (TS-1 Zeolite, Bismuth Titanate) and Photocatalytic Activity Testing

3.4.1 TS-1 Zeolite Synthesis (Phonthammachai, 2006).

Hydrothermal syntheses were carried out using microwave irradiation and a sample mixture containing an initial molar composition of $xSiO_2:yTiO_2:0.31TPA^+: 0.4NaOH:114H_2O$ (where x:y = 100, 50, 33, 25, 20 and 12). The mixture was aged at room temperature for 110 h and heated in a microwave at 150 °C for various ranges of reaction time, depending on the Ti loading; the higher the Ti-loading, the longer the reaction time, as discussed in Phonthammachai's work (Phonthammachai, 2006). Hydrothermal treatment by microwave heating technique was conducted on ETOH SEL, Milestone Microwave Laboratory System (Spec 2500 W and 2450 MHz). Samples were heated in a Teflon tube. The TS-1 zeolite product was washed several times with distilled water, dried at 60 °C overnight and calcined at 550 °C for 2 h at a heating rate of 0.5°C/min.

FTIR: 960 cm^{-1} ν(Si-O-Ti), 550 cm^{-1} δ(Si-O-Si) and 800 cm^{-1} ν(Si-O-Si). DR-UV: 210 nm (tetracoordinated titanium). XRD: $2\theta = 24.4^\circ$ (Orthorhombic symmetry of TS-1).

3.4.2 Bismuth Titanate Synthesis (Thanabodeekij, 2005)

Bismuth (III) nitrate pentahydrate was dissolved in nitric acid (Labscan Asia Co.). The stoichiometric amount of titanium glycolate was added to the bismuth (III) nitrate solution with vigorously stirring until the mixture turned clear. The pH of the mixture was adjusted to 5.0 using 0.1 M nitric acid and 0.1 M ammonium hydroxide (Carlo Earba). After stirring for 1 h, the mixture was centrifuged to separate the precipitate out, followed by washing with water until the filtrate became neutral. The white solid obtained was dried at 60 °C and then calcined at 600 °C for 3 h using a heating rate of 1 °C/min.

FT-IR: 457 cm^{-1} (weak Bi–O rocking), 525 cm^{-1} ν(O-Bi-O), 586 cm^{-1} ν(O-Bi-O), 663 cm^{-1} ν(O-Ti-O). DR-UV: 500 nm (visible absorption of intrinsic band transition of indirect gap bismuth titanate semiconductor). XRD: $2\theta = 24.7°$: [220], 27.7°: [310], 30.4°: [222], 32.9°: [321].

3.4.3 Photocatalytic Decomposition of Reactive Black 5 Dye

The photocatalytic reactions were carried out in a 500 ml batch reactor (Vt = 600 ml, Ø=14 cm) equipped with a cooling water jacket to control the temperature at 25 °C. The lamp was vertically immersed in the suspension and illuminated using a commercial 6 W UV lamp (Hg Philip; emission 320–400 nm). Reactive black 5 (RB5) purchased from Sigma-Aldrich was added into the continuously, magnetically stirred mixture solution at a concentration of 40 ppm, followed by bismuth titanate or TS-1 zeolite at Si/Ti molar ratios of 100, 50, 33, 25, 20 and 12. The activation energy of the reaction was studied at temperature ranging from 15–35°C (288–508 K). Hachem *et al.* (2001) pointed out that the adsorption equilibrium of the bismuth titanate system is quite fast, and the equilibrium concentration should be reached within about 45 minutes. Lee *et al.* (2003) found that for the TS-1 system, adsorption equilibrium is attained around 60 min. Thus, in this study, the adsorption/degradation equilibrium of the suspensions was established by magnetically stirring in the dark for 60 min. The concentration of catalyst was fixed at 0.5 g/l using various amounts of H_2O_2 (10, 20, 30 mM/l). The samples were taken out, filtered and then analyzed to determine the concentration of RB5 using

Shimadzu UV-240 spectrophotometer and the total organic content (TOC) using Shimadzu TOC-VCSH Analyzer. Kinetic analysis of this process was also studied.

3.5 Preparation of Hierarchical $Bi_{12}TiO_{20}$ Architecture

Bismuth nitrate pentahydrate (3.08 g) was dissolved in 100 ml of EG in a round-bottom flask. The stoichiometric amount of titanium butoxide was slowly dropped into the bismuth nitrate pentahydrate solution and stirred for 1 h. The mixture was heated under nitrogen atmosphere at 150 °C for 30 min, 1 h, and 2 h to precipitate out. The obtained powder, denoted as bismuth titanate precursor, was washed with acetronitrile three times and dried in a vacuum dessicator at room temperature for further calcination in a carbolite muffle at 600 °C for 30 min to achieve bismuth titanate.

3.6 Characterization

FE-SEM (SEM; Hitachi/S-4800) was used to observe the morphological appearance of the samples. FT-IR spectra (Nicolet iS10: FT-IR spectrometer) was used to investigate the chemical structure of organic functionality with a spectral resolution of 4 cm^{-1}, using transparent KBr pellets. TG-DTA was carried out using a Perkin Elmer thermal analysis system with a heating rate of 10 $°C.min^{-1}$ over a temperature range of 30–750°C to determine its thermal property. The surface area of all samples was measured using Quantachrom (Model Autosorp-1) surface area analyzer. The crystalline structure of the samples was analyzed on a Rigaku X-ray diffractometer system (RINT-2200) with a Cu tube for generating CuK_{α} radiation (1.5406 Å) and a nickel filter, a generator voltage of 40 kV, and a generator current of 30 mA. The scan speed of 5° (2θ)/min with a scan step of 0.02 (2θ) was used for a continuous run in a 5° to 60° (2θ) range. UV–visible measurements were performed on a Shimadzu UV-2550 with the ISR-2200 integrating sphere attachment, using $BaSO_4$ as a reference. Diffuse reflectance ultraviolet spectroscopy was obtained on a Shimatzu UV-2550 spectrometer. The reflectance output was converted using the Kubelka–Munk algorithm. The Si/Ti ratio was investigated using Perkin Elmer Optima 4300 DV, inductively coupled plasma (ICP) spectrometer. Solid state carbon-13 nuclear magnetic resonance spectrum was done on Varian-INOVA ^{13}C-NMR-500 MHz. Mass spectrum was recorded on a gas chromatography-mass spectrometer (GC-MS, micrOTOF-Bruker Daltonics) equipped with Positive-ESI source and run in a range of 50–3000 m/z.