

CHAPTER III EXPERIMENTAL

3.1 Materials

All syntheses were carried out with careful exclusion of extraneous moisture by purging under an atmosphere of UHP grade nitrogen; 99.99 % purity was obtained from Thai Industrial Gases Public company Limited (TIG). Argon gas (99.9% purity) for growing CNTs was purchased from Air Products and Chemicals, Inc., UK.

Fumed silica (SiO_2 , average particle size of 0.007 μm), titanium dioxide (TiO_2), Tin (IV) oxide (SnO_2 , purity 99%), 4-nitrophenol (4-NP, $\text{C}_6\text{H}_5\text{NO}_3$), rhodamine-B (Rh-B, $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$), poly(vinyl alcohol) (PVA, $M_w = 72,000$ Da and degree of hydrolysis $\geq 98\%$), nitric acid (HNO_3), acetic acid (CH_3COOH), benzyl alcohol (BA, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), toluene ($\text{C}_6\text{H}_5\text{CH}_3$), and ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) were purchased from sigma-Aldrich Chemical Company. Ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$) was purchased from J.T. Baker Co., Ltd. Triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$) was supplied by Carlo Erba Reagenti. Acetonitrile (CH_3CN) was purchased from Lab-Scan Company Co., Ltd. Tetrapropylammonium bromide (TPA^+Br^-) was purchased from Fluka Chemical AG. Hydrochloric acid (HCl) was purchased from BDH Laboratory Supplies. Sodium hydroxide (NaOH) was purchased from EKA chemicals. These chemicals were used as received. Commercial grade triethylenetetramine (TETA, $\text{C}_6\text{H}_{18}\text{N}_4$) purchased from Facai Polytech. Co. Ltd., was distilled prior to use.

All glassware is cleaned by soaking in a sodium hydroxide cleaning solution bath, followed by washing, rinsing with water, and then drying in an oven at 60 °C prior to use.

3.2 Instruments

3.2.1 Thermogravimetric Analysis (TGA)

TGA thermograms were carried out on a Perkin-Elmer Pyris Diamond TG/DTA over a temperature range of 30–900 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopic analysis was conducted using Bruker Instrument (EQUINOX55) with resolution of 2 cm⁻¹. The solid samples were prepared by mixing 2 mg sample with 60 mg of dried KBr.

3.2.3 X-Ray Diffraction (XRD)

A Rigaku XRD system, equipped with a RINT 2000 wide angle goniometer using a Cu tube for generating a CuK α radiation ($\lambda = 1.54 \text{ \AA}$), nickel filter as the K β filter at generator voltage and current of 40 kV and 30 mA, respectively, a scan speed of 5 °(2 θ)/min with a scan step of 0.02 °(2 θ) in the 5 to 90 °(2 θ) range, was used. The set goniometer parameters were divergence slit = 1°(2 θ); scattering slit = 0.3 nm. Sample (0.1–0.2 g) was spread on a glass slide.

3.2.4 Scanning Electron Microscopy (SEM)

The scanning electron micrographs were carried out to identify the microstructure of a sample. The samples were characterized using JEOL Scanning Electron Microscope, model JSM 5200 and high resolution SEM, model JEOL 6340F FEG-SEM.

3.2.5 BET Surface Area Measurement

The surface areas of all samples were measured by the BET method using a Quantachrome Corporation Autosorb I gas sorption system (Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer and also as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2 h at 150 °C prior to exposure to the adsorbent gas.

3.2.6 Conductivity measure equipment

The electrical conductivity values of samples were measured by a custom-built two-point probe with copper as electrodes, coupled to a Keithley 6517A voltmeter (Keithley, Model 6517A). The current used was in the linear Ohmic regime.

3.2.7 Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-Vis was performed on pelletized samples in the reflectance mode, using a Perkin Elmer LAMBDA 850 spectrophotometer with an integrating sphere.

3.2.8 Microwave equipment

Hydrothermal treatment by microwave heating technique was conducted using Biotage-Microwave Synthesis and Flash Purification Instrument. Samples were heated in glass vial, using time-to-temperature programming.

3.3 Methodology

3.3.1 Silatrane Synthesis

Wongkasemjit's synthetic method was followed by mixing SiO_2 , and TEA in a simple distillation set using EG solvent. The reaction was done at the boiling point of EG under nitrogen atmosphere to remove water as a by-product along with EG from the system. The reaction was run for 10 h and the rest of EG was removed under vacuum (1.6 Pa) at 110 °C to obtain brownish white, followed by washing with acetonitrile for three times to obtain the final white powder. The purified product was characterized using XRD, TGA and FT-IR.

3.3.2 Titanium Glycolate Synthesis

A mixture of TiO_2 (0.025 mol, 2 g), TETA (0.007 mol, 3.7 g), used as a catalyst, and 25 mL of EG, used as a solvent, were heated to the boiling point of EG for 24 h, followed by separating the unreacted TiO_2 from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain crude white solid product. The crude product was then washed with acetonitrile and dried in a vacuum desiccator before characterization using FTIR and TGA.

3.3.3 Tin Glycolate Synthesis

A mixture of 15 g of SnO_2 and 14.6 g of TETA were mixed together, stirred vigorously in an excess amount of EG, and heated to 200 °C for 24 h. The resulting solution was placed *in vacuo* to remove excess EG, resulting in a crude precipitate. The crude white solid product was then washed with acetonitrile, dried in a vacuum desiccator, and characterized using FT-IR and TGA.

3.3.4 Electrospinning PVA/Silatrane Solution and Preparation of Silica Fiber

The PVA/silatrane solutions were first prepared by mixing 0.5 g of silatrane with 600 mL of water. The solution was then added into 8 mL of aqueous PVA solution. The concentration of the base PVA solution was varied between 6 and 13 wt% and the resulting mixture was constantly stirred for 4 h. The as-prepared solutions are referred to as the spinning solutions.

A schematic drawing of the e-spinning setup is shown in Figure 2.1. In a typical process, each of the spinning solutions was loaded into a plastic syringe. A blunt 20-G stainless-steel needle was used as a nozzle. Both the syringe and the nozzle were tilted $\sim 45^\circ$ from a horizontal baseline to maintain the constant presence of a droplet at the tip of the nozzle. A Gamma High Voltage Research UC5-30P power supply was used to charge the spinning solution by connecting the emitting electrode of positive polarity to the nozzle and the grounding electrode to an aluminum sheet wrapped around a rigid plastic backing, used as a collection device. The distance between the tip of the nozzle and the collection device defines a collection distance.

The PVA/silatrane composite fibers that were used to investigate the effect of calcinations temperature on the morphological appearance, properties, and structures of the post-calcined SiO_2 fibers were prepared from a spinning solution with a concentration of base PVA solution of 10 wt% under a fixed electric field of 15 kV/10 cm. The e-spun fibers were left exposed to ambient moisture (ca. $55\% \pm 2\%$ RH) for ~ 5 h and subsequently subjected to calcination in a Carbolite CFS 1200 furnace at a temperature ranging between 500° and 1100°C for 5 h to remove PVA. The heating program started from room temperature with a heating rate of $0.5^\circ\text{C min}^{-1}$.

3.3.5 Electrospinning PVA/Tin Glycolate Solution and Preparation of Tin(IV)Oxide fiber

PVA/tin glycolate solution was first prepared by mixing 0.04 g of tin glycolate with 20 μL of 8 M HNO_3 and 200 μL of water. It should be noted that only in the case where the effect of the acid type was investigated the type of the acid was

changed to either 8 M CH_3COOH or 8 M HCl . The solution was then added into 5 mL of an aqueous PVA solution. The concentration of the base PVA solution was varied between 6 and 13 wt% and the resulting mixture was constantly stirred for 5 min. The as-prepared solutions were referred to as the spinning solutions. The e-spinning process was the same as the PVA/silatrane composite fibers.

The PVA/tin glycolate composite fibers that had been prepared from a spinning solution with a concentration of the base PVA solution of 10 wt.% and 8M HNO_3 under a fixed electric field of 12.5 kV/15 cm were used to further investigate the effect of calcination temperature on the morphological appearance, properties, and structures of the post-calcined SnO_2 fibers. The e-spun fibers had been exposed to ambient moisture (about $55 \pm 2\%$ RH) for ~ 5 h before being calcined in a furnace over a temperature range of 400° to 1000°C for ~ 5 h. The heating program started from room temperature to each specified calcinations temperature at a heating rate of $0.5^\circ\text{C min}^{-1}$.

3.3.6 Titanium Silicate 1 Zeolite (TS-1) Synthesis

Silatrane and titanium glycolate were mixed with NaOH , H_2O , and tetrapropylammonium bromide (TPA^+), using the molar ratio for the reaction mixture of $\text{Ti}:\text{Si}:\text{TPA}^+:\text{NaOH} = 1:20:2:8$. The solution was stirred at room temperature for 60 h and subsequently heated in microwave at 150°C for 1.5 h. The product was filtered, washed with distilled water, dried at 60°C overnight, and finally calcined at 550°C in argon atmosphere for 6 h.

3.3.7 TS-1/CNT Hybrid Synthesis

Carbon nanotubes (CNTs) were first synthesized via a modified CVD process in a tube furnace reactor using ferrocene as the catalyst precursor and toluene as the feedstock. 4 wt% ferrocene was dissolved in 25 mL toluene and injected into an argon gas stream through a pre-heated injector (180°C) at a rate of 5.4 mL h^{-1} . The reaction was carried out in a quartz tube at 760°C . The average outer diameter of the nanotubes was 70 nm, the length was between 20 and 30 μm . The as-grown CNTs were heated in argon at 2000°C for about 5 h prior to their use in the hybrids.

The CNTs were dispersed in ethanol with the aid of ultrasonication for 10 min. Benzyl alcohol and water were then added and the solution was kept

stirring at room temperature. Silatrane, titanium glycolate, sodium hydroxide, water, and TPA⁺ were mixed, using the same concentration formula as that used for the TS-1 synthesis, and immediately added to the CNT suspension. The concentration of CNTs was varied from 5 to 50 wt% with respect to the expected mass of TS-1. The final suspension was aged at room temperature for 60 h and subsequently heated in microwave at 150 °C for 1.5 h. The product was washed with distilled water, dried at 60 °C overnight and calcined at 550 °C in argon atmosphere for 6 h.

3.3.8 Silatrane/CNT Hybrid Synthesis and Preparation of Silica Nanotubes

The CNTs were coated via a sol-gel process, followed by hydrothermal treatments either in air or in flowing argon up to temperatures of 1000 °C. Silatrane was used as the SiO₂ precursor, ethanol, and water to start gelation. Benzyl alcohol was chosen as a surfactant due to its ability to keep the particle size small and to provide better interaction with the hydrophobic CNTs. In a typical experiment, the CNTs were dispersed in ethanol with the aid of ultrasonication for 10 min. Benzyl alcohol and water were then added in the solution. The silatrane was dissolved in water, stirred for 40 min and slowly dropped into the CNT suspension, using the molar ratio for a reaction mixture of silatrane:BA:ethanol:water of 1:4:86:5. The final suspension was aged at room temperature for 12 h then subsequently heated in autoclave at varied temperature between 60 ° and 150 °C. The product was washed with distilled water, dried at 60 °C overnight.

The silatrane/CNT hybrids, that were used to investigate the effect of calcination temperature on the morphological appearance, properties, and structures of the post-calcined SiO₂ nanotubes, were prepared from a solution heated in autoclave 100 °C for 24 h. The silatrane/CNT hybrids were subjected to calcination in a furnace at a temperature ranging between between 500° and 1100 °C, during which amorphous silica almost completely transformed into cristobalite while preserving exactly the nanotube structure. The last step in the process was the oxidation in air at 550 °C for 2 h to remove the carbon nanotubes. The heating program started from room temperature with a heating rate of 0.5 °Cmin⁻¹.

3.4 Catalytic Activity Testing

3.4.1 Catalytic Testing of TS-1/CNT Hybrids

The samples were tested for the photocatalytic decomposition of 4-NP and Rh-B, under both UV ($\lambda = 254$ nm, 6 W) and visible (72 W, cutoff ~ 420 nm) lights. Typically, 60 mg of the samples were added into a quartz beaker containing 100 mL of distilled water with either 4 mg L⁻¹ of Rh-B solution (Solution 1), or 20 mg L⁻¹ of 4-NP and 30 mmol L⁻¹ of H₂O₂ (Solution 2). The suspensions were stirred in the dark for 30 min to ensure equilibrium of the dye adsorption on the surface of the photocatalysts. Upon illumination, an aliquot part of the solution was removed after every 20 min of the reaction, followed by centrifuging and analyzing by UV-Vis.