

CHAPTER III EXPERIMENTAL

3.1 Chemicals

Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) (Wako Pure Chemical Industries, Ltd.), tetraisopropyl orthotitanate (TIPT, Tokyo Chemical Industry Co., Ltd.), acetylacetone (ACA, Nacalai Tesque, Inc.), laurylamine hydrochloride (LAHC, Tokyo Chemical Industry Co., Ltd.), cetyltrimethylammonium bromide (CTAB, Tokyo Chemical Industry Co., Ltd.), cetyltrimethylammonium chloride (CTAC, Tokyo Chemical Industry Co., Ltd.), anhydrous ethyl alcohol (EtOH, Wako Pure Chemical Industries, Ltd.), ethylene glycol (EG, Nacalai Tesque, Inc.), and distilled water were used as starting materials. All chemicals are analytical grade and used as received without further purification. $\text{Sr}(\text{NO}_3)_2$ and TIPT were used as strontium and titanium precursors, respectively, for the synthesis of mesoporous-assembled SrTiO_3 nanocrystal photocatalysts. ACA was used for slowing down the hydrolysis reaction rate of the titanium precursor. EtOH, EG, and distilled water were used as solvent/co-solvent media. LAHC, CTAB, and CTAC were used as structure-directing surfactants. The commercially available SrTiO_3 nanopowder (Wako Pure Chemical Industries, Ltd.) was also used for comparative studies on photocatalytic activity.

For photocatalyst modification, the loaded metals were prepared from various precursors: Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%, Alfa Aesar), Chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aldrich Co., Ltd.), Nickel (II) nitrate hydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%, Wako Pure Chemical Industries, Ltd.), Silver nitrate (AgNO_3 , 99.8%, Nacalai Tesque), Iron (III) nitrate nanohydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.9%, Wako Pure Chemical Industries, Ltd.), and Cerium (IV) diammonium nitrate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, 95%, Chameleon Reagent).

The chemicals used for the experiments of photocatalytic hydrogen evolution reaction were as follows: Anhydrous methyl alcohol (MeOH, 99.8 % purity, Labscan Asia Co., Ltd.), Anhydrous ethyl alcohol (EtOH, 99.5 % purity,

Italmar Co., Ltd.), Anhydrous iso-propyl alcohol (2-PrOH, BDH Laboratory Co., Ltd.), D-glucose (Ajax Finechem), Sodium sulfite (Na_2SO_3 , Riedel-Dehaeh), Formic acid (HCOOH , analytical grade, Labscan Asia Co., Ltd.), Acetic acid (CH_3COOH , analytical grade, Labscan Asia Co., Ltd.), Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, analytical grade, Labscan Asia Co., Ltd.), Hydrochloric acid (HCl , 37% analytical grade, Labscan Asia Co., Ltd.), Sulfuric acid (H_2SO_4 , 40% analytical grade, Labscan Asia Co., Ltd.), Commercial SrTiO_3 nanopowder (Wako Pure Chemical Industries, Ltd.), and Commercial TiO_2 nanopowder (Degussa P-25, Tokyo Chemical Industry Co., Ltd.).

3.2 Photocatalyst Synthesis Methods

ACA was first added into TIPT at an equimolar, and the mixed solution was then allowed to cool to room temperature (Sakulkaemaruechai *et al.*, 2004; Sreethawong *et al.*, 2005, b). A surfactant solution of LAHC, CTAC, or CTAB was prepared by dissolving it in different solvents of distilled water, EG, EtOH, or a mixture of EtOH and EG. Afterwards, an appropriate amount of $\text{Sr}(\text{NO}_3)_2$ was added to the surfactant solution with continuously stirring at room temperature to obtain a clear solution. In the case of the metal-loaded mesoporous-assembled SrTiO_3 nanocrystal photocatalyst synthesized via a single-step sol-gel process, metal of various amounts was added to this clear solution to obtain different metal loadings, as being analogous to Pt-loaded mesoporous-assembled TiO_2 (Sreethawong and Yoshikawa, 2006). Afterwards, the LAHC- $\text{Sr}(\text{NO}_3)_2$ or LAHC- $\text{Sr}(\text{NO}_3)_2$ -metal solution was slowly dropped into the yellow mixture of the TIPT-ACA solution while stirring continuously at room temperature. The resulting mixture was kept at 80°C for 2 d to obtain complete gel formation. The resulting gel was dried at 80°C for 2 d. Finally, the obtained zero gel (dried residue) was calcined at two different heating rates of 1 or 2°C min^{-1} and four different temperatures of 600, 650, 700, or 750°C for 4 h to remove the surfactant and the remaining solvent from the framework to yield the mesoporous-assembled SrTiO_3 nanocrystal photocatalyst (synthesized SrTiO_3). The schematic diagram of the synthesis procedure is shown in Figure 3.1.

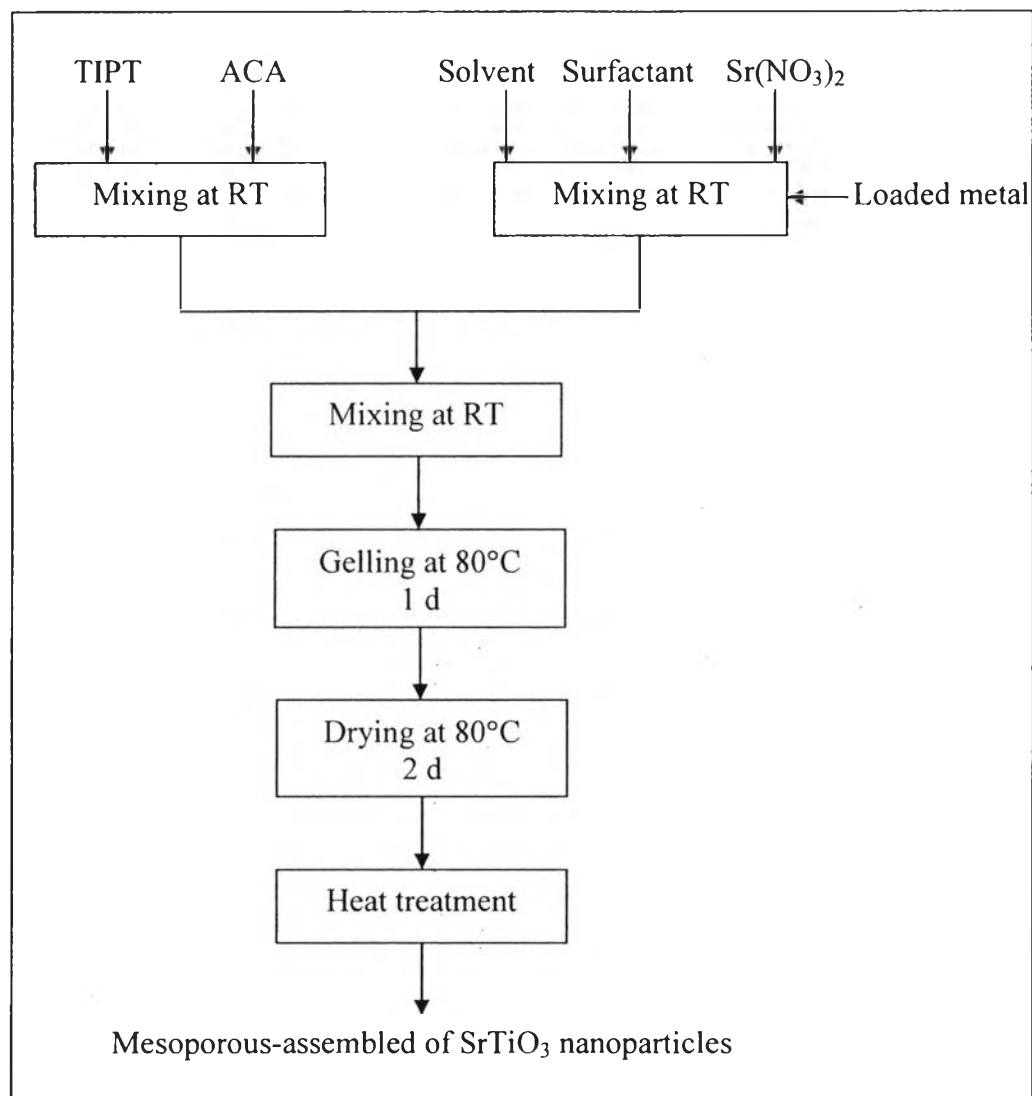


Figure 3.1 Schematic of the synthesis procedure.

3.3 Characterization Techniques

The thermal decomposition behavior of the zero gel and the suitable thermal treating conditions were investigated by using a TG-DTA apparatus (Shimadzu, DTG-50) with a heating rate of $10^{\circ}\text{C min}^{-1}$ in a static air atmosphere and with $\alpha\text{-Al}_2\text{O}_3$ powder used as the reference.

The crystallinity and purity of the synthesized SrTiO_3 and the commercial SrTiO_3 (Wako) were examined by X-ray diffraction (Rigaku, RINT-2100) with a rotating anode XRD generating monochromated $\text{CuK}\alpha$ radiation using the continuous

scanning mode at a rate of $2^{\circ}\text{C min}^{-1}$ and operating conditions of 40 kV and 40 mA. Crystallite size (D) was calculated from the line broadening of the corresponding X-ray diffraction peak according to the Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (3.1)$$

where K is the Sherrer constant (0.89), λ is the wavelength of the X-ray radiation (0.15418 nm for CuK_{α}), β is the full width at half maximum (FWHM) of the diffraction peak measured at 2θ , and θ is the diffraction angle.

The N_2 adsorption-desorption isotherms of the synthesized SrTiO_3 and the commercial SrTiO_3 (Wako) were obtained by using a nitrogen adsorption-desorption apparatus (BEL Japan, BELSORP-18 PLUS,) at a liquid nitrogen temperature of -196°C . The Brunauer-Emmett-Teller (BET) approach using adsorption data over the relative pressure ranging from 0.05 to 0.35 was utilized to determine the specific surface area. The Barrett-Joyner-Halenda (BJH) approach using desorption data was used to obtain a mean pore size and pore size distribution.

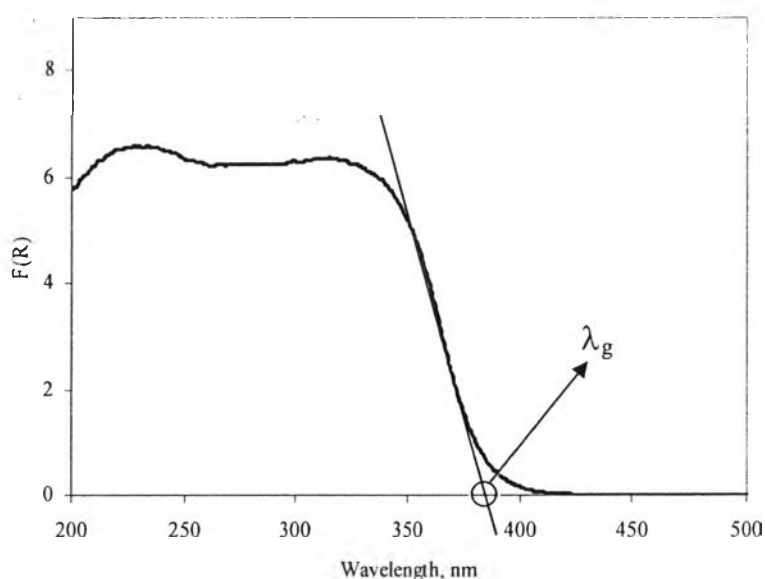


Figure 3.2 The plot between the Kubelka-Munk function ($F(R)$) as a function of wavelength (λ , nm) and the band gap wavelength (λ_g) estimation (Kamat *et al.*, 1999)

The diffuse reflectance spectra of the synthesized SrTiO₃ and the commercial SrTiO₃ (Wako) were obtained by using a UV-Visible spectrophotometer (Shimadzu, UV-2450) at room temperature with BaSO₄ as the reference. Afterwards, the diffuse reflectance spectra were analyzed to estimate the band gap energy (E_g , eV) by using the Kubelka-Munk function ($F(R)$), as expressed by the following equation:

$$F(R) = \frac{(1-R)^2}{2R} \quad (3.2)$$

where R is the ratio of the reflected light intensity to the reflected light intensity of the reference. The band gap wavelength (λ_g , nm) is the cross-section point between the line extrapolating of the onset of the rising part and x-axis of the plot of $F(R)$ as a function of wavelength (λ , nm), as shown in Figure 3.2. The E_g is then determined by using the following equation (Kamat *et al.*, 1999):

$$E_g = \frac{1240}{\lambda_g} \quad (3.3)$$

The synthesized SrTiO₃ and the commercial SrTiO₃ (Wako) morphologies were observed by a transmission electron microscope (JEOL, JEM-200CX) at 200 kV. The specimens for TEM analysis were prepared by ultrasonically dispersing pestled powders of the synthesized photocatalysts in 2-propanol and then placing drops of the suspension on a Cu microgrid with carbon film.

The actual metal loading was analyzed by an X-ray fluorescence spectroscope (Phillip, WD-XRF PW-2400) and the aggregated particle size distribution of the synthesized SrTiO₃ photocatalysts was analyzed by a light scattering particle size analyzer (laser technique) (Malvern / Mastersizer X, Malvern Instruments Ltd.), capable to measure in the range of 0.1 to 600 μm with the standard deviation of the mean aggregated particle size in the range of -9 to 9 μm

3.4 Photocatalytic Activity Testing

3.4.1 The Photodegradation of Methyl Orange

The photocatalytic activity of the synthesized SrTiO₃ and the commercial SrTiO₃ (Wako) were investigated using the photodegradation of methyl orange in aqueous solution under UV irradiation (Vilber Lourmat, VL 115L, 15 W, with a maximum emission wavelength at 365 nm) at room temperature. A quantity of 0.15 mg of methyl orange was dissolved in 15 ml of distilled water to yield a methyl orange concentration of 10 mg l⁻¹. An amount of 0.075 mg of the SrTiO₃ powders was suspended in the methyl orange solution by using a magnetic stirrer, and the suspension was photoirradiated at room temperature. The sample was periodically withdrawn (sampling time of 30 min), centrifuged to separate the photocatalyst powder from the solution, and used for the absorbance measurement. The absorbance of the sample was monitored by the UV-Visible spectrophotometer and was used to determine the percentage of methyl orange degradation. Moreover, the pseudo-first order rate constant (k , min⁻¹) for the photodegradation reaction of methyl orange was determined through the following relation:

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (3.4)$$

The k value is calculated from the plot between $\ln(C_0/C)$ and time (t), where C_0 and C denote the methyl orange concentration at $t = 0$ and $t = t$, respectively. The percentage of methyl orange degradation and the pseudo-first order rate constant were used as the indicators for evaluating the photocatalytic activity of the synthesized SrTiO₃, compared with the commercial SrTiO₃ (Wako).

3.4.2 The Photocatalytic Hydrogen Production

The photocatalytic activity of the synthesized SrTiO₃ photocatalysts for the photocatalytic hydrogen production is investigated by using the hydrogen production rate as the indicator. The photocatalytic water splitting experiment was performed in an outer-irradiation and air-tight Pyrex glass reactor (750 ml), connected to a water-cooling system, as shown in Figure 3.3. In a typical run, a specified amount of the SrTiO₃ photocatalyst is suspended in the aqueous solution of

a scavenger mediator (hole scavenger) by using a magnetic stirrer. Prior to the reaction testing, the suspension is left in the dark simultaneously with being thoroughly deaerated by purging with Ar gas for 20 min.

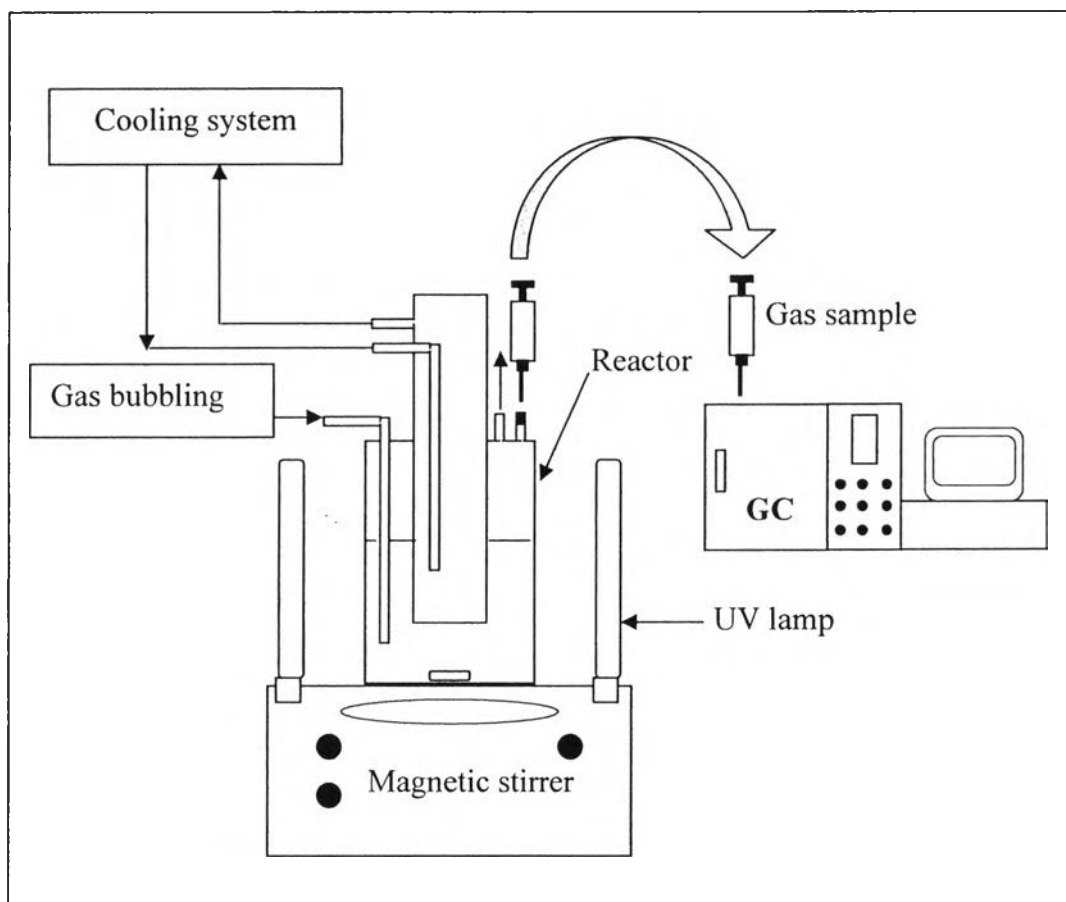


Figure 3.3 The photocatalytic hydrogen production system used in this study.

Afterwards, the Ar purging is stopped and the suspension is then photoirradiated by the UV light (A set of 176 W Hg lamps (16 lamps, TUV 11 W PL-S, Phillip), which emitted light of more than 95% with a wavelength of 254 nm with total irradiance of 2.3 mW cm^{-2}) or visible light (a 300 W Xe lamp (KXL-300, Wacom Electric) combined with a UV cutoff filter (ATG, B-485), which allowed only the visible light with wavelengths longer than 400 nm to pass with total irradiance of 2.6 mW cm^{-2}) at room temperature. To control the reaction temperature, the cooling water is circulated through an inner cylindrical jacket of the reactor. A

gas sample in the headspace of the studied reactor was periodically withdrawn at 1 h intervals and analyzed for its hydrogen, oxygen, carbon dioxide, and carbon monoxide concentrations by using a gas chromatograph (Hayesep D100/120, PERKIN ELMER) equipped with a thermal conductivity detector (TCD).

3.5 References

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