

## CHAPTER VII

### SYNTHESIS AND CHARACTERIZATION OF CNT-SILATRANE HYBRID MATERIAL AND SILICA NANOTUBE

#### 7.1 Abstract

Use of benzyl alcohol as a surfactant enables SiO<sub>2</sub> to interact with the hydrophobic surface of pristine CNTs without the need of covalent functionalisation. The quality of the SiO<sub>2</sub> coating is strongly affected by various reaction conditions, including the order of mixing, the presence of benzyl alcohol, and the reaction temperature. Furthermore, the effect of heat treatment on the crystallization of amorphous SiO<sub>2</sub> to cristobalite is discussed in detail. The key achievement of this work is the control of morphology and structure of the cristobalite nanotubes after removal of the CNTs. This process allows the production of the silica structure with a high surface area-to-mass ratio and for desired applications.

**(Key-words:** Hybrid material; Silatrane; Silica nanotube)

#### 7.2 Introduction

Carbon nanotubes (CNTs) are important structural blocks for preparation of hybrid composites with the outstanding optical, electrical, and mechanical properties [1]. Recently, the surface decorations of CNTs with silica nanoparticles are gaining attention as they provide an excellent platform for the development of biosensors as well as for optical, magnetic, and catalytic applications. Surface decoration of CNTs with silica was achieved by a number of methods [2], each of which emphasized on the usefulness of the silica coating as a way to preventing tube-tube contacts. The assembly of silica on CNTs may also provide an interface between living cell and biosensors. The controlled assemblies of silica nanoparticles on CNTs have been reported by many researchers [2,3]. In literature, surface decorations of carbon nanotubes were achieved under strong oxidizing conditions, e.g., refluxing in

concentrated  $\text{HNO}_3$  for the introduction of carboxylic acid groups. Although these strong oxidizing treatments functionalize the CNTs, they introduce defects to the pristine CNTs and thus compromise the electronic and mechanical properties, which is undesirable. In this work, we demonstrate the in situ fabrication of silica nanoparticles on pristine carbon nanotubes via a sol-gel process.

In a traditional sol-gel process, the sol of a given precursor is prepared and some chemical and physical changes (usually hydrolysis and condensation) take place. The sol, grows in size and forms gel [4]. Those primary sol particles can serve as the nuclei or seeds for further particle growth. Based on this feature, if heterogeneous fine objects were introduced into the sol-gel systems to serve as nuclei or seeds for the further particle growth, those heterogeneous seeds would be enwrapped and become the bulk of particles. This mechanism has been widely used by researchers to produce heterophase nanoparticles. Moreover, this process provides particularly good control from the molecular precursor to the final product, as well as giving high purity and homogeneity [5, 6]. In our study, carbon nanotubes were introduced into the sol-gel system as nuclei for the further growth of silica nanoparticles.

Generally, a large specific surface area of  $\text{SiO}_2$  is crucial to achieve high catalytic activities as well as good dispersions of adsorbed metals and metal-organic compounds. Hence, the fabrication of this material in nanoscale morphology is of considerable interest. Nanotubes and nanofibrils have a particular advantage in the way that they enable three-dimensional mechanically coherent architectures, providing high-surface area for catalysis applications [7-10].

In recent years, there has been considerable progress in the production of novel functional materials by coupling  $\text{SiO}_2$  with other inorganic/organic materials [11-15]. For instance, Lopez *et al.* [11] reported that novel sol-gel silica coatings reinforced with multi-walled carbon nanotubes (MWCNTs) have been prepared using the organic sol-gel route. The sol suspension was prepared from tetraethylorthosilicate (TEOS), phosphoric acid, and distilled water in the molar ratio of 1:0.01:11. Su *et al.* [14] revealed that alkali salts of poly(2-acrylamido-2-methylpropane sulfonate) (PAMPS)- $\text{SiO}_2$  and single-walled carbon nanotubes (SWCNTs)- $\text{SiO}_2$ -PAMPS (poly(2-acrylamido-2-methylpropane sulfonate)) could be

used as composite materials to make a humidity sensor. The SiO<sub>2</sub>-PAMPS composite was prepared by copolymerization of hydrolytic TEOS and monomeric AMPS [16]. The results indicated that the H<sup>+</sup> form of the PAMPS-SiO<sub>2</sub> composite film had the highest electrical conductance.

It is evident that all of these previous reports utilized TEOS as the source of silica. As TEOS is highly sensitive to moisture, handling and controlling the property of the resulting sol suspension over the course of the fabrication process could be problematic. The use of another silica source that possesses greater stability towards moisture could alleviate such obstacles. Silatrane is one such structure that possesses a very good moisture stability property [17]. The present manuscript is, therefore, aimed at exploring a non-destructive, simple process to coat CNTs with SiO<sub>2</sub> by using silatrane as precursor and benzyl alcohol as surfactant. The  $\pi$ - $\pi$  interactions of its benzene ring enable the use of pristine CNTs without the need of covalent functionalisation and thus provide an interesting alternative for the synthesis of various other CNT-inorganic hybrid materials. However, a detailed understanding of the coating process and of subsequent heat treatments is crucial in order to control the morphology and structure of the SiO<sub>2</sub> coating, to enhance the specific surface area, and to synthesize the ideal CNT-SiO<sub>2</sub> hybrid materials for the desired electrical, catalytic and sensor applications.

## **7.4 Experimental section**

### **7.4.1 Preparation of Carbon Nanotubes**

Multi-walled carbon nanotubes (CNTs) were grown via a modified CVD process in a tube furnace reactor using ferrocene as the catalyst precursor and toluene as the feedstock. These reactants were vaporized into a hydrogen/argon atmosphere at 760°C. Iron particles were produced by the decomposition from the ferrocene, which then acted as catalysts for the carbon nanotubes growth. The average outer diameter of the nanotubes was 70 nm, the length was between 20 and 30  $\mu$ m. However both dimensions can be controlled by the reaction conditions [18].

#### 7.4.2 Preparation of Silatrane

The method for the preparation of silatrane was described previously [17]. Briefly, a mixture of 6 g of silica (0.10 mol; amorphous precipitates; 100% purity; Sigma-Aldrich, Steinheim, Germany) and 18.6 g of triethanolamine (TEA, 0.12 mol; 98% purity; Merck (NJ)) was stirred vigorously in an excess amount of ethylene glycol (EG, 100 mL; 100% purity; Merck, USA) and heated to 200°C for 10 h. The resulting solution was placed *in vacuo* to remove unreacted EG, resulting in a crude precipitate. The crude white solid product was then washed with acetonitrile (99% purity; Labscan (Asia), Thailand), dried in a vacuum desiccator, and characterized using fourier-transformed infrared spectroscopy (FT-IR) and thermo gravimetric analysis (TGA).

FT-IR: 3422  $\text{cm}^{-1}$  ( $\nu$ O-H), 2986–2861  $\text{cm}^{-1}$  ( $\nu$ C-H), 2697  $\text{cm}^{-1}$  ( $\nu$ N-Si), 1459–1445  $\text{cm}^{-1}$  ( $\nu$ C-H), 1351  $\text{cm}^{-1}$  ( $\nu$ C-N), 1082  $\text{cm}^{-1}$  ( $\nu$ Si-O-C), 579  $\text{cm}^{-1}$  ( $\nu$ N-Si) [12]. TGA: a majority of weight loss occurred at  $\sim 390$  °C with a ceramic yield of  $\sim 19\%$ – $23\%$ .

#### 7.4.3 Preparation of CNT-Silatrane Hybrid Material and Silica Nanotube

The CNTs were coated *via* a sol-gel process, followed by hydrothermal treatments in argon up to temperatures of 1100°C. Silatrane was used as the silica precursor, ethanol as solvent and water to start gelation. Benzyl alcohol (BA) was chosen to study as a surfactant due to its ability to keep the particle size small [19-21], and to provide better interaction with the hydrophobic CNTs [19].

In a typical experiment, the CNTs were dispersed in ethanol with the aid of ultrasonication for 10 min. BA and water were then added into the solution and provided ultrasonication for another 5 minutes. Silatrane was dissolved in water and slowly dropped into the CNT suspension, so that the final molar ratio for a reaction mixture of silatrane: BA: ethanol: water was 1:4:86:33. After 12 h of stirring at room temperature, the sample was put in autoclave for 24 h then the precipitates were vacuum-filtered, washed in distilled water and dried at room temperature.

For the preparation of the CNT-Silatrane hybrid material, the following parameters were varied to investigate their effect on the morphological appearance of the obtained nanotubes: the effect of benzyl alcohol (BA) (i.e., with

BA vs without BA using the condition; Si: BA: EtOH: H<sub>2</sub>O of 1: x: 86: 33 where x = 0 or 4), the synthesis method (i.e., *in-situ* process vs *ex-situ* process over a fixed reaction condition; Si:BA:EtOH:H<sub>2</sub>O of 1:4:86:33), and the reaction temperature (i.e., room temperature to 150°C using the in-situ process and a fixed reaction condition; Si:BA:EtOH:H<sub>2</sub>O of 1:4:86:33). For these studies, all samples were obtained by combining both methods, involving a) filtering the precipitates to remove any unreacted precursor as well as most of solvents, but not to complete dryness, and b) slowly drying the remaining wet sample in a Petri dish at room temperature before further characterization.

The CNT-Silatrane hybrid materials that were used to investigate the effect of calcinations temperature on the morphological appearance, properties, and structures of the postcalcined silica nanotubes were prepared from a solution with a condition of Si:BA:EtOH:H<sub>2</sub>O of 1:4:86:33 using *in-situ* process, aged at room temperature 12 h and heated in autoclave 100°C for 24 h. The hybrid materials were left exposed to ambient moisture (ca. 55% ± 2% RH) for 24 h and subsequently subjected to calcination in a furnace where flowing argon with exclusion of oxygen for 4 h at a temperature ranging 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.

#### 7.4.4 Characterization

The morphological appearance and size of the CNT-Silatrane hybrid material and the as calcined silica nanotube were studied by high resolution scanning electron microscopy (SEM), using a JEOL 6340F FEG-SEM. Functional groups of the materials were observed by FT IR over the wave number range of 400–4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> using the KBr pellet method. Specifically, each sample was thoroughly crushed, mixed with KBr at an approximate weight ratio between the sample and KBr of 1:100, and pressed into a thin pellet. The samples were characterized with energy-dispersive X-ray spectroscopy (EDS) using JEOL JSM-580LV, and with X-ray diffraction (XRD) using a Bruker D8 Advance with Cu-Kα radiation, 40 kV and 40 mA, λ = 1.5406°Å. WAXD was used to investigate the

microstructure of the as-calcined silica nanotube. Lastly, the BET surface area of both the pre- and the postcalcined hybrid material was measured using a Quantasorb JR Autosorp-1 gas sorption system (Quantachrome, Boynton Beach, FL). All of the samples were degassed at 250°C before measurement.

## 7.5 Results and Discussion

### 7.5.1 CNT-Silatrane Hybrid Materials

#### 7.5.1.1 *Effect of surfactant*

Without benzyl alcohol (BA), the SiO<sub>2</sub> coating on pristine CNTs (as synthesised) was highly non-uniform in thickness, with much of the oxide being present as particles (Figure 7.1a). This can be explained by the fact that pristine CNTs are typically hydrophobic and thus need to be functionalised with hydrophilic organic groups to provide attractive interaction with the sol. i.e titanium, silica, zinc sol etc. [22-23]. Two major challenges remain: (1) the improvement of the interface between SiO<sub>2</sub> and the CNT surface, and (2) the control of size and morphology of the SiO<sub>2</sub> particles during crystallization. In this research we present an alternative route that enables SiO<sub>2</sub> to uniformly coat pristine CNTs without the need for covalent functionalization by adding benzyl alcohol (BA) as surfactant (Figure 7.1b). Furthermore, the use of BA provides an excellent tool to control the size of the deposited SiO<sub>2</sub> particles upon crystallization.

Benzyl alcohol enhances the coating of pristine CNTs with SiO<sub>2</sub>. Figure 7.1b shows that the SiO<sub>2</sub> coating was indeed very uniform in thickness with a smooth surface. Presumably, BA acts as a weak surfactant and enhances the dispersion of pristine CNTs in the reaction solution, which helps to achieve a uniform distribution of SiO<sub>2</sub>. In absence of BA, SiO<sub>2</sub> precipitated in form of large clusters, and only few CNTs were coated. By adding a small amount of BA more CNTs were coated and fewer SiO<sub>2</sub> particles remained in solution. From these results we assume that the SiO<sub>2</sub> coating is not formed via a Si–O–C bond, as is the case for acid-treated CNTs [19], but rather via  $\pi$ - $\pi$  interaction between the aromatic CNT surface and the benzyl ring of BA [24]. Presumably, BA adsorbs at the CNTs'

surface via  $\pi$ - $\pi$  interactions with its benzene ring, while at the same time providing hydrophilic hydroxyl groups for the hydrolysis of the silatrane precursor. Hence, despite their hydrophobic surface, pristine CNTs can indeed be used as a template without the need of covalent functionalization by simply adding a small amount of BA to the reaction mixture [19]. Moreover, the hydroxyl groups of BA would then coordinate with the silica and may further induce condensation to form a Si–O–Si network via the so-called “benzyl alcohol route” [20, 21]. Finally, the dispersion of pristine CNTs could be significantly improved with the addition of BA, thus also enabling the coating of individual CNTs with SiO<sub>2</sub>. The conformation of two BA molecules on the CNT surface is shown in Scheme 1.

#### 7.5.1.2 Effect of synthesis method

To investigate the effect of the synthesis route on the morphological appearance of the obtained hybrid material, the method was compared between *in-situ* and *ex-situ* process. The CNT-silatrane hybrid solutions were prepared at fixed the condition; Si:BA:EtOH:H<sub>2</sub>O of 1:4:86:33, kept stirring at room temperature 12 h and heated in autoclave 100°C for 24 h. Figure 7.2 (a and b) show representative SEM images of the CNT-silatrane hybrid materials. The sample shown in Figure 7.2a was produced by adding a solution of silatrane in water slowly to a suspension of pristine CNTs in ethanol, water and BA, so that the silica precursor could react directly at the surface of the CNTs (*in-situ* process). For comparison, a suspension of CNTs in ethanol was added to a readily prepared solution of silatrane, BA, ethanol and water (*ex-situ* process). In contrast to the uniform gray color of the collected material in the previous experiment, the resulting material appeared speckled with white and black spots. SEM revealed the presence of uncoated carbon nanotubes mixed with large SiO<sub>2</sub> particles (Figure 7.2b). This is in agreement with Yan *et al.*, who observed that dispersing acid-functionalised SWCNTs into an aged TiO<sub>2</sub> sol (*ex-situ*) resulted in unstable dispersions and uncoated CNTs. [23] Hence, the best coating was obtained when the silica precursor reacted in situ with the hydroxyl groups of the BA molecules, adsorbed at the CNT surface, thus confirming our previous results.

#### 7.5.1.3 Effect of reaction temperature

To investigate the effect of the reaction temperature on the morphological appearance of the obtained hybrid materials, the temperature of the reaction was varied at room temperature, 60°, 100° and 150°C. The synthesis formula is Si:BA:EtOH:H<sub>2</sub>O of 1:4:86:32. The solution was kept stirring at room temperature 12 h and heated in autoclave for 24 h at x°C. Representative SEM images of the obtained hybrid are shown in Figure 7.3. At room temperature, the large particle size of silica is precipitated with lower conversion to silica coating on CNTs' surface and presented a large amount of cluster. When the temperature increased to 100°C (see Figure 7.3 b and c), the particle size became smaller and provided uniform coating in thickness along the tubes until the temperature reached to 150°C (Figure 7.3d). At this temperature, the gelation was occurred because the hydrolysis and condensation reactions of silatrane cause the polymerization to form the network [25]. Moreover, increase temperature, increase hydration and cross-link density leading to a more open and stronger gel network resulting in size of particles was increased and presented non uniform coating again [26].

## 7.5.2 Preparation of Silica Nanotube

### 7.5.2.1 *Effect of Calcination Temperature*

The CNT-Silatrane hybrid materials used to investigate the effect of calcination temperature on the morphological appearance, properties, and structures of the postcalcined silica nanotubes were prepared from a solution with a condition of Si:BA:EtOH:H<sub>2</sub>O of 1:4:86:33 using *in-situ* process, aged at room temperature 12 h and heated in autoclave 100°C for 24 h.

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removed prior to the argon heat treatment, then the tube morphology of the cristobalite is lost.

The final step in the process was the oxidation in air at 550°C for 2 h to remove the carbon nanotubes. The oxidation temperature was carefully selected to be sufficiently high to oxidize the tubes but not so high as to destroy the cristobalite nanotube morphology. These silica nanotubes were identified with XRD (Figure 7.6 (c-e)) to be 100 % cristobalite with no graphitic present. Interestingly, the temperature needed for this complete removal of carbon is significantly lower than that required to oxidize a pure nanotube sample (650°C) [19]. Eder *et al.* reported that the area underneath the TGA peaks, which corresponds to the heat evolved during combustion of carbon in air, was calculated to be 115 kJ mol<sup>-1</sup> C for the coated CNTs and 180 kJ mol<sup>-1</sup> C for the uncoated CNTs. Hence, the particle coating promoted the formation of C–O bond to produce CO or CO<sub>2</sub> using lattice oxygen, similar to the Mars–van Krevelen mechanism [27], thus explaining the observed decrease in oxidation temperature.

Figure 7.4 shows selected SEM images of the pristine CNT, the CNT-silatrane hybrid material and the silica nanotubes that had been calcined in argon with exclusion of oxygen for 4 h at temperature 700°C and followed by calcination in air at 550°C for 2 h. The pristine CNTs (see Figure 7.4a), grown by CVD with an average diameter of approximately 70 nm and lengths of up to 50 mm, were smooth with diameters of 210 ± 71 nm. Figure 7.4b shows typical SEM image for the CNT-silatrane hybrid and reveal that the CNTs were indeed covered completely by a layer of small particles, uniform in size (14-25 nm) and regular in shape. Figure 7.4c shows the nanotube morphology in the cristobalite phase after removal of the carbon nanotube template after calcinations at 700°C. The nanotubes were typically several microns long, with the length being limited to some extent by the cracking of the amorphous silica coating.

The chemical integrities of the hybrid and the post calcined products were further investigated by FT-IR, as graphically shown in Figure 7.5. According to the FT-IR spectrum, the postcalcined hybrid exhibited an absorption peak at ca. 1100 cm<sup>-1</sup>, which is much more pronounced than that observed in the

spectrum of the precalcined, hybrid materials and they attributed to the formation of either Si–O–C or Si–O–Si bonds [28]. In addition to this absorption peak, the peaks at ca. 485 and 795  $\text{cm}^{-1}$ , which were absent in the spectrum of the precalcined, CNT-Silatrane hybrid, were clearly visible in the spectra of the as calcined nanotube. Emphatically, these three absorption peaks that are associated with the Si–O–Si bonds [29] became more evident in the spectra of the nanotube that had been calcined at temperatures  $\geq 700^\circ\text{C}$ . Interestingly and surprisingly, an additional absorption peak at ca. 623  $\text{cm}^{-1}$ , corresponding to the pseudolattice vibration of  $\beta$ -cristobalite [30]. As a conclusion, the CNT-silatrane hybrid was successfully transformed into  $\text{SiO}_2$  nanotube.

The structural organization of the postcalcined nanotube was further investigated with WAXD, and the results are shown in Figure 7.6. Only one broad scattering peak, centering at  $\sim 21.9^\circ$ , was observed for the fibers that had been calcined at  $550^\circ\text{C}$ , which could be an indication of the amorphous nature of the obtained silica nanotubes at such a temperature. Apparently, phase transformation from amorphous silica to cristobalite takes place at a temperature ranging from  $1000$ – $1400^\circ\text{C}$  [31–34]. Here, the transformation to cristobalite occurred at a much lower temperature, i.e.,  $\sim 700^\circ\text{C}$ . Interestingly at calcinations temperatures  $> 550^\circ\text{C}$ , four major diffraction peaks, characteristic of a crystalline nature of some sorts, were observed at the  $2\theta$  angles of  $21.9^\circ$ ,  $28.3^\circ$ ,  $31.2^\circ$ , and  $36.0^\circ$ . While the peaks at  $21.9^\circ$  and  $36.0^\circ$  could be both assigned to the (101) and (200) planes of  $\alpha$ -cristobalite [JCPDS 76-938] and the (111) and (220) planes of  $\beta$ -cristobalite [33,35], the peaks at  $28.3^\circ$  and  $31.2^\circ$  could be assigned to reflection planes of  $\alpha$ -cristobalite [33]. In general,  $\beta$ -Cristobalite was found to exist after amorphous silica powder had been calcined at temperatures  $\geq 1100^\circ\text{C}$ , with evidence of its a polymorph being observed when the amorphous silica powder was calcined at temperatures  $\geq 1350^\circ\text{C}$  [33]. Based on the evidence reported in the literature [33,35] and the WAXD results obtained in this work, it is proposed that the use of silatrane as the source of silica favors the formation of cristobalite.

EDS was carried out to probe the composition of the attached nanoparticles. It confirmed the presences of Si, O, C on the surface of the nanotubes

and provides Si: O: C ratio of 23.4: 28.34: 47.05. A closer look with XRD of pre-calcined hybrid reveals the broad scattering peak, centering at  $\sim 21.9^\circ$ , and the 002 diffraction peak of carbon ( $2\theta = 26.4^\circ$ ), which is in good agreement with the observation by SEM. Therefore, the combined and results from SEM, EDS and XRD confirm that the coatings are indeed composed of silica. Furthermore, the use of benzyl alcohol has enabled the synthesis of CNT-hybrids with maximum interfacial area and excellent control of morphology.

Lastly, the BET surface area of both the CNT-silatrane hybrid and the post-calcined nanotube was also determined. The surface area of the pre-calcined CNT-Silatrane hybrid was determined to be about  $33 \text{ m}^2\cdot\text{g}^{-1}$ , while those of the as-calcined nanotubes at  $550^\circ$ ,  $700^\circ$ ,  $900^\circ$ , and  $1100^\circ\text{C}$  were 421, 325, 242 and  $127 \text{ m}^2/\text{g}$ , respectively. The observed decrease in the BET surface area with increasing calcinations temperature is likely a result of the increase in the grain size of cristobalite crystals. Recently, Eder *et al.* reported that the rutile nanotube was calcined at  $900^\circ\text{C}$  obtained surface area  $70 \text{ m}^2\cdot\text{g}^{-1}$  while the BET surface area of anatase nanoparticles was only  $11.5 \text{ m}^2\cdot\text{g}^{-1}$  [36]. Moreover, Wongkasemjit *et al.* [37] found that the BET surface area of ultrafine silica fibers which was prepared from the e-spun PVA/silatrane composite fibers and calcined at  $700^\circ\text{C}$  was  $198 \text{ m}^2\cdot\text{g}^{-1}$ . Based on the previous reported in the literature [36-37] and the BET results obtained in this work, it is believed that the nanotubes will be able to produced architectures that can provide full access to their surface area.

## 7.6 Conclusions

The CNT-SiO<sub>2</sub> hybrid material was successfully prepared using silatrane, as inexpensive and moisture stable precursor and BA as surfactant. The  $\pi$ - $\pi$  interactions of its benzene ring enable the use of pristine CNTs without the need of covalent functionalization and thus provide an interesting alternative for the synthesis of various CNT-inorganic hybrid materials. By just adding a small amount of BA, very small and uniform cristobalite nanocrystals with very high specific surface areas ( $127$ – $421 \text{ m}^2\cdot\text{g}^{-1}$ ) were produced. In addition, pure silica nanotubes were successfully

prepared for the first time using a carbon nanotube template for the deposition of an amorphous silica coating, and subsequently to support it during the phase transformation to cristobalite. The EDS analysis confirmed the presence of Si on the surface of CNTs and revealed the advantage of using BA which has enabled the synthesis of CNT-hybrids with maximum interfacial area and excellent control of morphology. Both FT-IR and WAXD results confirmed that the microstructure of the nanotubes, obtained from the hybrid and calcined at temperatures  $\geq 700^{\circ}\text{C}$ , were composed predominately of cristobalite, a high-temperature polymorph of crystalline silica.

### 7.7 Acknowledgements

This research work was supported by the Center for Petroleum, Petrochemicals and Advanced Materials (C-PPAM), the Ratchadapisake Sompote Fund, the Thailand Research Fund (TRF); and D. Eder is grateful to the Austrian Academy of Science (APART - Austrian Program for Advanced Research and Technology) for financial support.

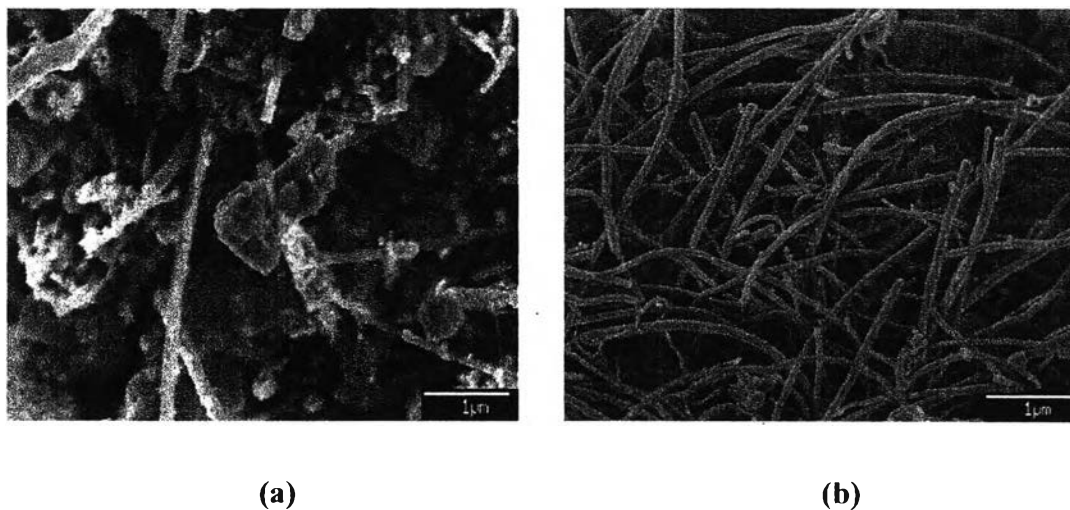
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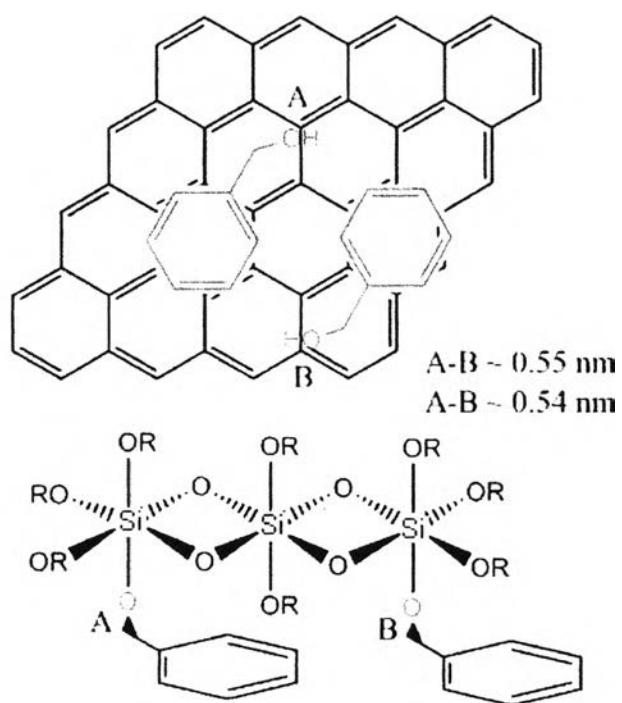
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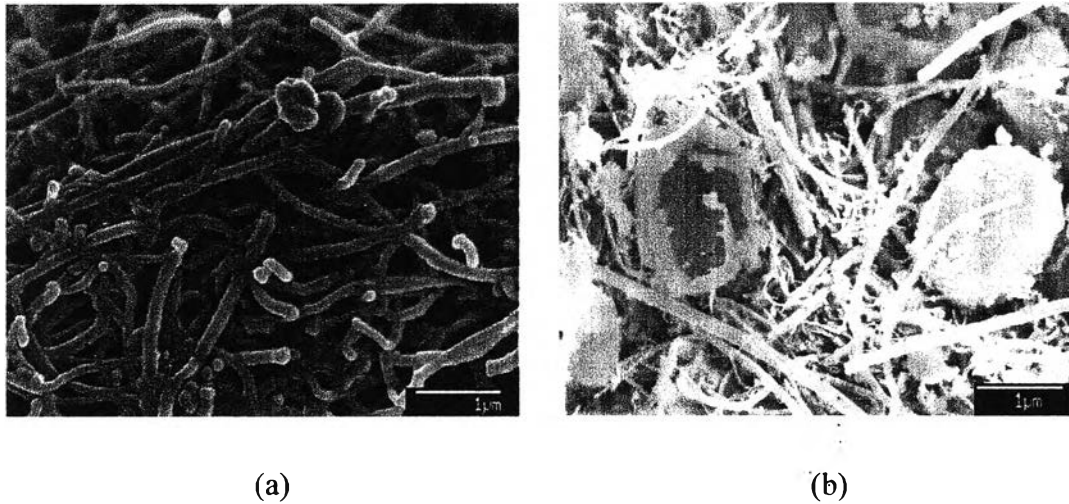


**Figure 7.1** Selected SEM images illustrating the morphological appearance of pristine CNTs coated with silatrane using an in-situ sol-gel process with a standard reaction mixture Si: BA: ethanol: water of 1: x: 86: 33, heated in autoclave 100°C for 24 h and after vacuum filtration: (a) without BA ( $x = 0$ ) and (b) with BA ( $x = 4$ ).

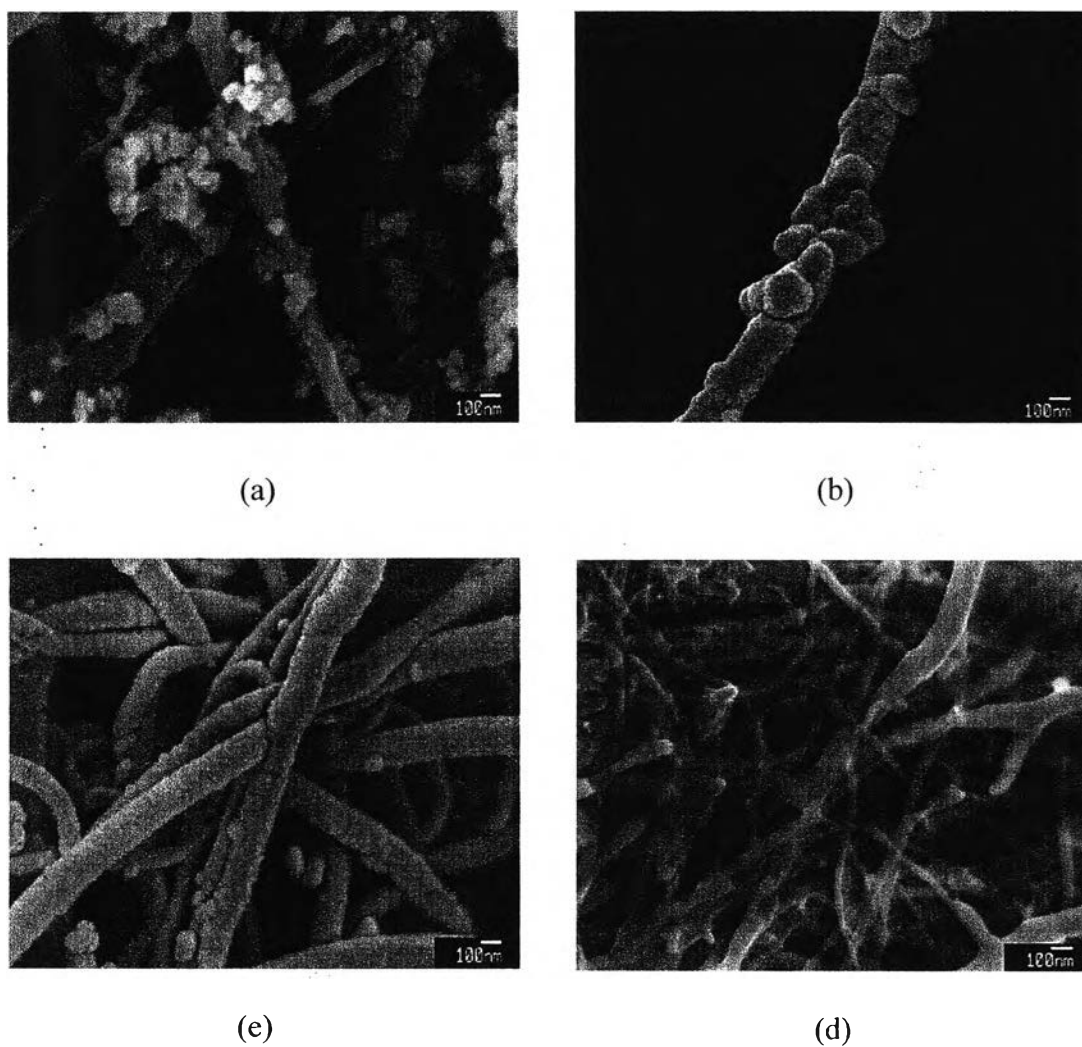




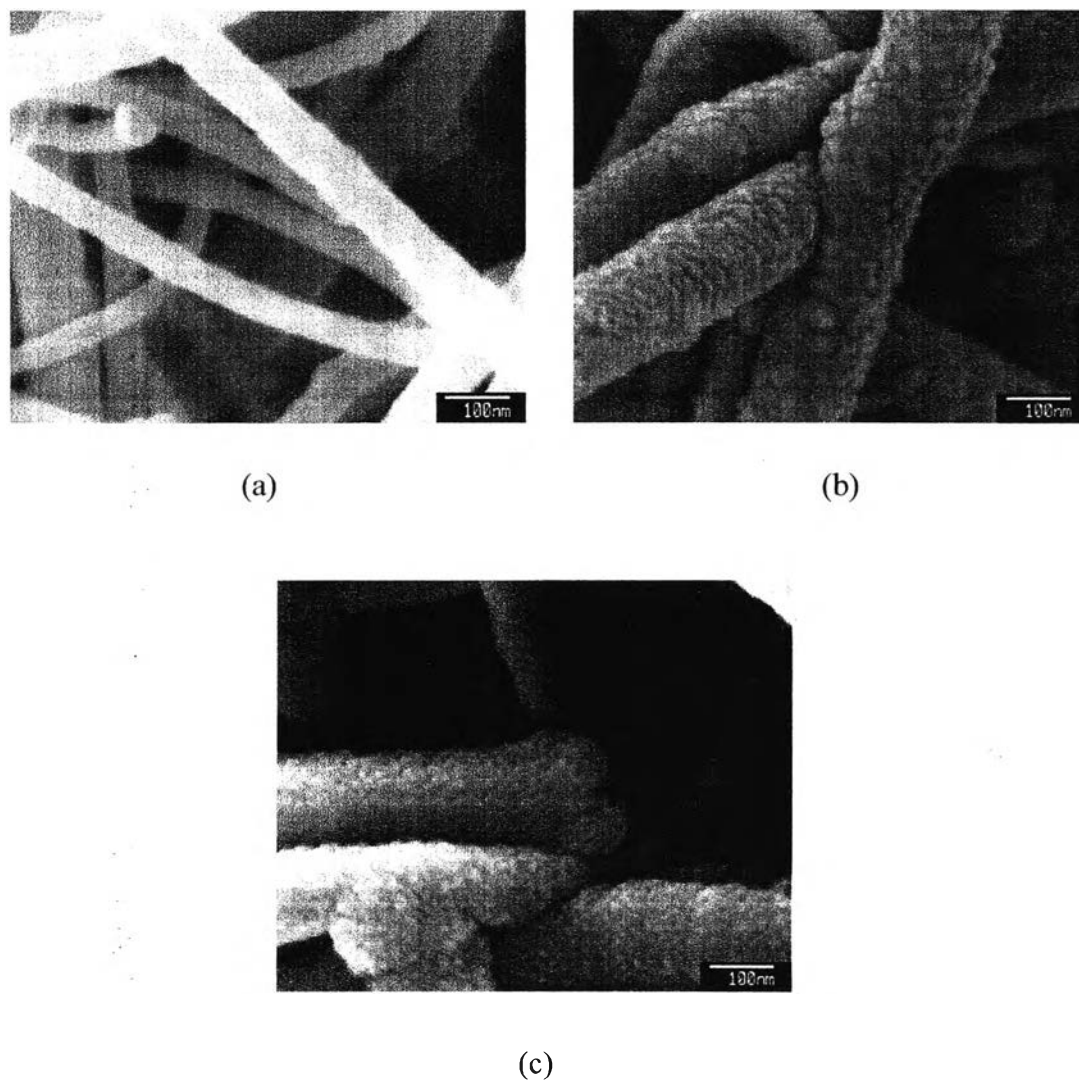
**Scheme 1** Suggested conformation of BA molecules adsorbed on the CNT surface.



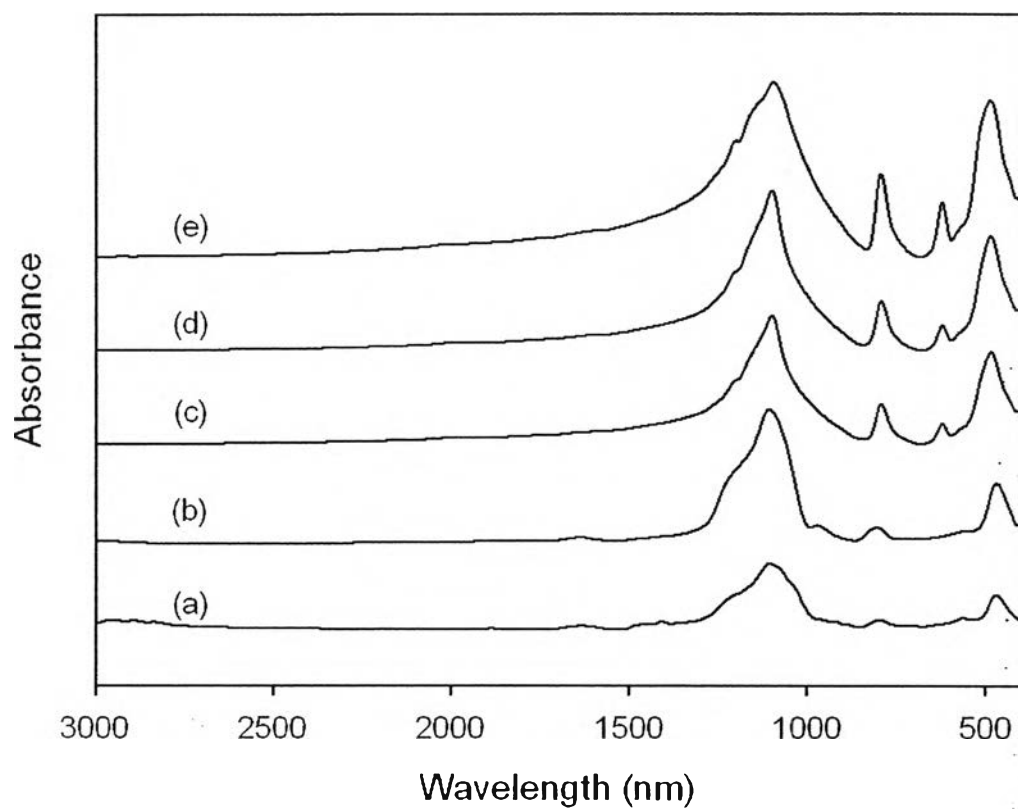
**Figure 7.2** Selected SEM images illustrating the morphological appearance of pristine CNTs coated with silatrane fixed a standard reaction mixture Si: BA: ethanol: water of 1: 4: 86: 33; using (a) an *in-situ* sol-gel process, (b) *ex-situ* sol-gel process after heated in autoclave 100°C for 24 h and vacuum filtration.



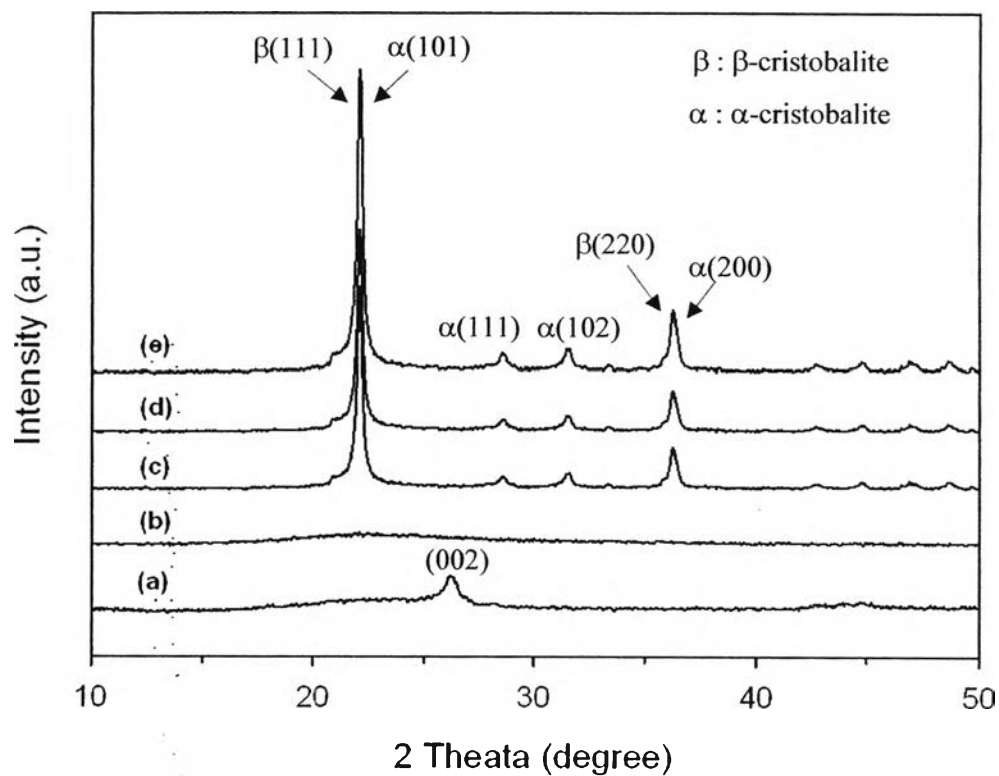
**Figure 7.3** Selected SEM images illustrating the morphological appearance of CNT-Silatrane hybrid material prepared from the solution of Si: BA: ethanol: water of 1: 4:86:33 after (a) left at room temperature for 24 h or heating in autoclave at various temperatures of (b) 60°, (c) 100°, and (d) 150°C.



**Figure 7.4** Selected SEM images illustrating the morphological appearance of (a) pristine CNT (b) pre-calcined the CNT-Silatrane hybrid material prepared from the solution of Si: BA: ethanol: water of 1: 4:86:33 after heat in autoclave 100°C 24 h and (c) post-calcined silica nanotube obtained from the calcinations at 700°C.



**Figure 7.5** FT-IR spectra of (a) pre-calcined the CNT-Silatrane hybrid material prepared from the solution of Si: BA: ethanol: water of 1:4:86:33 after heat in autoclave 100°C 24 h and silica nanotubes obtained from calcinations at various temperatures of (b) 550°, (c) 700°, (d) 900°, and (e) 1100°C.



**Figure 7.6** WAXD patterns of (a) pre-calcined the CNT-Silatrane hybrid material prepared from the solution of Si: BA: ethanol: water of 1:4:86:33 after heat in autoclave 100°C 24 h and silica nanotubes obtained from calcinations at various temperatures of (b) 550°, (c) 700°, (d) 900°, and (e) 1100°C.