CHAPTER II
REVERSE MICELLES MICROEMULSION FOR NANO-METAL OXIDE
SYNTHESIS

2.1 Abstract

Nanoparticle synthesis is part of an emerging field in nanotechnology. Applications take advantage of the high surface area and confinement effects, which lead to nanostructures with properties different from those of conventional materials. The main focus of this work was on the study of the use of reverse micelle microemulsion for metal oxide synthesis. Two microemulsion systems were used. The first system was anionic surfactant system of n-heptane/water/NaCl/ sodium bis (2-ethylhexyl) sulfosuccinate (AOT) for synthesis TiO_2. The second system was non-ionic surfactant system (brine solution/1-hexanol/Triton X-100/cyclohexane) for synthesis TiO_2 and Nb-TiO_2. The effects of prepaparation conditions, such as salinity concentration, temperature and co-surfactant on the micellar size change were investigated. The results showed that increasing NaCl concentration in anionic surfactant system strongly influenced a reducing in micellar size. On the other hand, temperature and the addition of cosurfactant caused a significantly reduce in reverse micellar size of non-ionic surfactant. The synthesized powders had very uniformity in size and shape, high in specific surface area, high crystallinity in the anatase phase.

2.2 Introduction

For the past 10 years, many researchers have focused on the synthesis of nanoparticles because it is believed that they have the ability to improve mechanical, electrical, optical, and chemical properties as compared with conventional polycrystalline materials (Higgins and Goldsmith, 1999; Wu *et al.*, 1999). New physical properties of nanoparticles such as high hardness combined with good fracture toughness and corrosion resistance for coatings (Xiao *et al.*, 2000), large contact area for catalytic applications such as oxidation and reduction (Li *et al.*, 2002; Hong *et al.*, 2002), and high surface area which promotes rapid interactions of

active material with surrounding media (Tanner *et al.*, 2002; Song *et al.*, 2002), have led to a major interdisciplinary area of research.

It has been found that the properties of nanoparticles depend on the method of preparation. A variety of synthetic methods (Xiao *et al.*, 2000), such as hydrolysis, sol-gel processing (Debuigne *et al.*, 2000; Jung and Park; 1999; Moran-Pineda *et al.*, 2002), bulk-precipitation, spray drying (Jiang *et al.*, 2002), freeze drying, hot spraying, laser vaporization and controlled condensation (LVCC), hydrothermal techniques (Wu *et al.*, 1999), and microemulsions (or reverse micelles) (Boutonet *et al.*, 1982; Leung *et al.*, 1988; Clint, 1992; Lisiecki *et al.*, 1995; López-Quintela *et al.*, 1997; François and Ginzberg, 1998; Calandra *et al.*, 1999; Li and Park, 1999; Bagwe and Khilar, 2000; Lade *et al.*, 2000; Ju *et al.*, 2002) have been studied to prepare nanoparticles. Of these methods, the microemulsion technique is the most interesting because it allows easy control of particle size (Tojo *et al.*, 1998; Zarur *et al.*, 2000).

There are three types of microemulsions that can be formed in the different compositions of organic phase, aqueous phase and surfactant. First is an oil-in-water (o/w) microemulsion (type I), in which oil droplets are surrounded by a sheath of amphiphile and separates the oil core from the continuous aqueous phase. Second, a water-in-oil (w/o) microemulsion (type II) is a reverse of the type I microemulsion, in which the aqueous phase is dispersed as microdroplets surrounded by a monolayer of surfactant molecules in a continuous organic phase. Third is a bicontinuous structure microemulsion (type III) in which the surfactants form interfaces of rapidly fluctuating curvature and both oil and water domains are continuous. Type II microemulsion has been used as a constraint microreactor for synthesizing ultrafine particles with a narrow size distribution by controlling the growth inside a water drop (Bourrel and Schechter, 1988). It is interesting to learn how the reverse micelle influences the final particle sizes and their properties. Factors influencing the size of nanoparticles (Higgins and Goldsmith, 1999; Calandra *et al.*, 1999; Lade *et al.*, 2000; Lisiecki *et al.*, 1995) may include the conditions of preparation and the intermicellar exchange rate. The variables in the preparation include times and temperatures of calcination and reaction, and composition of the microemulsion solution. In addition, the intermicellar exchange rate depends on variables that include organic

solvent, organic additives, the volume ratio of water to oil, the nanosized reactor or the molar ratio of water to surfactant, and the structure of reverse micelles.

This work focused on the effects of salinity scan on type II microemulsion of anionic surfactant (sodium bis (2-ethylhexyl) sulfosuccinate, AOT) for TiO_2 synthesis and the effect of temperature and cosurfactant on type II microemulsion of nonionicsurfactant (Triton-X 100) for TiO_2 and Nb-TiO_2 synthesis. A second reactant, ammonia, was used for precipitation of nanoparticles in the microemulsion. Dynamic light scattering (DLS) (Quinlan *et al.*, 2000; Fu and Qutubuddin, 2001), water content by using a coulometer, x-ray diffraction (XRD) pattern (Pillai and Shah, 1996; Quinlan *et al.*, 2000; Kim and Hahn, 2001), scanning electron microscopy study (SEM) (François and Ginzberg, 1998), transmission electron microscopy study (TEM) (Pillai and Shah, 1996; Quinlan *et al.*, 2000; Kim and Hahn, 2001), and surface area analysis (Kim and Hahn, 2001) were used for characterizing the oxide particles produced.

2.3   Experimental

2.3.1   Materials

High purity (98%) anionic surfactant (sodium bis(2-ethylhexyl) sulfosuccinate Aerosol OT; AOT), nonionic surfactant (Triton X-100) and 1-hexanol (+98 %) obtained from Fluka (Switzerland) was used for preparing microemulsion solutions. The analytical reagents (AR) consisted of 99% *n*-heptane or cyclohexane as the oil phase, 99% sodium chloride (NaCl) for salinity scan of microemulsion formation, and 99.5% acetone for rinsing the titanium dioxide precipitate (Lab-Scan, Thailand). Ammonium hydroxide (NH_4OH, AR grade) was purchased from J. T. Baker (U.S.A.). Niobium (V) chloride was purchased from Sigma-Aldrich (Germany). 99.5% titanium dioxide (TiO_2, P25) was obtained from Degussa (GmbH) and 40% hydrofluoric acid (HF) from Riedelde Haën AG (Germany). Perchloric acid (56%, $HClO_4$) was purchased from Carlo Erba (Italy). Deionized water was used throughout the experiments.

Titanium tetrachloride solution ($TiCl_4$) in concentrated HCl was prepared from TiO_2 by dissolving P25 TiO_2 in hot concentrated HF solution (80 $^\circ$ C) until the clear solution of TiF_4 was obtained (Kirk and Othmer, 1981; Barksdale, 1996). Further heating reduced the solution volume to 2-3 milliliters. Then, a few milliliters of $HClO_4$ was added to react with TiF_4 in the solution and the solution was further heated to remove HF. Concentrated HCl was added to the solution and finally, $TiCl_4$ was obtained as shown in the following reactions:

$$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O \qquad (2.1)$$
$$2TiF_4 + HClO_4 + 7HCl \rightarrow 2TiCl_4 + 4F_2 + 4H_2O \qquad (2.2)$$

2.3.2 Formation of the Microemulsion

The system of anionic microemulsion (AOT/n-heptane/$TiCl_4$/NaCl brine solution) was prepared by mixed the same ratio of the brine (0.3 M $TiCl_4$, 4-8 %wt NaCl) with oil phase of 6% wt of AOT in n-heptane using a vortex mixer, (Genie-2 G560E, Scientific Industries, U.S.A.). The solution was left in a temperature controlled water bath (DT2, Heto, Denmark) at 30°C for 2 days until it reached equilibrium and a microemulsion was observed.

The system of nonionic microemulsion (NaCl/1-hexanol/Triton X-100/cyclohexane) was prepared by mixing 3.84 ml of aqueous phase in the oil phase. The oil phase was prepared by mixing 66.78 g of TX-100 and 53.00 g of n-hexanol with 210.33 g of cyclohexane. For the aqueous phase, the preparation was performed under N_2 atmosphere. The aqueous phase was prepared by weighing 0.06079 gram of $NbCl_5$ followed by the addition of 10 ml of 36.46% wt of HCl and 5 ml of 1.5 M $TiCl_4$ and then adding deionized water until 25 ml of solution was obtained. The solution was left in temperature controlled water bath (DT2, Heto, Denmark) at 30-50°C for 2 days until it reached equilibrium and a microemulsion was observed.

2.3.3 Preparation of Metal Oxide Particles in the Microemulsion

The microemulsion phase was separated for subsequent precipitation. Ammonia gas, obtained by bubbling air through concentrated NH_4OH solution at a

constant flow rate of 20 ml/min, was transferred into the microemulsion to precipitate titanium dioxide at the optimum pH of 6.0.

The precipitate was separated by a high speed and low temperature centrifuge (Sorvall super T21, DuPont, U.S.A.) at the speed of 10,000 rpm for 10 min, washed twice with ethanol and acetone to remove the oil and the surfactant from the precipitated particles, dried at 80°C for 24 h to remove water, and calcined at 460°C for 5 h prior to characterization of the nanoparticles.

2.3.4 Characterization of Microemulsions

The apparent hydrodynamic diameter (D_h) of the microemulsion was determined using dynamic laser light scattering (DLS) (Coherent, U.S.A.) at a constant angle of 90°, pinhole 100, wavelength 514.3 nm (Ar^+, Laser light source, 100 mW), and a constant temperature of 30°C. Three milliliters of microemulsion solution in a quartz cell was measured by DLS.

Water content in the microemulsion phase was determined using a coulometer (Metrohm 737 KF, Switzerland). Fifty microliters of microemulsion solution was titrated with a hydramal coulomat solution. The water content reported was an average of three runs.

2.3.5 Characterization of Particles

The phase analysis of TiO_2 and $Nb-TiO_2$ particles was performed using an x-ray diffractometer (D/max-2200, Rigaku, Japan) at room temperature. X-ray diffraction (XRD) patterns of all titanium dioxide particles were obtained by using a Phillips PW 1830/00 No. SY 1241 diffractometer equipped with a graphite monochromator and a Cu tube for generating a $CuK\alpha$ radiation (wavelength 1.5406 Å). The particles were spread on a glass slide specimen holder and its diffraction angles were examined between 5 and 90° at a scanning rate of 2θ of 1.5° per minute with 0.02° increments. The x-ray source was operated at 40 kV, 30 mA, and 1.20 kW. The digital output of the proportional x-ray detector and the goniometer angle measurements were sent to an online microcomputer to store the data, which were analyzed by a PC-APD version 3.5B. Peak positions were compared with the standard files to identify crystalline phases.

The size and shape of TiO_2 and Nb-TiO_2 particles were observed using a transmission electron microscope, TEM (2010 Jeol, Japan). Precipitated TiO_2 and Nb-TiO_2 samples were placed on a copper stub and were coated with gold at 40 mA for 4 minutes. The TiO_2 and Nb-TiO_2 samples were examined by using the scanning electron microscope at a constant accelerating voltage of 25 kV. The specimens for the transmission electron microscope were prepared by placing a small amount of sonicated precipitated titanium dioxide sample dispersed in an acetone solution on a 300-mesh carbon film coated copper grid. The particle sizes of the precipitated TiO_2 and Nb-TiO_2 were determined at a constant accelerating voltage of 100 kV.

The Brunauer-Emmett-Teller (BET) surface area of TiO_2 and Nb-TiO_2 was measured by using surface area analyzer (Autosorb I, Quanta Chrom, U.S.A.). TiO_2 and Nb-TiO_2 particles were first outgased to remove moisture and volatile adsorbents under vacuum at 300 °C for three hours before starting the analysis to determine the surface area. Autosorb ANYGAS Version 2.10 (U.S.A.) was used to analyze the results. The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation.

2.4   Results and Discussion

2.4.1 Microemulsion Preparation

2.4.1.1 Effects of salinity on micellar size and water content on the anionic surfactant system

Reverse micelle microemulsion of anionic surfactant was prepared with various NaCl concentration as shown in Figure 2.1 (a). It can be seen that as the concentration of NaCl continuously increased, average micelle diameters decreased from 40 nm to 15 nm. This might be due to the effect of salt binding, which caused the decrease in repulsive force between the head groups of the surfactant, resulting in a decrease of micellar size. Figure 2.1 (b) shows the water content in the microemulsions. Water was decreased from 6 to 3% wt with the addition of NaCl from 4 to 8 %wt.

2.4.2.2 Effects of temperature and cosurfactant on micellar size of nonionic surfactant system

Figures 2.2 shows micellar size change with the addition of n-hexanol (a) and without the addition of n-hexanol (b). The temperature varied from 30°-50°C. Dynamic laser light scattering results indicated that without the addition of hexanol, an increase temperature from 30° to 50°C caused the micellar size to decrease from 85 to 20 nm. It might be corresponded to the dehydrated water, from the polar head group (poly-oxyethylene) of TX-100, which was removed at higher temperature and thus decreased the CMC of surfactant and the size of reverse micelle. On the other hand, the additions of n-hexanol as a cosurfactant caused a drastic reduction of micellar size while the temperature showed no significant effect on change of micellar size. The addition of cosurfactant reduces the repulsive force of the surfactant head groups and hence reduced the micellar size. The smallest size of 4 nm was achieved with the addition of n-hexanol.

2.4.2 Synthesis of Metal Oxide Particles in Microemulsions

2.4.2.1 TiO$_2$ Synthesis in anionic surfactant system

After precipitation, the synthesized TiO$_2$ was calcined at temperatures of 460°C for 5 hours. Powders were subsequently characterized by a BET specific surface area analyzer and by XRD. Table 2.1 shows the results of BET specific surface area and phase of the TiO$_2$ particles. The phase analysis was done by calculating the area under the anatase peak at 25.3° 2θ and under the rutile peak at 27.5° 2θ (Jung and Park, 1999). It was found that the amount of rutile decreased and the amount of anatase increased with an increased NaCl concentration. Above 6 %wt of NaCl, the rutile phase could not be detected. The highest surface area of 98 m^2/g was obtained from powder prepared from 8% wt of NaCl addition.

TEM results for titanium dioxide heated to 460°C for 5 hours (Figures 2.3 (a)-(c)). The average particle size decreased from 33 to 13 nm as NaCl concentration increased from 4.0 to 8.0 %. The size of the micellar reactor and the amount of the NaCl in the reverse micelle control the growth or the size of TiO$_2$. These results showed the same trend as reported in the literature (Wu *et al.*, 1999; Kim *et al.*, 2001; Kim and Hahn, 2001); that is, the micellar size is controlled by the

water-to-surfactant ratio. The obtained TiO_2 was found to be in a narrow size distribution. In this work the micelle acts as a constraint microreactor in a w/o microemulsion that can be controlled by the addition of NaCl, and the size of which decreased with an increasing amount of NaCl. This also controlled the growth and structure of titanium dioxide.

2.4.2.2 TiO_2 and Nb-TiO_2 synthesis in nonionic surfactant system

The synthesized TiO_2 and Nb-TiO_2 from nonionic surfactant were calcined at 550°C and 950°C for 5 hours. Powders were subsequently characterized by XRD and BET specific surface area analyzer. XRD result of TiO_2 presented only in anatase structure at 550°C but almost 90% of rutile structure was obtained at 950°C. On the other hand, Nb-TiO_2 presented only pure anatase structure even calcined at 950°C. BET specific surface area of TiO_2 drastically reduced from 118 m^2/g to 25 m^2/g when the temperature increased up to 950°C. In case of Nb-TiO_2, when the calcinations temperature increased from 550°C to 950°C, BET specific surface area was decreased from 167 m^2/g to 120 m^2/g. Comparatively, less change of BET specific surface area was observed in case of Nb-TiO_2.

The TEM result revealed the crystal sizes of TiO_2 and Nb-TiO_2 after calcined at 550°C about 8 nm and 4 nm, respectively (Fig. 2.4 (a) and (c)). At 950°C, crystal size of pure TiO_2 and Nb-TiO_2 were 150-200 nm and 10 nm, respectively (Fig. 2.4 (b) and (d)). Pure TiO_2 showed the drastic increase in crystal size while the rate of agglomeration was retarded in case of Nb-TiO_2. For the nano structural study, the HR-TEM of Nb-TiO_2 clearly showed the d-spacing of anatase structure plane 101 at 3.52 Å even at 950°C, which agreed well with XRD result (Fig. 2.5).

2.5 Conclusions

Nanometer size of TiO_2 and Nb-TiO_2 particles was successfully synthesized using microemulsion system of both anionic and nonionic surfactants. Increasing NaCl concentration influenced the micellar size as well as water content in case of anionic surfactant system. On the other hand, an increase in temperature and an addition of cosurfactant played important role in nonionic surfactant system. Both

TiO$_2$ and Nb-TiO$_2$, obtained from two microemulsion systems, were small and uniformed in size and large in specific surface area. In addition, Nb dopant slowed down the rate of agglomeration; the nanocrystal size could be maintained with pure anatase structure.

2.6 Acknowledgements

2.7 References

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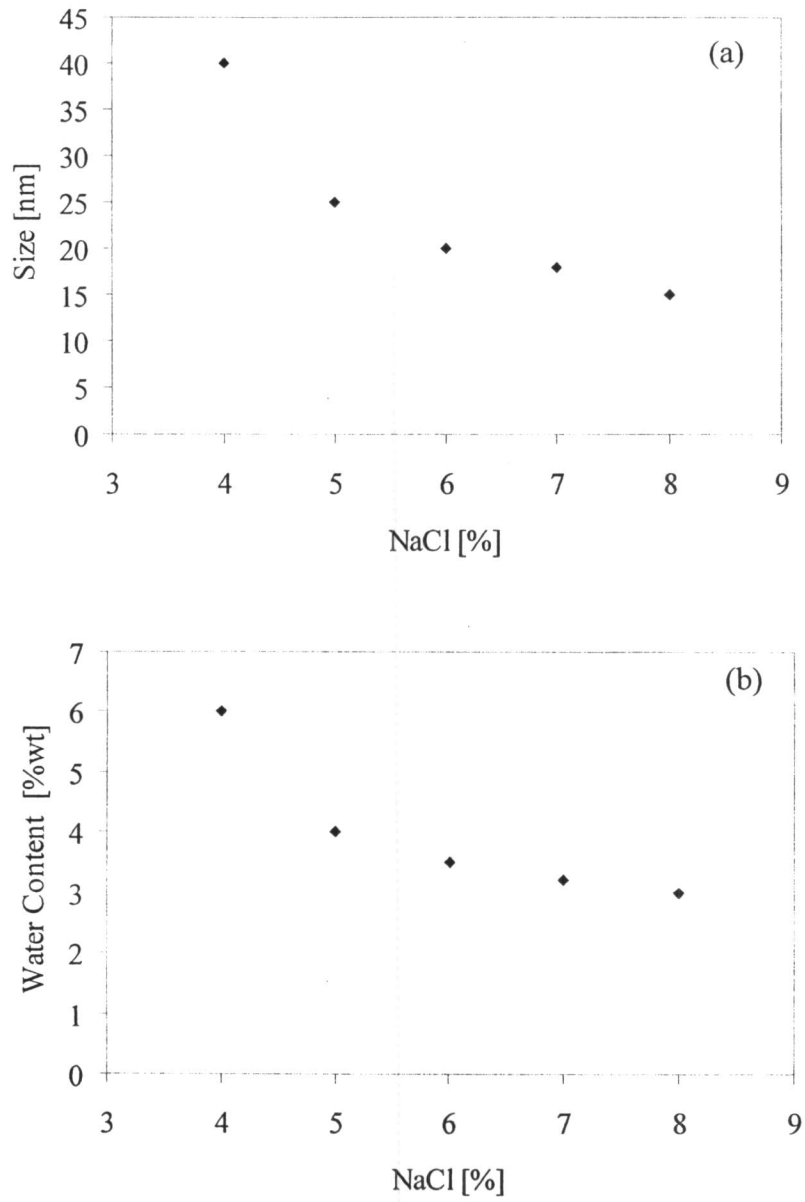
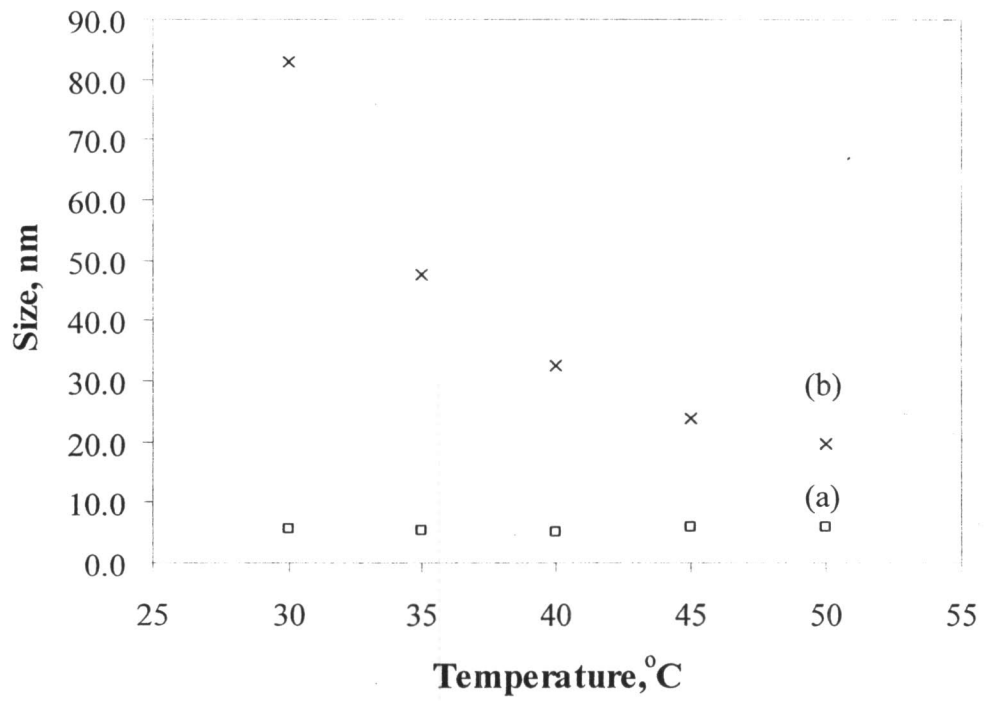**Figure 2.1** Micellar sizes (a) and water contents (b) in anionic surfactant system.

Figure 2.2 Effect of tempearure on nonionic surfactant system; with addition of *n*-hexanol (a) and without the addition of *n*-hexanol (b).
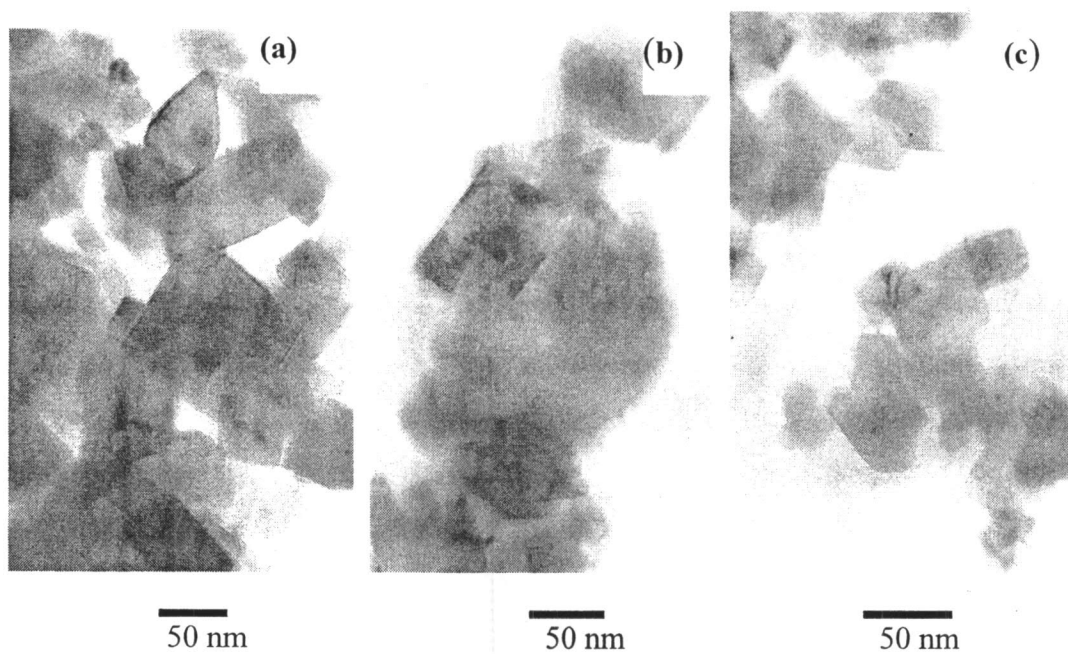
Figure 2.3 Transmission electron micrographs of titanium dioxide obtained from (a) 4.0% NaCl, (b) 6.0% NaCl, (c) 8.0% NaCl microemulsions.
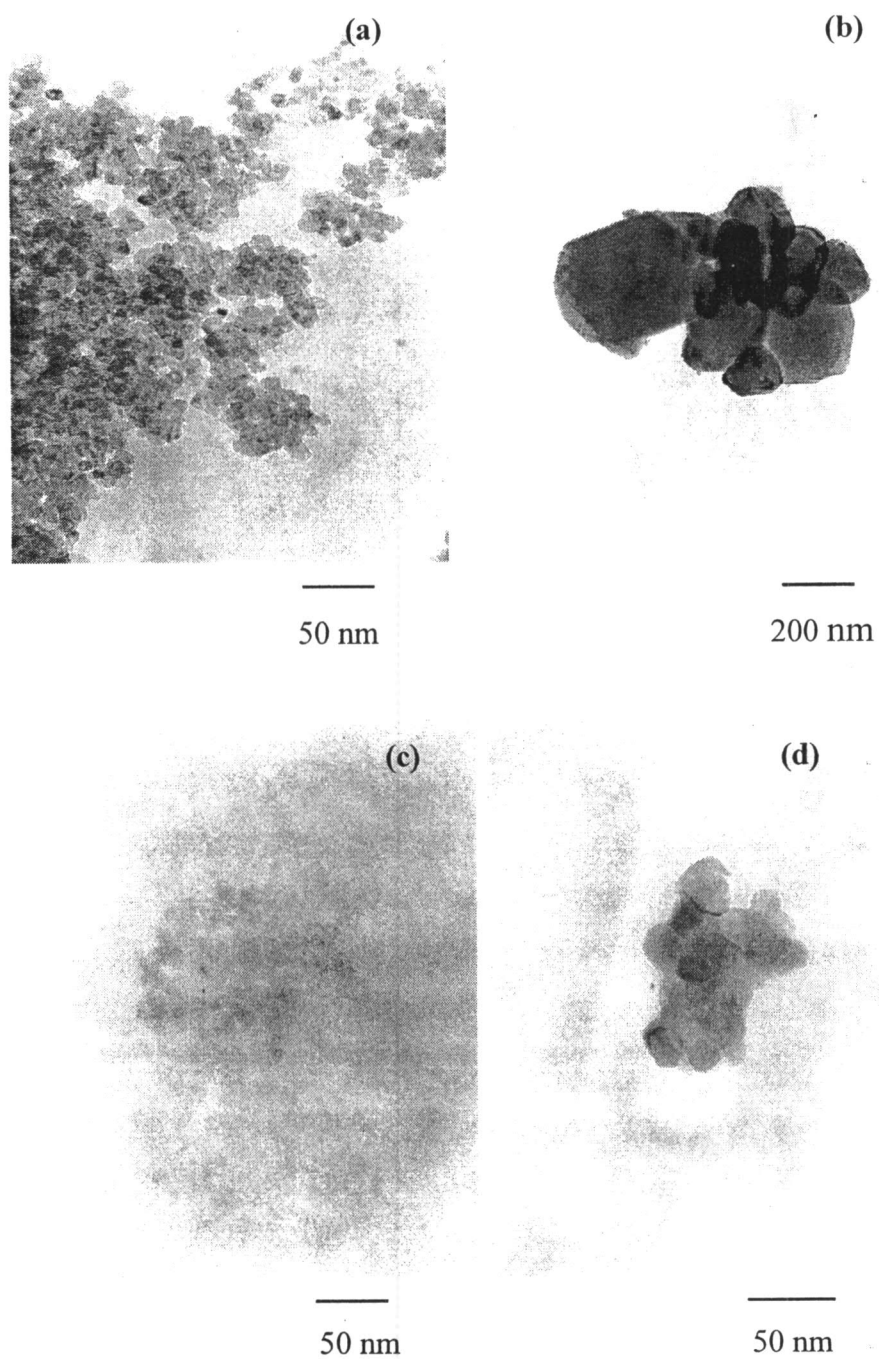
Figure 2.4 The TEM picture of TiO_2 after calcined at 550^oC (a) and 950^oC (b) and Nb-TiO_2 after calcined at 550^oC (c) and 950^oC (d).
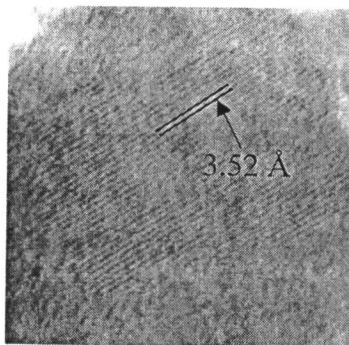
Figure 2.5 HR-TEM of anatase plane 101 of Nb-TiO$_2$ calcined at 950°C.

Table 2.1 BET specific surface area and XRD phase of titanium dioxide particles synthesized from different types of microemulsions heated to 460^0C for 5 h and commercial titanium dioxide

Samples	% NaCl	BET Surface area (m^2/g)	XRD, % Rutile
TiO$_2$ synthesized in w/o microemulsion	4.0	40	19
TiO$_2$ synthesized in w/o microemulsion	6.0	68	0
TiO$_2$ synthesized in w/o microemulsion	8.0	98	0