CHAPTER IV
RESULTS AND DISCUSSION

4.1 Modified Surface Composition Investigation by EDS

The film formed on mica was subjected to elemental analysis by EDS. The results showed an average 0.07%Ti, 7.5%Si, 7%Al, and 50 % C. The EDS result confirmed formation of titanium on the mica surface. High percentage of carbon indicated that there was some surfactant still remaining on the surface which could not be removed by washing in the surfactant removal step. While the observation of Al and Si indicated the composition of mica which was used as substrate.

4.2 Triton X-100® in 10% Isopropanol Solution in Water on Mica

The structure of Triton X-100® adsorbed on mica for 24 hours in 10% isopropanol aqueous solution was investigated using tapping mode AFM at scan size 2 μm (Figure 4.1). The surface is covered with patches of Triton X-100$^{®}$, with the average patch more than 400 nm in width and 0.5nm in height. The parallel stripes found in all images are artifacts caused by deflection of the laser, which may occur with very flat surfaces.

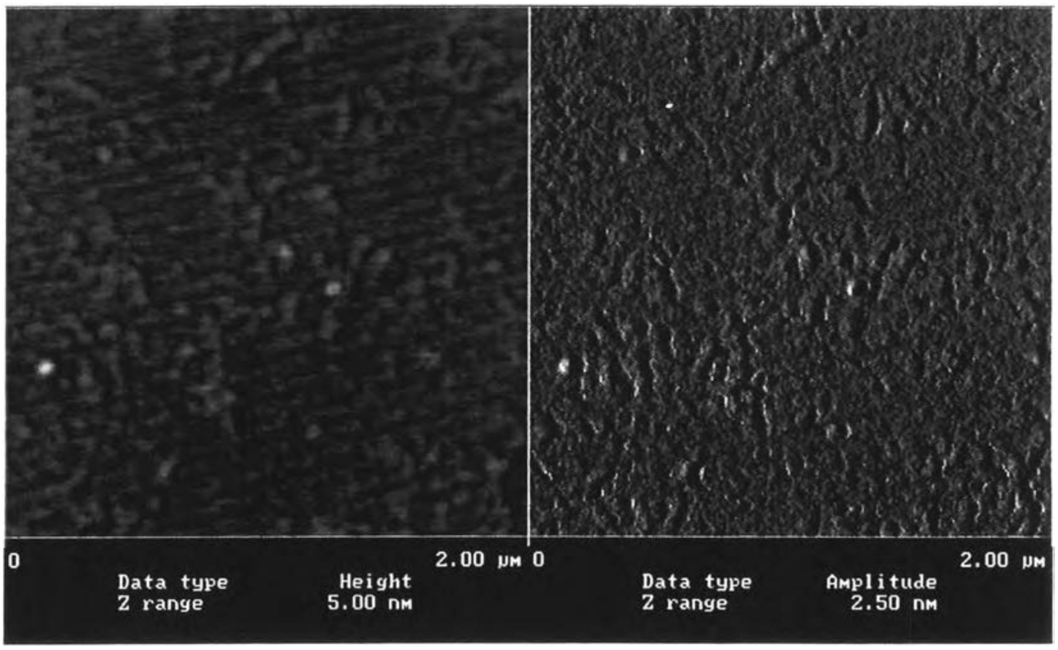

Figure 4.1 AFM topography (left) and amplitude (right) image of Triton X-100® in 10 % isopropanol solution in water adsorbed on mica surface. (Scan size 2 μm with z range 5 nm and 2.5 nm respectively).

4.3 Effect of Surfactant on Film Topography

In order to reveal the role of surfactant on film formation, samples were prepared with and without surfactant. Figure 4.2 (a)-Fig. 4.4(a) are the AFM amplitude images of surfaces which were modified with 0.01 μM TBOT precursor in 0.2 mM Triton X-100® solution while Fig. 4.5(a)-Fig. 4.7(a) are the AFM amplitude images of surfaces which were modified with 10 μM TBOT precursor in 0.2 mM Triton X-100® solution. Figure 4.2 (b)-Fig. 4.4(b) are the AFM amplitude images of surfaces modified by 0.01 μM TBOT in the absence of surfactant while Fig. 4.5(b)-Fig. 4.7(b) are the AFM amplitude images of surfaces modified by 10 μM TBOT in the absence of surfactant.

The systems containing both TBOT and surfactant clearly show a smooth and homogeneous surface with highly ordered and connected particles ranging in size from 20 – 30 nm in diameter with 0.2 - 0.5 nm in height. Besides connected particles that were found on surface, fibrous structure can also be found on surface in size of 20-30 nm in diameter with length longer than 100 nm but these fibrous structures were random and minority when compared to the highly ordered particles which cover the entire surface. The systems modified with TBOT alone show randomly dispersed titania particles ranging in size from 20 nm to a hundred nm in diameter. These particles did not cover the entire surface, as can be observed in Figure 4.2 (b)-Fig. 4.7(b). The morphology of the particles formed in the absence of surfactant were random and not experimentally controllable (Wei-Li *et al.*, 2001).

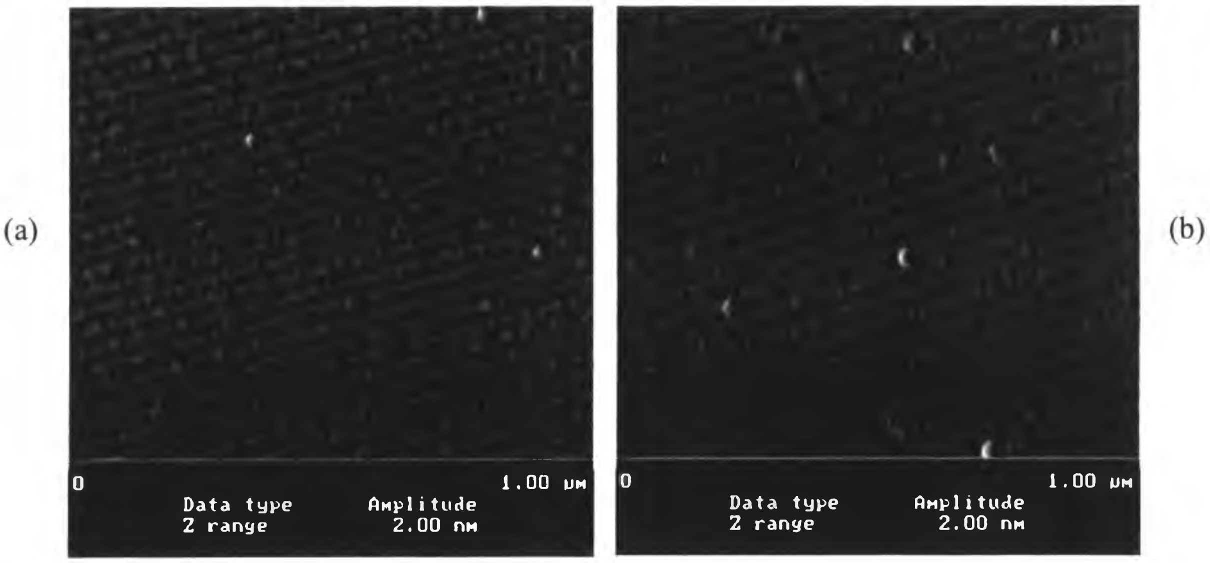

Figure 4.2 AFM amplitude images of titania film from 0.01 µM TBOT at reaction time of 10 minutes in 0.2 mM Triton X-100® (a) and in the absence of surfactant (b). (Scan size 1 µm, z height of 5 nm).

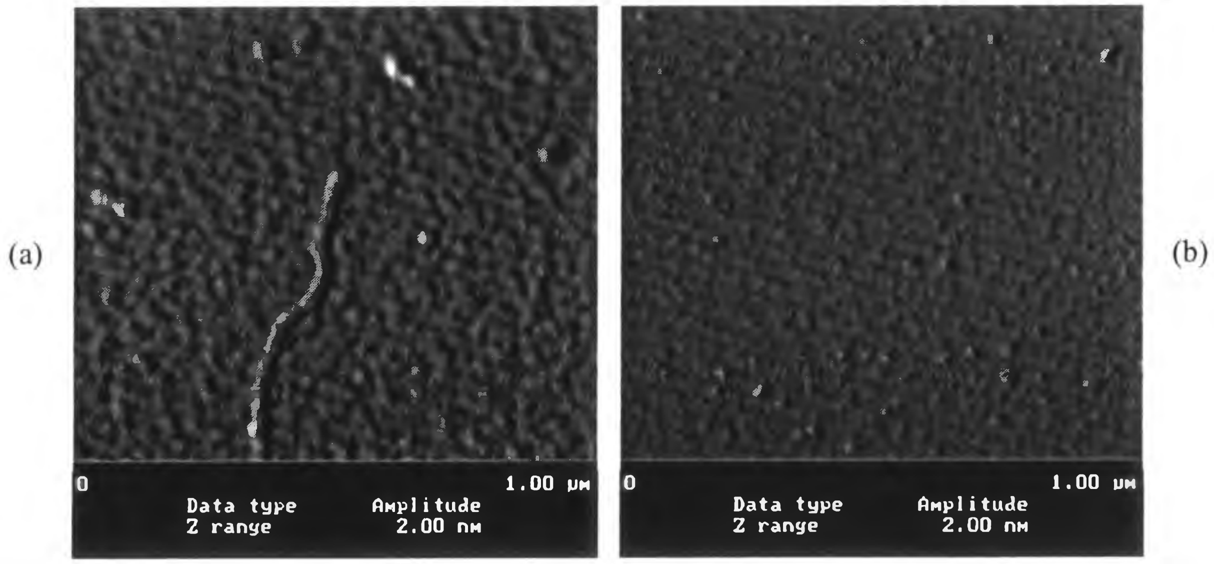

Figure 4.3 AFM amplitude images of titania film from 0.01 µM TBOT at reaction time of 6 hours in 0.2 mM Triton X-100® (a) and in the absence of surfactant (b). (Scan size 1 µm, z height of 5 nm).

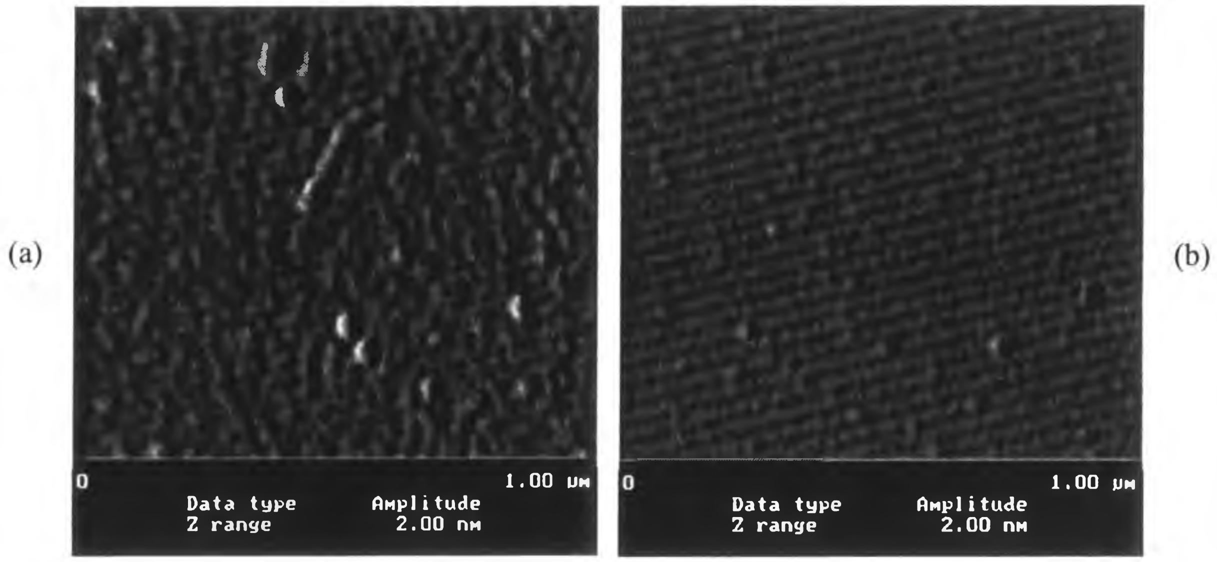

Figure 4.4 AFM amplitude images of titania film from 0.01 µM TBOT at reaction time of 24 hours in 0.2 mM Triton X-100® (a) and in the absence of surfactant (b). (Scan size 1 µm, z height of 5 nm).

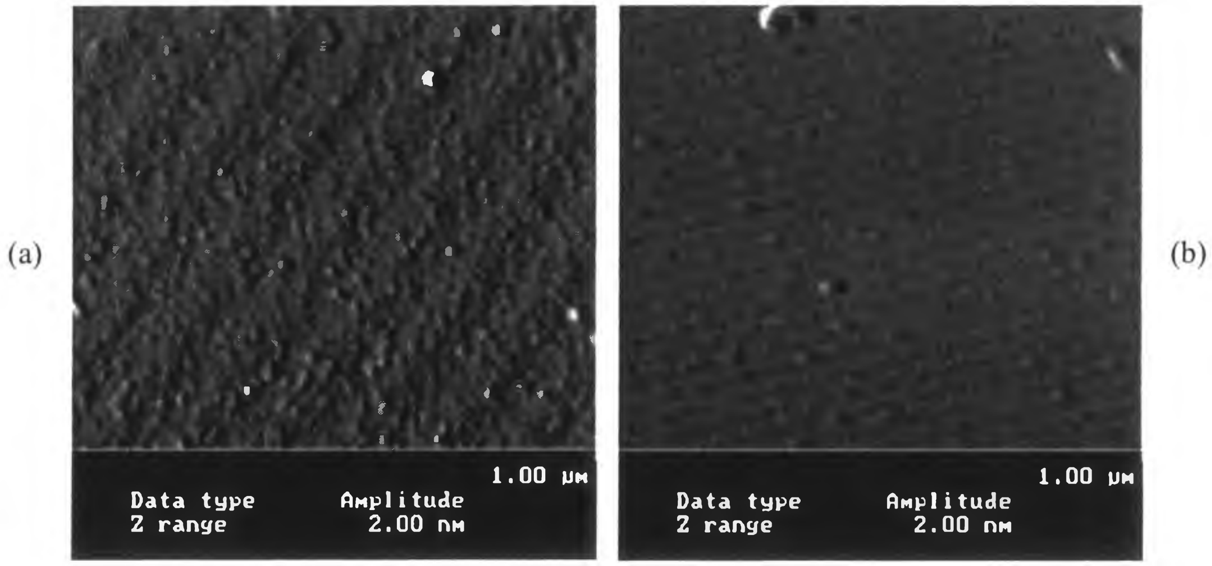

Figure 4.5 AFM amplitude images of titania film from 10 µM TBOT at reaction time of 10 minutes in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

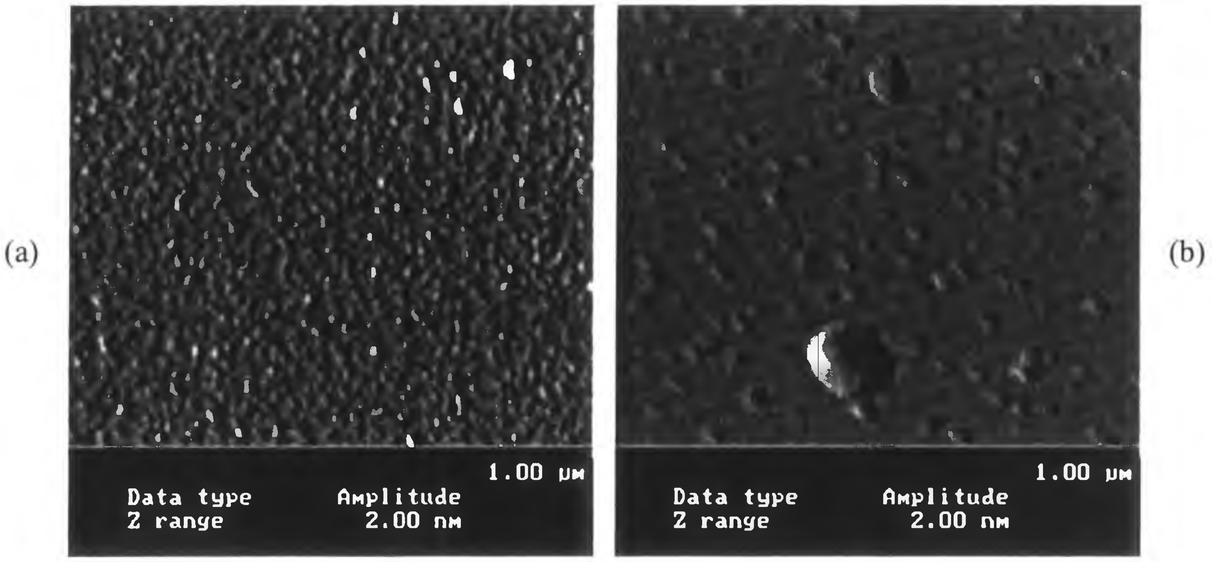

Figure 4.6 AFM amplitude images of titania film from 10 µM TBOT at reaction time of 6 hours in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

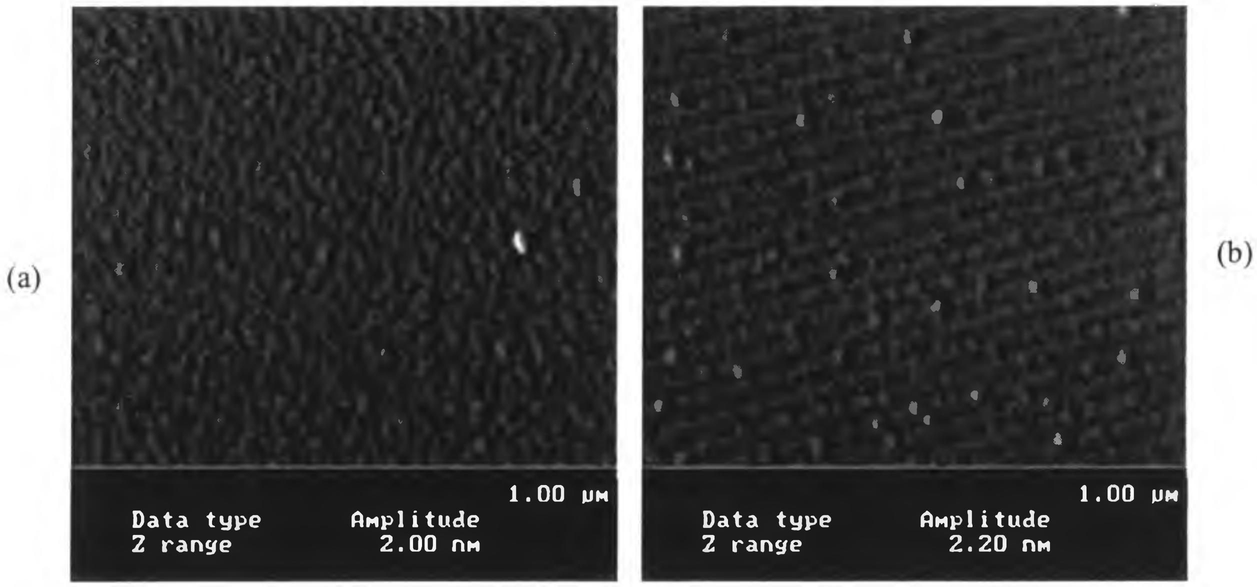

Figure 4.7 AFM amplitude images of titania film from 10 μM TBOT at reaction time of 24 hours in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 μm, z height of 5 nm).

Surfaces modified with TIPP precursor in surfactant solution are shown in Fig. 4.8(a)-Fig. 4.10(a) and Fig. 4.11(a)-Fig. 4.13(a). The images clearly show that the surface is fully covered with interconnected titania particles ranging in size from 20-30 nm in diameter and 0.8-1.5 nm in height. Surfaces showed a smooth and homogeneous adsorbed layer that was similar to the film formed using TBOT precursor, with difference only in film thickness. The difference in height between TBOT and TIPP systems is because TIPP has a higher hydrolysis rate than TBOT (Falaras and Xagas, 2002). Since the mechanism of the polymerization to produce TiO_2 network includes a nucleophilic attack of the titanium metal center, steric hindrance by the presence of the alkyl groups is expected to play a crucial role. Thus, the more bulky butoxide ligand is expected to impede the access to the titanium atom, thus inhibiting propagation of the hydrolysis more than the less bulky isopropoxide. (Babonneau *et al.*, 1988).

The surface topography clearly shows that surfactant has an effect on film formation. First, the presence of surfactant appears to help titania particles adhere to the surface, as the hydrolysable ligand molecule of the titanium alkoxide precursor can form hydrogen bond with the terminal hydroxyl group of the surfactant bilayer (Pinnavaia, 1998). Surfaces formed in the presence of surfactant were fully covered with titania particles. Secondly, during the polymerization process, diffusion of precursors into the admicelles controls the availability of precursor for hydrolysis reaction on the surface. Since the admicelle has a much lower concentration of water compared to the bulk, hydrolysis of precursor is retarded within the admicelle and the rate of film growth is somewhat controlled (Muller and Birkhahn, 1967). Thus homogeneous and smooth surfaces can be observed in the systems containing surfactant.

From the observation of fibrous structure, it is interesting to note that the fibrous structures can be found on the surfaces which were fabricated in TBOT only. The fabrication of fibrous structures may come from the difference in the ability to diffuse of precursors into the admicelle. TBOT which has longer chain alkoxide may have slower diffusion rate than TIPP which has shorter alkoxide chain (Rosen, 1989). Slower diffusion rate may cause the frequency of collision of the particles to be lesser than the faster diffusion rate. This will make the coalescence of the particles from slower diffusion rate precursor less. Moreover, the slower diffusion rate may leas to the inside of admicelle not having enough precursor to form 3-D particles, thus 2-D fibrous structures were formed instead. Thus TBOT precursor may have more possibility to form fibrous structure than TIPP precursor.

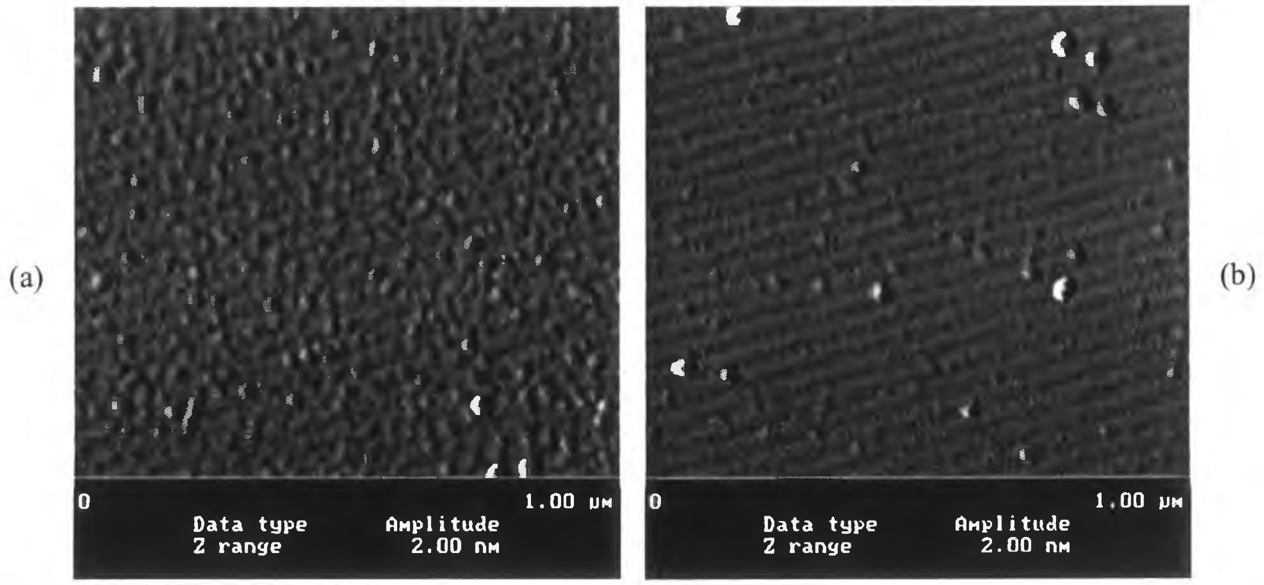

Figure 4.8 AFM amplitude images of titania film from 0.01 µM TIPP at reaction time of 10 minutes in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

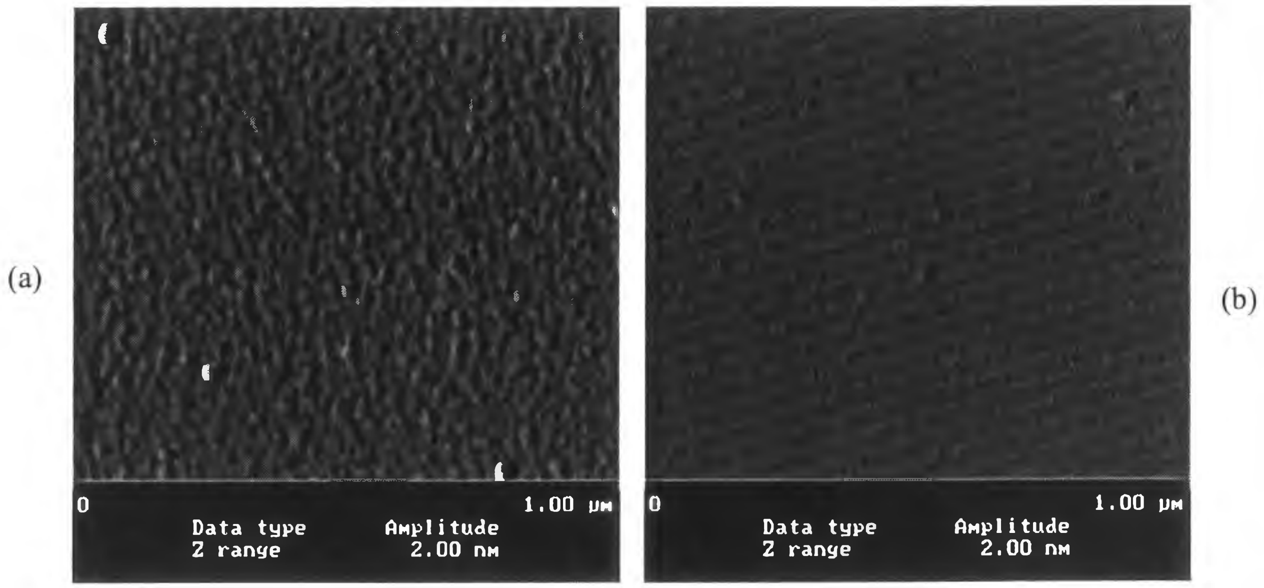

Figure 4.9 AFM amplitude images of titania film from 0.01 µM TIPP at reaction time of 6 hours in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

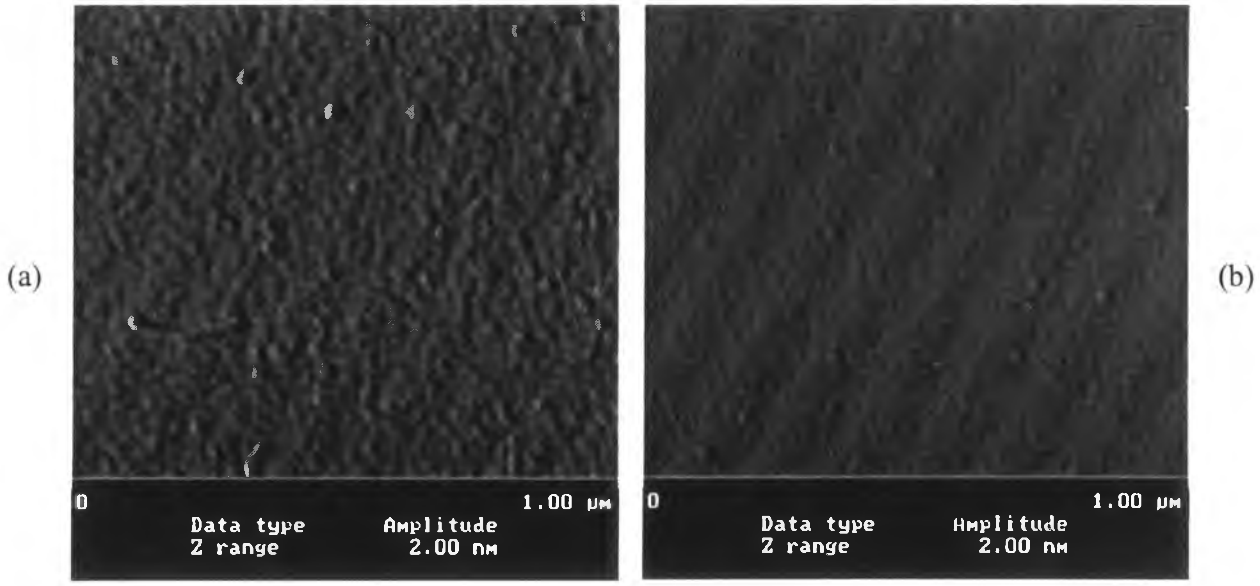

Figure 4.10 AFM amplitude images of titania film from 0.01 µM TIPP at reaction time of 24 hours in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

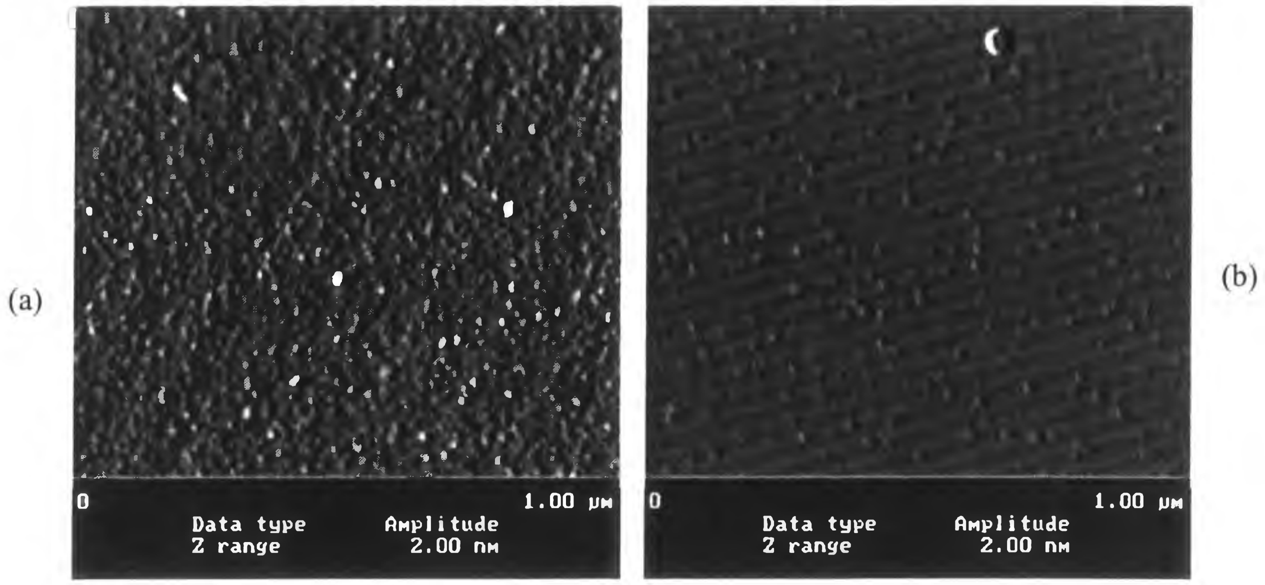

Figure 4.11 AFM amplitude images of titania film from 10 µM TIPP at reaction time of 10 minutes in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

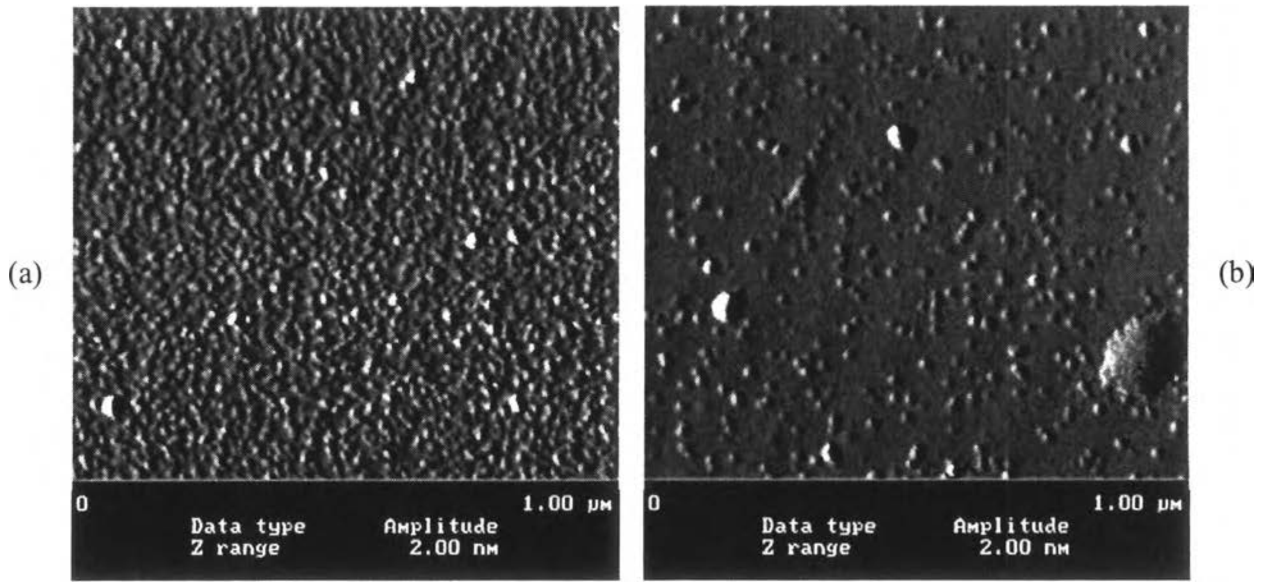

Figure 4.12 AFM amplitude images of titania film from 10 µM TIPP at reaction time of 6 hours in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

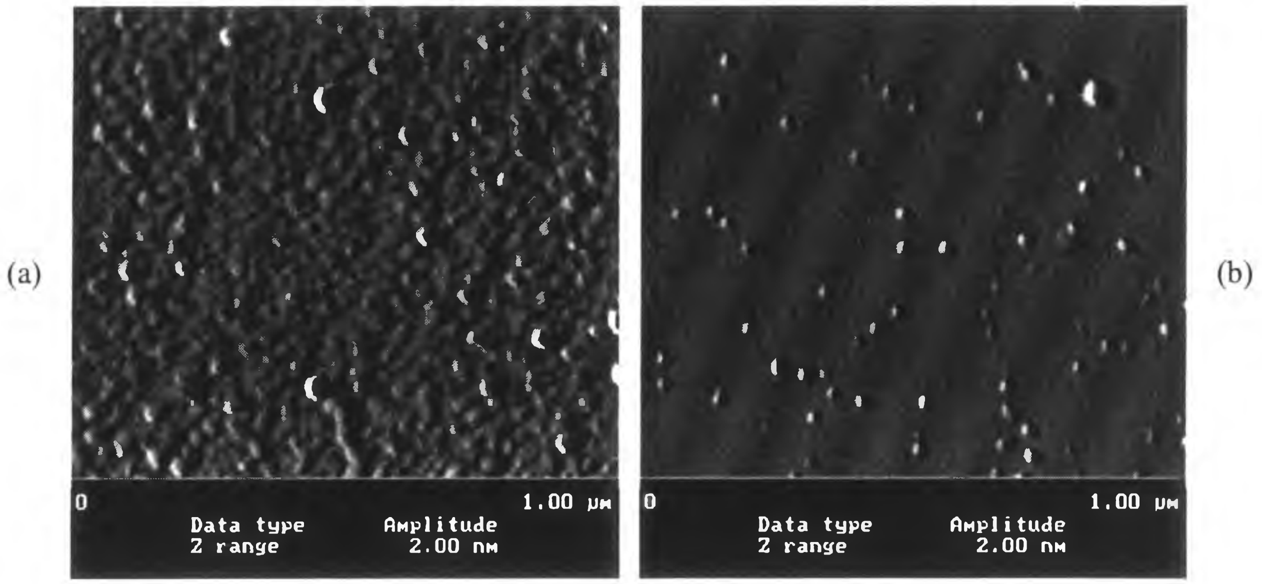

Figure 4.13 AFM amplitude images of titania film from 10 µM TIPP at reaction time of 24 hours in 0.2 mM Triton X-100® (left) and in the absence of surfactant (right). (Scan size 1 µm, z height of 5 nm).

4.4 Effect of Precursor Concentration on Film Topography

The effect of precursor concentration on film morphology was investigated by forming films at precursor concentrations of 0.1 μM, 10 μM and 500 μM. The AFM images in Figures 4.14-4.16 illustrate the effect of TBOT precursor concentration at a reaction time of 24 hours. Figure 4.14, with 0.01 μM precursor, shows that a uniform titania film had been fabricated with nearly all particles approximately 20 nm in diameter. When the concentration of TBOT precursor was increased, the size distribution of titania particles formed became broader. At 500 μM TBOT, two distinct particle sizes may be seen, as shown in Table 4.1

Table 4.1 Titania particle size distribution at various TBOT or TIPP precursor concentrations and reaction times

Sample Details		Fine particle	Large particle
TBOT/TIPP concentration (μM)	Reaction time (hr.)	(20-50 nm)	(larger than 50 nm)
0.01	0.17	✓	-
	6	✓	-
	24	✓	-
10	0.17	✓	-
	6	✓	-
	24	✓	-
500	0.17	✓	✓
	6	✓	✓
	24	✓	✓

The fine particles, which range in size from 20-50 nm in diameter, are found at all precursor concentrations and reaction times. These particles can cover the entire surface and are only found in the systems containing surfactant. The large particles, which are greater than 60 nm in diameter with height approximately 4-20 nm, can be found only at high precursor concentration (500 μM) and at all reaction times. These large particles may have formed in bulk solution because the height of these large particles were much higher than the thickness of admicelle. Moreover, the inconsistency of height of large particles indicated that the formation of large particles were not controlled by surfactant. After large particles were formed in bulk solution, they may then deposit on the substrate, which has been covered with the smaller fine titania particles. This is reasonable since there would be no difference in surface characteristics between the film and the coexisting particles being grown simultaneously. These large particles adhere tightly on the substrate since they cannot be washed away by washing solution which was used to stop reaction by getting rid of the excess precursor and surfactant.

The TIPP precursor, shown in Fig.4.17-4.19, exhibits the same trends. At 0.01 μM TIPP (Fig. 4.17) the surface was covered solely by titania particles ranging from 30-40 nm in diameter. At higher precursor concentrations, the particle size distribution becomes broader and, at 500 μM TIPP, two distinct sizes of titania particles can again be seen. The smaller particles range from 20-50 nm and the larger ones are larger than 50 nm in width (Fig. 4.19).

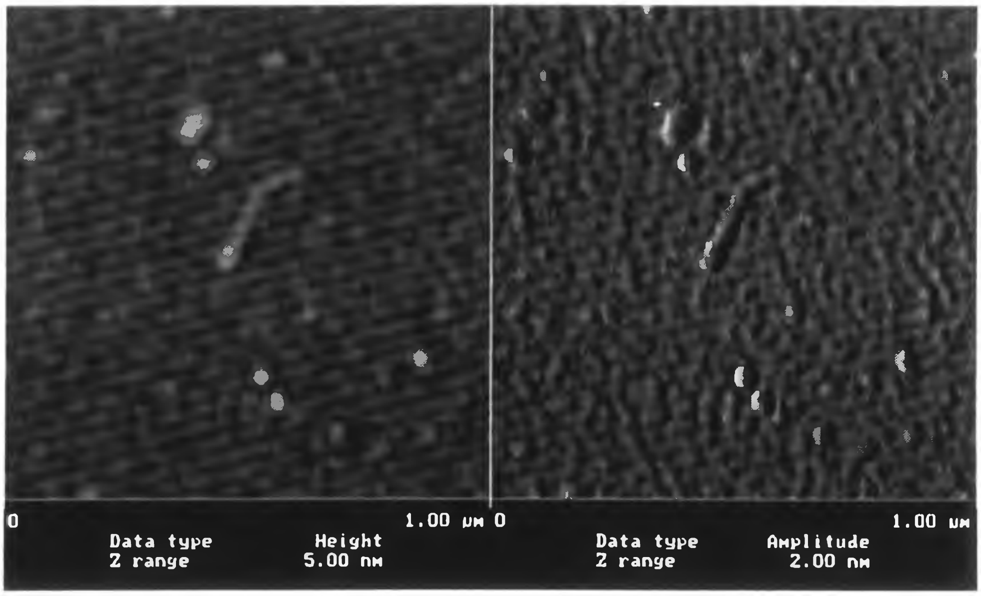

Figure 4.14 AFM topography (left) and amplitude (right) image of titania film at 24 hours reaction time and 0.01 µM TBOT in 0.2 mM Triton X-100®. (Scan size 1 µm x 1 µm, z height 5 nm).

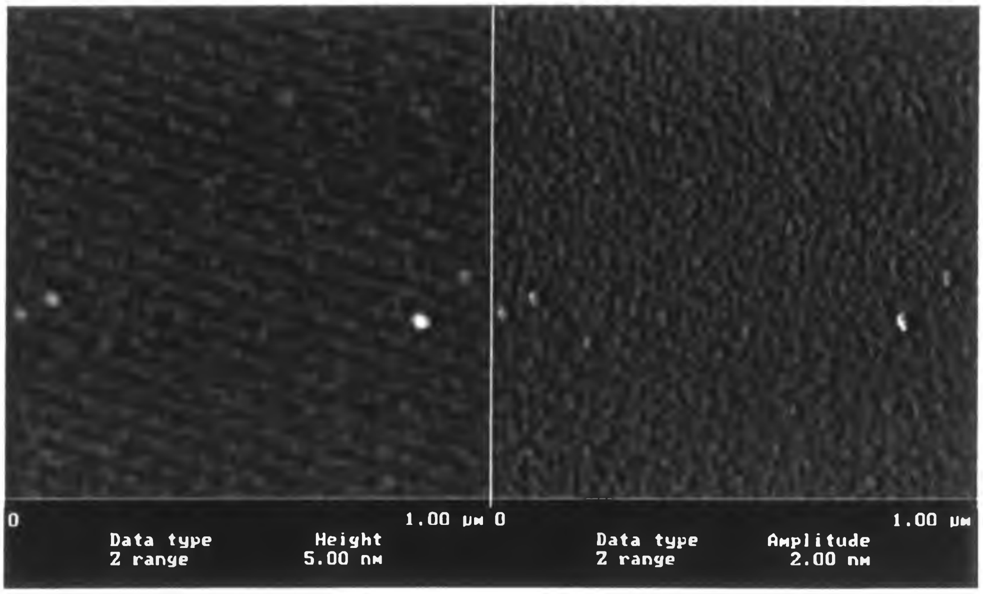

Figure 4.15 AFM topography (left) and amplitude (right) image of titania film at 24 hours reaction time and 10 µM TBOT in 0.2 mM Triton X-100®. (Scan size 1 µm x 1 µm, z height 5 nm).

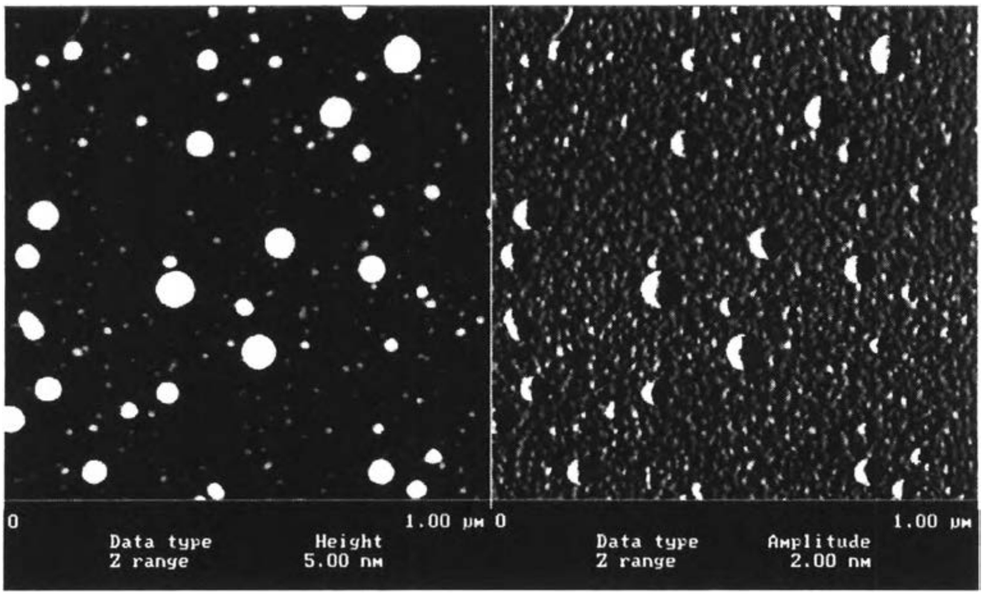

Figure 4.16 AFM topography (left) and amplitude (right) image of titania film at 24 hours reaction time and 500 µM TBOT in 0.2 mM Triton X-100®. (Scan size 1 µm x 1 µm, z height 5 nm).

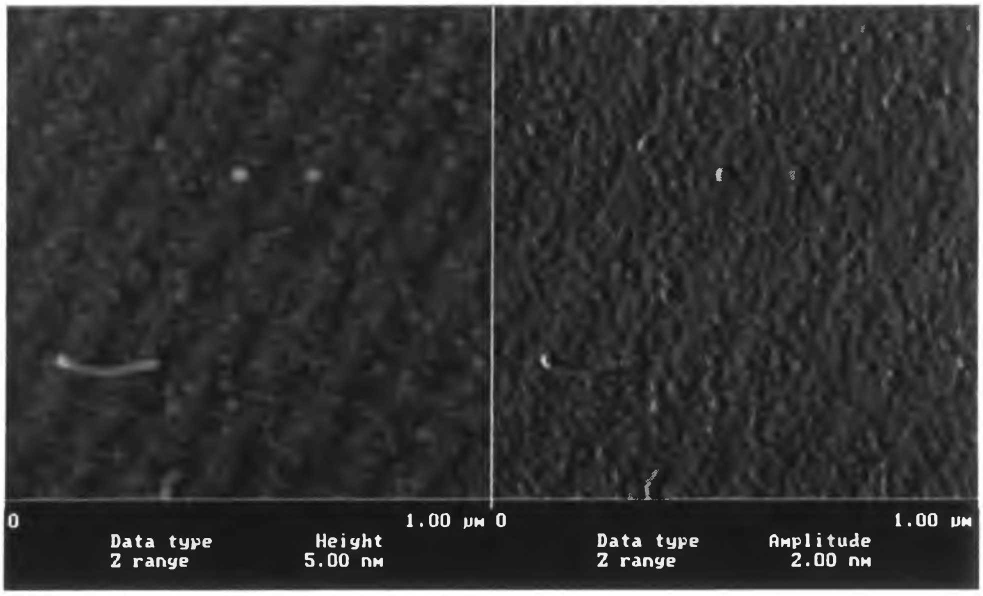

Figure 4.17 AFM topography (left) and amplitude (right) image of titania film at 24 hours reaction time and 0.01 µM TIPP in 0.2 mM Triton X-100®. (Scan size 1 µm x 1 µm, z height 5 nm).

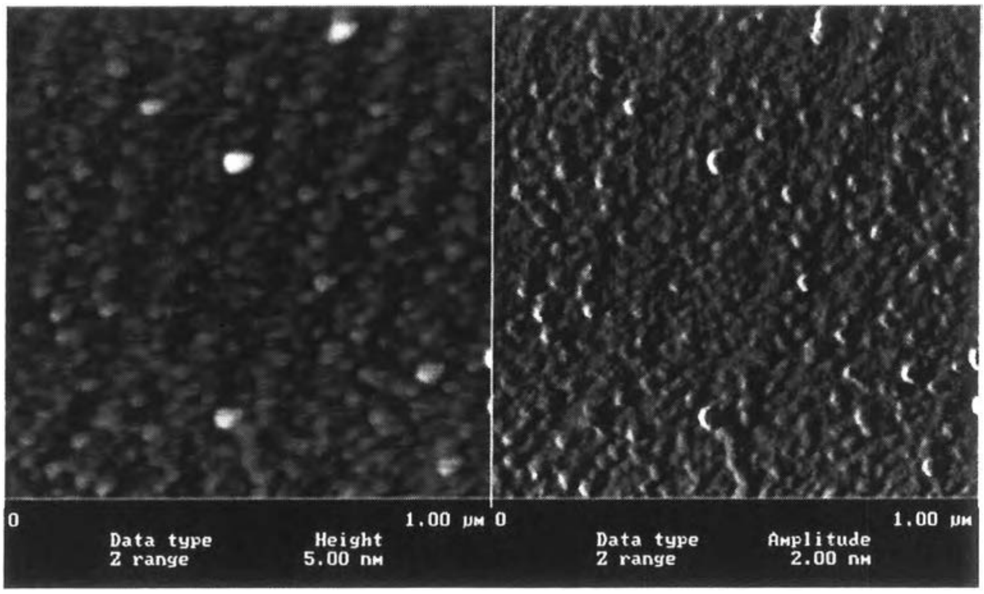

Figure 4.18 AFM topography (left) and amplitude (right) image of titania film at 24 hours reaction time and 10 µM TIPP in 0.2 mM Triton X-100®. (Scan size 1 µm x 1 µm, z height 5 nm).

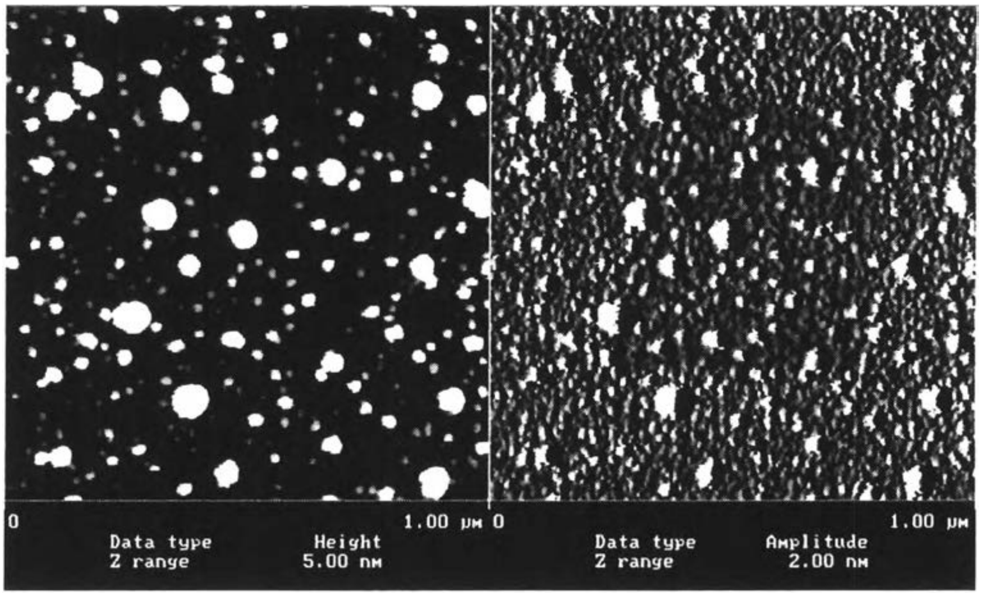

Figure 4.19 AFM topography (left) and amplitude (right) image of titania film at 24 hours reaction time and 500 µM TIPP in 0.2 mM Triton X-100®. (Scan size 1 µm x 1 µm, z height 5 nm).

4.5 Effect of Reaction Time on Film Topography

Figures 4.20-4.22 show the AFM amplitude images of the titania surface film on mica prepared from 10 µM TBOT precursor in 0.2 mM Triton X-100® at varying reaction time of 10 minutes (0.17 hours), 6 hours and 24 hours respectively. It can be seen that the entire surface was already covered by a titania film at 10 min. As the reaction time increased to 6 hours, more complete surface coverage occurred, as can be clearly seen in Fig. 4.21. The titania particles increase in size from approximately 20 nm at a reaction time of 10 minutes to approximately 25 nm at a reaction time of 6 hours. The aggregates are also closer together at the longer reaction time. When the reaction time was increased to 24 hours, titania particle size increased to approximately 30 nm. The increase in particle size indicates that titania film growth on the substrate was not due to the formation of colloidal particles in bulk solution with subsequent deposition on the surface, but rather from in-situ growth (Okudera and Yokogawa, 2001). Thus the titania film forms on the substrate as the precursor is adsobilized into admicelle followed by hydrolysis with water in the admicelle. The same changes with reaction time were seen at the intermediate TBOT concentration (10 μM). Figure 4.23 summarizes the effect of reaction time on titania particles size at TBOT and TIPP concentrations of 0.01 μM and 10 μM, respectively.

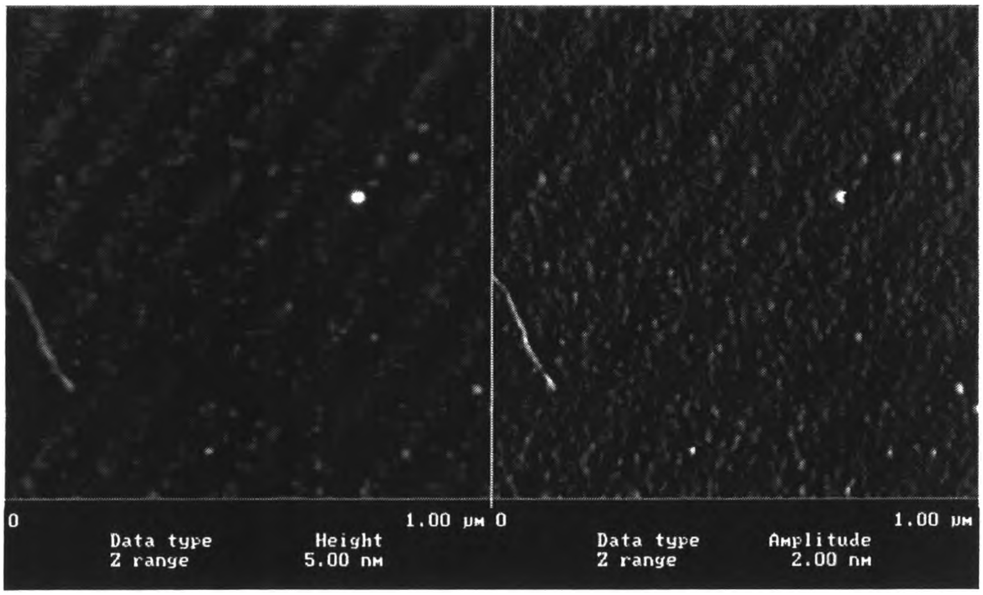

Figure 4.20 AFM topography (left) and amplitude (right) from 10 μM TBOT in 0.2 mM Triton X-100® and a reaction time of 10 minutes. (Scan size 1 μm x 1 μm, z height 5 nm).

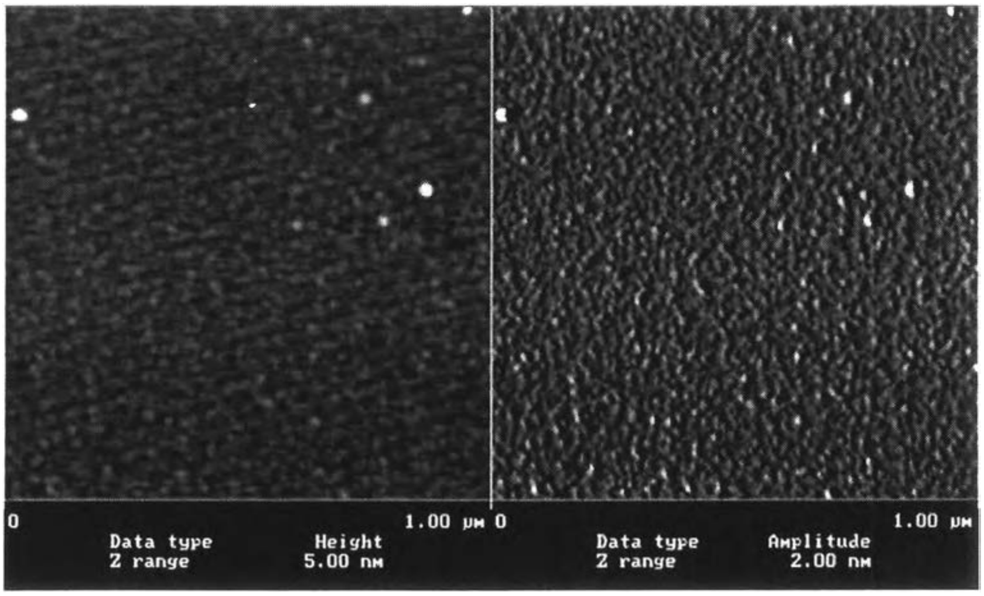

Figure 4.21 AFM topography (left) and amplitude (right) from 10 µM TBOT in 0.2 mM Triton X-100® and a reaction time of 6 hours. (Scan size 1 µm x 1 µm, z height 5 nm).

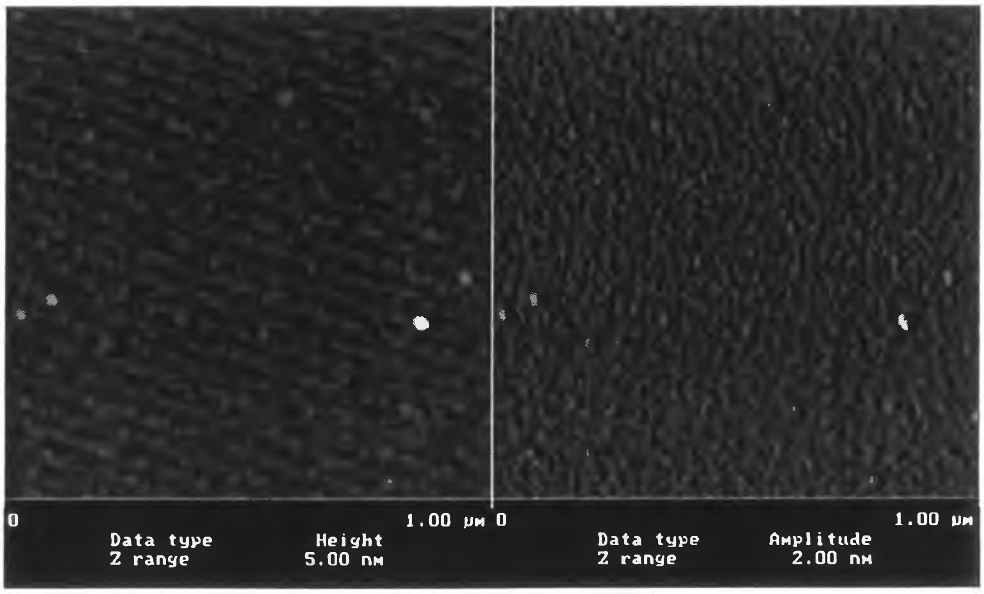

Figure 4.22 AFM topography (left) and amplitude (right) from 10 µM TBOT in 0.2 mM Triton X-100® and a reaction time of 24 hours. (Scan size 1 µm x 1 µm, z height 5 nm).

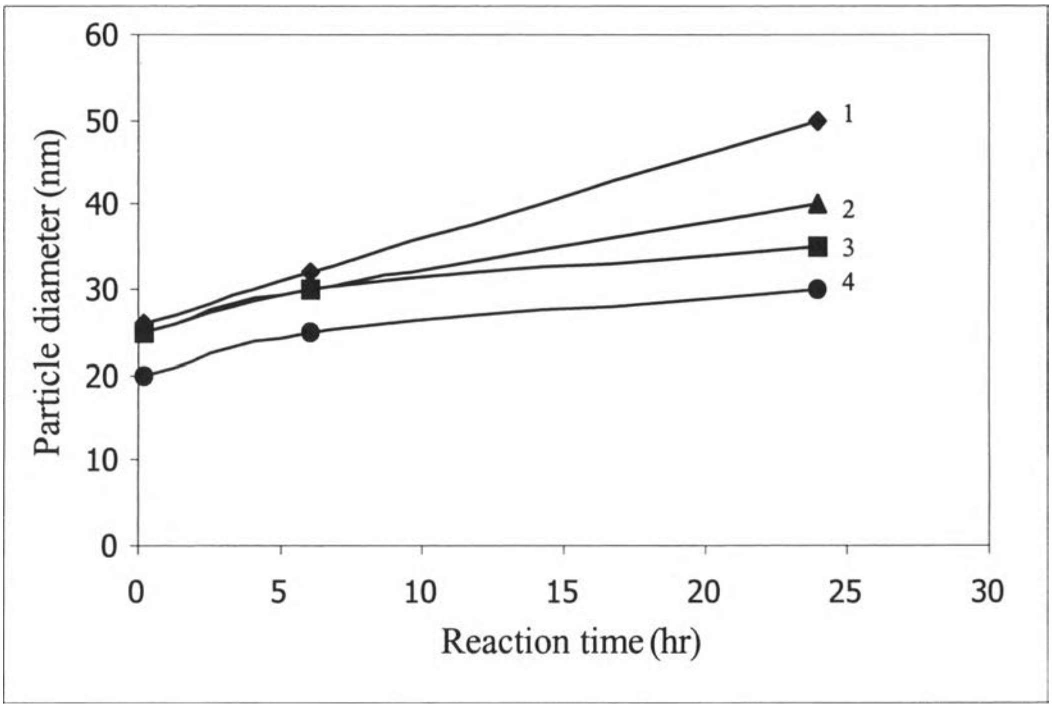

Figure 4.23 The effect of reaction time on titania particle size. Curve 1 represents 10 μM TIPP precursor, Curve 2 0.01 μM TIPP precursor, Curve 3 10 μM TBOT precursor and Curve 4 0.01 μM TBOT precursor.

The data in Figure 4.23 again illustrate that TIPP produces larger titania particles than TBOT. Since TIPP has a higher hydrolysis rate than TBOT (Falaras and Xagas, 2002) TIPP has a lower induction time than TBOT. Since induction time is a strong inverse function of average growth rate and nucleation rate (Hartel and Berglund, 1986) TIPP should provide a faster growth rate and nucleation rate than TBOT.

Samples prepared with 500 μM TBOT precursor do not show the effect of reaction time. At this concentration, the precursor has already formed large aggregates at 10 minutes reaction time which persists at all longer times.

Systems formed from the TIPP precursor exhibit the same patterns as can be seen in Figure 4.24-Figure 4.26.

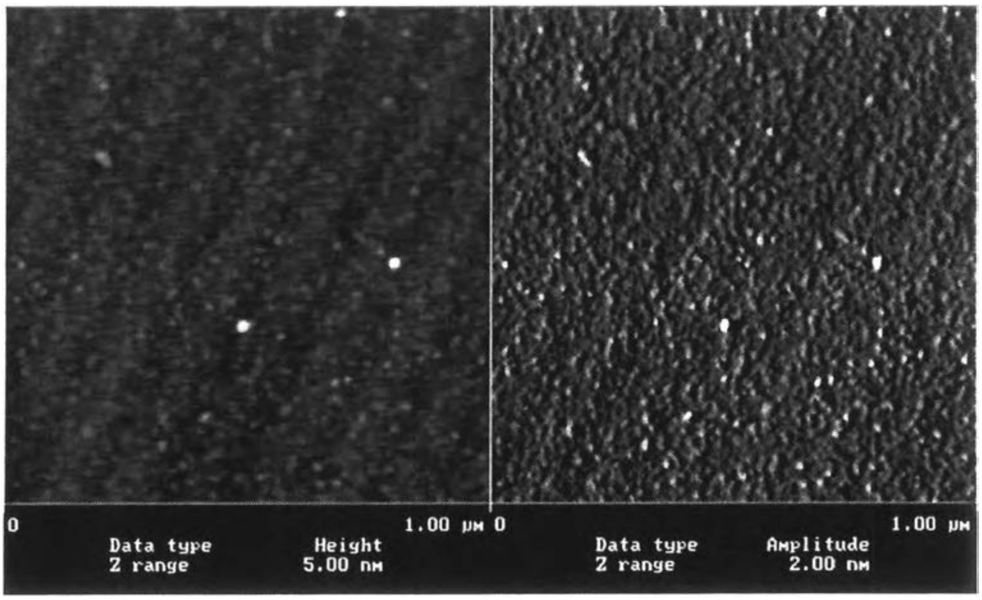

Figure 4.24 AFM topography (left) and amplitude (right) from 10 µM TIPP in 0.2 mM Triton X-100® and a reaction time of 10 minutes. (Scan size 1 µm x 1 µm, z height 5 nm).

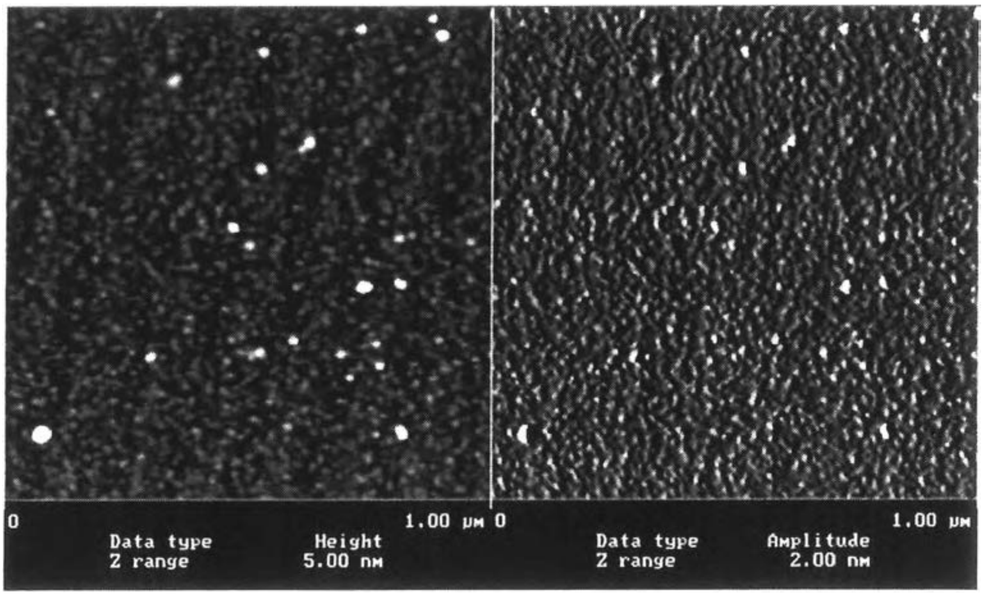

Figure 4.25 AFM topography (left) and amplitude (right) from 10 µM TIPP in 0.2 mM Triton X-100® and a reaction time of 6 hours. (Scan size 1 µm x 1 µm, z height 5 nm).

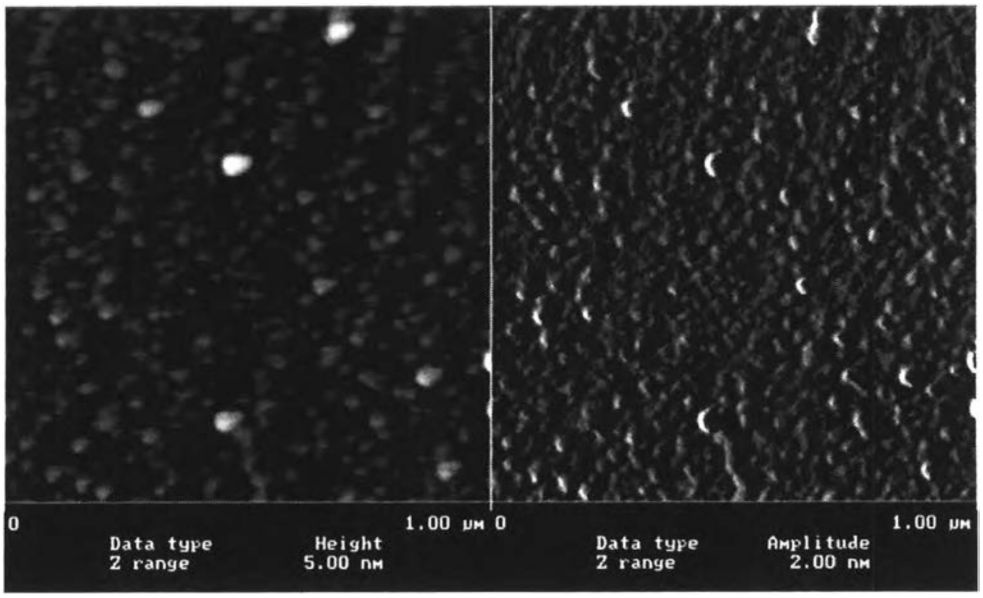

Figure 4.26 AFM topography (left) and amplitude (right) from 10 μM TIPP in 0.2 mM Triton X-100® and a reaction time of 24 hours. (Scan size 1 μm x 1 μm, z height 5 nm).