

Materials and Methods

This chapter details the various materials and reagents as well as the experimental techniques used in this investigation. It also describes the various techniques used to identify and characterize the nano materials synthesized.

3.1 Materials

- i. Titanium Tetrachloride (TiCl_4) anhydrous having M.W 189.71, with minimum argentometric assay of 99% was purchased from Spectrochem Pvt. Ltd. Density (d_4^{20}) = 1.729-1.730 g/m. It was used as the precursor for synthesizing titania in all the techniques.
- ii. Hydrochloric acid (HCL), I.R grade having M.W 36.5, with minimum acidimetric assay of 35-38% was purchased from s.d fine chem. Ltd. Density (d_4^{20}) = 1.18 g/ml.
- iii. Sodium Hydroxide (NaOH) pellets, purified I.R grade having M.W 40.00 with minimum assay of 97% were purchased from s.d fine chem. Ltd. It was used as the precipitating agent in hydrolysis method. Hydrochloric acid and sodium hydroxide were used in the hydrolysis and hydrothermal methods.
- iv. Cyclohexane ($\text{CH}_2(\text{CH}_2)_4(\text{CH}_2)$), LR grade having M.W 84.16 with minimum GLC assay of 99% was purchased from s.d fine chem. Ltd. Density(d_4^{20}) = 0.776-0.780 g/m;
- v. n-hexanol (1-hexanol, n-hexyl alcohol ($\text{CH}_3(\text{CH}_2)_5\text{OH}$) having M.W 102.8 with GC essay > 98% was purchased from Lobachemie Ltd. Density (d_4^{20}) = 0.818-0.819 g/ml.
- vi. Triton X-100 ($(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4(\text{C}_2\text{H}_4\text{O})_{9.5}\text{OH}$), LR grade having M.W 646.87 with minimum iodometric assay of 98% was purchased from s.d. fine chem. Ltd. Density (d_4^{20}) = 1.064-1.067 g/ml.
- vii. Ammonia solution (25%) extra pure having M.W with minimum assay of 25-28% was purchased from s.d fine chem. Ltd. It was the aqueous phase in microemulsion II and served as the precipitating agent. Density (d_4^{20}) = 0.91 g/ml.
- viii. Methanol (CH_3OH) having M.W 32.04, with minimum GC assay of 99.0% was purchased from s.d fine chem. Ltd. Density (d_4^{20}) = 0.790-0.793 g/ml.

- ix. Chloroform (CHCl_3) having M.W 119.38 with minimum GLC assay of 99.5% was purchased from Qualigens fine chemicals. Density (d_4^{20}) = 1.48 g/ml. Methanol and chloroform were both used for washing the precipitate obtained from microemulsions.
- x. Acetone ($\text{C}_3\text{H}_6\text{O}$) having M.W 58.08 with minimum GC assay of 99.0% was purchased from s.d fine chem. Ltd. Density (d_4^{20}) = 0.789-0.792 g/ml.
- xi. Propan-1-ol (n-propyl alcohol, ($\text{C}_3\text{H}_8\text{O}$), LR grade having M.W 60.10 with minimum GC assay of 99.0% was purchased from s.d fine chem. Ltd. Density (d_4^{20}) = 0.803-0.805 g/ml. Acetone and n-propanol were used as the dispersing media.
- xii. Benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$), LR grade having M.W 108.10 with minimum GC assay of 99.0% was purchased from s.d fine chem. Ltd. Density (d_4^{20}) = 1.041-1.046 g/ml. Benzyl alcohol was used as a solvent for TiCl_4 .
- xiii. Butyl alcohol ($\text{C}_4\text{H}_9\text{OH}$), LR grade having M.W 74.12 with minimum GC assay of 99.0% was purchased from s.d fine chem. (d_4^{20}) = 0.81-0.815 g/ml. Butyl alcohol was used as a solvent.
- xiv. Cadmium Nitrate-Tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), LR grade having M.W. having minimum assay of 99.0 % was procured from Loba Chemicals. Cadmium Nitrate-Tetrahydrate was used as precursor for CdSe preparation.
- xv. Selenium powder, AR grade, having minimum assay of 99.6% was procured from Loba Chemicals. It was used as a precursor for CdSe preparation.
- xvi. Sodium Selenite, Na_2SeO_3 , AR grade, Colourless Solid, having minimum assay of 99 % was procured from Loba Chemicals. It was used as a precursor for CdSe preparation.
- xvii. Hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), AR grade, M.W 50.56, procured from Loba chemicals. it was used as reducing and templating agent.

All reagents were used without further purification. The water used was RO water or demineralized water.

3.2 Equipment and glassware

In none of the experimental runs involving synthesis of semiconductor nanomaterials an special experimental set up was used the requirements were mostly three necked round bottom flask, condenser, stirring arrangement, water bath,

filtration and centrifuging assembly. Experimental set up was rigged up whenever required. Remi make laboratory centrifuge model no was used having capability to rotate at 10000 rpm. Powders were dried in vacuum oven and calcined in a muffle furnace capable of working up to a temperature of 925⁰ C. Laboratory glassware of borosilicate glass of Corning make, Durga trading Co. make were used. Care was exercised to maintain clean and aseptic conditions.

3.3 Experimental Techniques

Titanium dioxide (Titania) as well as cadmium selenide were synthesized by a number of methods namely microemulsion, sol-gel, hydrolysis and hydrothermal techniques. The outline of these procedure of synthesis route is as detailed below.

3.3.1 *Microemulsion method for Titania synthesis*

Cyclohexane, n-hexanol, Triton X-100 are the components of the microemulsion system where cyclohexane was the continuous phase, Triton X-100 was the surfactant and n-hexanol was used as cosurfactant.

Procedure:

Microemulsion system	:	Triton X-100 as surfactant
		n- hexnol as co-surfactant
		Cyclohexane as continuous oil –phase and
		Electrolyte solution as dispersed aqueous phase

Microemulsions were prepared by solubilizing different electrolytes into Triton X-100 / n-hexanol / cyclohexane solutions. Two microemulsions (microemulsion I and microemulsion II) with identical composition but in a different aqueous phase are taken. The aqueous phase in microemulsion I was an aqueous solution of 0.3 M TiCl₄, whereas the aqueous phase in microemulsion II was the precipitating agent 1.2 M aqueous hydroxide solution. The composition in weight percent of the reagents used is given in Table 3.1. The volumetric composition was calculated by using the density of the reagents. The densities of the aqueous solutions were estimated using specific gravity bottle.

Table 3.1: Composition of a sample microemulsion systems used for syntheses reaction

Components	Microemulsion 1	Microemulsion 2	Wt. %
Aqueous phase	TiCl ₄ solution (0.3M)	Ammonia solution (1.2 M)	8
Surfactant	Triton X-100	Triton X-100	19
Cosurfactant	n-hexanol	n-hexanol	15
Oil phase	Cyclohexane	Cyclohexane	58

3.3.1.1 Preparation of microemulsion

The aqueous solutions of 0.3 M TiCl₄ and ammonium hydroxide were prepared in advance before starting the preparation of microemulsions. The aqueous TiCl₄ solution should be prepared at low temperature in an ice bath. Two conical flasks of same volume are taken. Cyclohexane was first taken in a 250 ml conical flask and to it n-hexanol was slowly added with vigorous stirring according to the composition given in Table 3.1.

Vigorous stirring is to provide complete mixing. Triton X-100 was then added drop-wise with stirring. With addition of few drops of triton -100, the system may turn into slight white colored but with more addition of triton X-100 and much vigorous stirring the solution becomes colorless. Some procedure was followed to prepare the second microemulsion system in the other conical flask. The two microemulsions should be colorless.

Now, the respective aqueous phases are introduced into two microemulsions. Certain volumes of TiCl₄ solution and ammonium hydroxide solution was added drop by drop with stirring to the microemulsion I and microemulsion II respectively. The solution turned white colored at the beginning, but later with much stirring, both turned colorless. The final solutions are colorless.

The two microemulsions were mixed with vigorous stirring at room temperature. The microemulsions II which serves as the precipitating agent was slowly added to the microemulsion I. Due to the continuous collisions and coalescence of the droplets of water-in-oil micro-emulsions, the reacting species in

microemulsions I and II (TiCl_4 and ammonium hydroxide, respectively) come in contact with each other and react. This leads to the precipitation of titanium hydroxide within the aqueous cores of the microemulsion. With more addition of microemulsion II, the precipitation increases which can be observed clearly. A schematic diagram for the preparation of TiO_2 particles in microemulsion is shown in fig 3.2. The particles thus prepared in the constrained micro reactors of microemulsion droplets are expected to be fairly uniform and homogeneous and have a higher surface area with very small particle size.

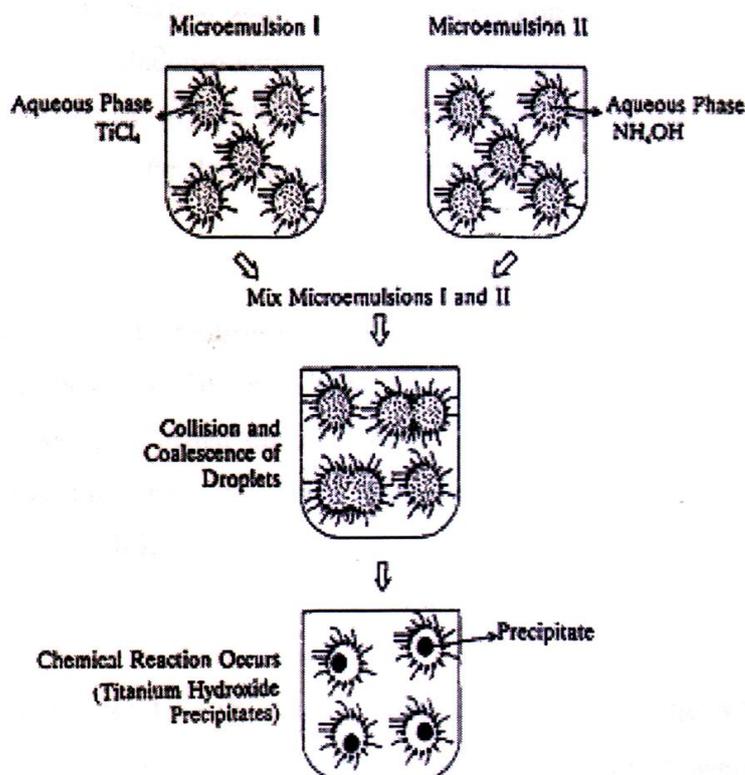


Fig 3.1 Schematic diagram showing the preparation of TiO_2 particles in microemulsions

The precipitate was separated in a high speed centrifuge at 10,000 rpm for about 10 min. The precipitate was then thoroughly washed in a 1:1 mixture of methanol and chloroform followed by pure methanol to remove contaminated oil and surfactant from the particles. The precipitate was then dried and characterized.

3.3.1.2 Microemulsion synthesis of CdSe

Microemulsion synthesis of CdSe proceeded with the preparation of aqueous solution of cadmium nitrate tetrahydrate and sodium selenite by taking known amount of each salt (2.78 mM/ml) and dissolving in deionized water. Surfactant (Triton X 100) 10 ml and n-heptane 50 ml were taken in three necked flat bottom flask to which a condenser was attached. This mixture was stirred at ambient temperature using magnetic stirrer. 1 ml Cadmium nitrate tetrahydrate (2.78 mM/ml) was added dropwise into solvent-surfactant solution. The reaction system formed reverse micelle with Cd salts in the inner core of micelle.

Thereafter, 1 ml Sodium selenite (2.78 mM/ml) was mixed with 5 ml of hydrazine hydrate in a separate beaker. The solution became dark red from colourless indicating the formation of Se^{2-} ions. This solution was added dropwise over a period of 30 seconds to original reaction mixture when the temperature of the mixture reached around 70°C. The reaction between Cd ions and selenium ions (perhaps also in reverse micelles) took place due to interaction of these reverse micelles in the reaction mixture.

The reaction content was refluxed with continuous stirring and at around 70°C for about 3 hours. The color of mixture changed from yellow (at the initial reaction between cadmium and selenium) to orange to red then to deep dark red indicating of precipitation of CdSe particles. When the reaction was completed after 3 hours, the reaction mixture was allowed to cool at room temperature. Then, the product was separated by centrifuging at around 5000 rpm followed by repetitive washing with deionized water to remove any ions that may still be present in the sample. Finally, the product was dried overnight at room temperature in closed oven to remove the remaining water from the product.

3.3.1.3 Hydrolysis method for Titania synthesis

Titanium tetrachloride (TiCl_4) was used as the starting material without any further purification. The procedure for preparation of TiO_2 powder is shown as flow char in Fig. 3.2 TiCl_4 was slowly added to the distilled water in an ice bath. TiCl_4 reacts violently with water and air giving off white dense fumes. So it should be added slowly drop by drop with stirring. Each drop is added only after the dense fume

disappears. The concentration of titanium tetrachloride was adjusted to certain molarities. When TiCl_4 was dissolved in distilled water, the heat of the exothermic reaction explosively generated the formulation of orthotitanic acid $[\text{Ti}(\text{OH})_4]$. Because the formation of this species disturbed homogeneous precipitation, 5 ml of hydrochloric acid (35% HCl) per 100 ml of distilled water was previously added to prevent formation of orthotitanic acid.

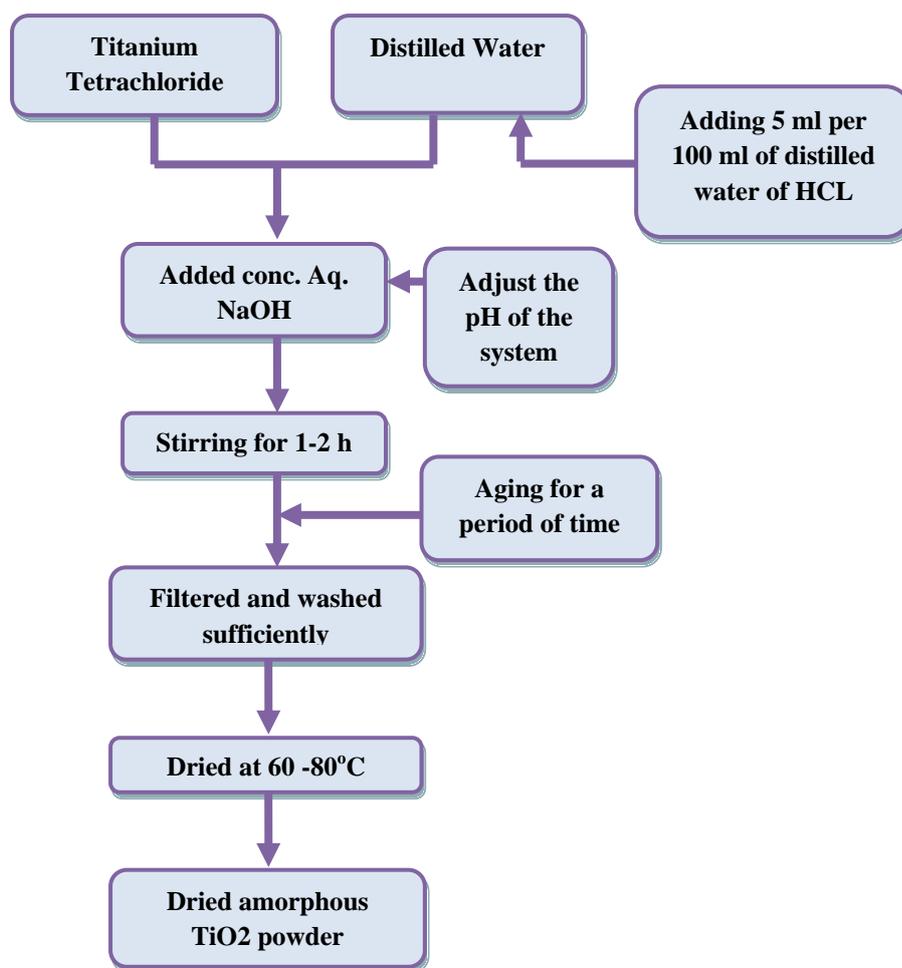


Fig 3.2 Procedure for preparation of TiO_2 powder

The initial pH of the solution was found to be very less that cannot be measured. A 1N solution of sodium hydroxide, NaOH in water was added drop wise to the TiCl_4 solution until the pH raises to the desired level. Here sodium hydroxide serves as the precipitating agent. The hydrolysis and condensation reactions starts immediately upon mixing, as indicated by the rapid increase in turbidity and the formation of large, visible flocs, which precipitated to the bottom of the reaction vessel. The mixture was kept under high-speed constant stirring on magnetic stirrer for 1-2 h at room temperature. Subsequently, the precipitated titanium dioxide

($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) was filtered and repeatedly washed with distilled water to make $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ free of chloride ions. The hydrous oxide was then dried at $60\text{-}80^\circ\text{C}$.

3.3.1.4 Hydrothermal Method for Titania

The procedure for making the initially TiCl_4 solution was the same as that of hydrolysis method. After adjusting the pH using NaOH, the solution was kept for stirring for 1-2 h at room temperature. The solution was then subjected to hydrothermal conditions. The hydrothermal preparations were conducted in the temperature range of $85 - 220^\circ\text{C}$ for 1- 4 h. The influences of concentration of TiCl_4 solution, pH in reaction medium, temperature, on formation, phase, morphology, and particle size of TiO_2 were examined. After the specific time period of heating, the product was cooled to room temperature in 2 h. It was then filtered and washed sufficiently with distilled water. The precipitate was separated in a centrifuge and dried at 80°C . Better results can be obtained by washing the precipitate several times with cold distilled water.

3.3.1.5 Hydrothermal Method for CdSe synthesis

In this synthesis method, initially aqueous solution of Cadmium nitrate tetrahydrate and sodium selenite were prepared each having 2.78 mMol/ml concentration by taking appropriate amount of each salt and dissolving in deionized water. From the Cd stock solution, one (1) ml solution of Cadmium nitrate tetrahydrate (2.78 mMol/ml) and 20 ml deionized water were taken in 100 ml beaker. This mixture was stirred and heated using magnetic stirrer. The color of initial solution was milky white color.

Thereafter, a mixture of one (1) ml aqueous solution of Sodium selenite (2.78mMol/ml), 10 ml hydrazine hydrate and 20 ml deionized water was prepared in separate beaker. The solution turned from colourless to dark red indicating formation of Se^{2-} ions. This selenium solution was added in a dropwise manner over duration of 30 seconds to original reaction mixture when the temperature of the mixture reached around 70°C . The reaction between Cd^{2+} ions and Se^{2-} ions in aqueous media takes place in the reaction mixture.

The reaction content was under constant stirring and heating so as to maintain the temperature around 70°C for about 3 hours. The color of final mixture changed

from yellow at the initiation of reaction between cadmium and selenium to orange to red then to deep dark red indicating of precipitation of CdSe particles. When the reaction was completed after 3 hours, the reaction mixture was allowed to cool to room temperature. Then, the deep dark red precipitate in the final reaction mixture was separated by centrifuging at around 5000 rpm followed by repetitive washing with deionized water to remove any ions that may still be present in the sample. Finally the product was dried overnight at room temperature in closed oven to remove the remaining water from the sample.

The experiments were performed for base case, molar ratio (1:1) of Cadmium nitrate tetra-hydrate to Sodium selenite as well as for excess Cd where the molar ratio of Cadmium nitrate tetra-hydrate to Sodium selenite was maintained at 2:1 and also excess Se where the molar ratio of Cadmium nitrate tetra-hydrate to Sodium selenite was maintained at 1:2, to investigate the effect of precursor mole ratio on the CdSe particles and their respective characteristics. The experiments were also performed by varying amount of hydrazine hydrate and water (reaction media) to investigate the effect of the same on synthesis of CdSe particles and their characteristics. Table 3.2 summarizes the experimental runs performed.

Table 3.2: Various experimental cases for Hydrothermal method

Sample run	Cd Salts	Se Salts	N ₂ H ₄ *H ₂ O	Deionized Water in Cd Salts	Deionized Water in Se Salts
	Mmol	mmol	ml	ml	ml
RB1	2.78	2.78	10	20	20
RB2	2.78	2.78	5	20	20
B1	2.78	2.78	20	100	100
B2	2.78	2.78	10	100	100
B3	2.78	2.78	5	100	100
B4	2.78	2.78	0.42	100	100

3.3.2 Sol–Gel Method

The sol-gel method is a versatile process used in making various ceramic materials. In a typical sol-gel process, a colloidal suspension, or a sol, is formed from

the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides.

The reaction between TiCl_4 and benzyl alcohol is a simple and nonaqueous procedure for the synthesis of highly crystalline titania nanoparticles at a temperature ~ 40 °C. XRD measurements prove the exclusive presence of the anatase phase. The particle growth depends strongly on temperature.

In a typical preparation, TiCl_4 was slowly added to anhydrous benzyl alcohol with vigorous stirring at room temperature. The reaction vessel was covered with a Petri dish and the sol was heated at 60, 80 and 100 °C with constant stirring.

- In the first step of the synthesis titanium tetrachloride was added dropwise to the benzyl alcohol. The benzyl alcohol to titanium chloride ratio was 80:2 (mL). Vigorous stirring is necessary to prevent precipitation.
- The reaction mixture is yellow, orange or deeply red, depending on the amount of TiCl_4 .
- The aging time was determined by applied temperature and the concentration of the titanium tetrachloride. The reaction at 70 °C temperature or higher led to the formation of titania nanoparticles within 30-50 minutes. Usually, for a given temperature lower titanium tetrachloride concentrations increase the aging time.
- The reaction mixture turned from red to white thick suspension. The product was recovered by centrifugation.
- Subsequent washing with ethanol and drying in air yielded a brittle and hard solid. After grinding, a white powder in good yield (ca. 90% with respect to TiCl_4) was obtained.
- For a constant ratio of benzyl alcohol to titanium tetrachloride, the temperature was varied from 60 to 100 °C.

Similarly, Sol-gel Method was performed using different types of alcohols like Isopropanol, Methanol, Butanol, and Ethanol. Synthesis of TiO_2 was carried out with different Calcination temperature and temperature effect on nano particles also studied.

3.4 Characterization of Powders

Powders were characterized on their material character and their morphology by the following techniques:

3.4.1 X-Ray Powder Diffraction (XRPD)

Powder X-ray diffraction pattern (XRD) were recorded on a Philips X'Pert PRO, PAN Analytical, Netherlands, using a Ni-filtered equipped with Cu K α 1 radiation (1.5405 Å) source (Cu anode), Solid-state Germanium detector with spinning sample stage.

3.4.2 Fourier transform infrared spectroscopy (FTIR)

The Infrared (FT-IR) spectra of samples were recorded in the range from 400 to 4000 cm⁻¹ on a Perkin Elmer (Model-Spectrum One) FT-IR spectrophotometer. Approximately 2 mg of the sample was mixed thoroughly with 100mg of KBr (dried) and then compressed to form discs using one cm diameter pellets, IR spectra was recorded with resolution of 4.00 cm⁻¹ and 16 scans each for sample at room temperature.

3.4.3 Fourier Transform Raman spectroscopy (FT-Raman)

Raman spectra of purified and dried samples were recorded by using a FT-Raman Spectrometer (Model: RFS 100/S, Bruker Optik) equipped with a 750 mW Helium : Neon laser source operating at 1064 nm having laser power 350 mW and liquid nitrogen cooled germanium detector, scanning range from (+) 4000 cm⁻¹ to (-) 2000 cm⁻¹ and number of scans fifty.

3.4.4 Photoluminescence Spectra

Photoluminescence spectra serves as an optical fingerprint by which the effect of process parameters on the size and overall intensity of quantum dots can be analyzed. Semiconductor nanocrystal emissions were performed using a Shimadzu RF-5301 PC fluorimeter and displayed as a peak that may be Gaussian. The peak of the curve corresponds to the emission wavelength from the mean size of the nanoparticle. The width of the peak, typically reported as the full-width-at-half-maximum (fwhm), is one common method used to evaluate the particle size

distribution. Thus, the emission spectra represent size distributions of individual emissions. The fwhm serves as a statistic that can accurately represent the size distribution.

3.4.5 Scanning electron microscopy (SEM)

Surface morphology and shape of the samples were examined with scanning electron microscope (Model-Quanta-200, Make-FEI Company, The Netherlands). The samples were mounted with carbon tape on a double-sided adhesive with spot size 5, an accelerated voltage of 15 kV and a current of 20 mA prior to observation.