

Synthesis of Multi-Walled Carbon Nanotubes by Chemical Vapor Deposition on Natural Silk Carbon Fibers

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Abstract

Multi-walled carbon nanotubes were synthesized by chemical vapor deposition using silkworm cocoons as the carbon source. The impregnation method with iron metal as a catalyst was utilized for growth of multi-walled carbon nanotubes. Morphology and microstructure of the synthesized multi-walled carbon nanotubes were investigated by scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy techniques. Results indicated that multi-walled carbon nanotubes with a diameter of about 20 nm were successfully synthesized by the decomposition of an acetylene-hydrogen mixture using an iron catalyst at 850°C. Silkworm cocoons were used as a low-cost natural carbon source for high-quality multi-walled carbon nanotube growth.

Keywords : Chemical vapor deposition, Multi-walled carbon nanotubes, Silkworm cocoons

1. Introduction

Biosensors are devices composed of a transducer and a biological element as an enzyme, antibody or nucleic acid. The transducer acts as a microelectronic element that detects and transmits an electrical signal, while the biological element acts as a sensor by interacting with the analyte. Carbon fibers and carbon nanotubes show great promise as electronic components because of their remarkable mechanical properties. For example, carbon fibers have been applied to form microbial biosensors to detect toxic substrates [1] and single carbon fiber microelectrodes have been used to measure real-time chemical release from single cells [2].

Carbon fibers have certain disadvantages which include only a limited surface area. Therefore, sensitive detection instrumentation is required to deal with the weak electronic signals

[2]. One possible solution to overcome this obstacle is to place carbon nanotubes (CNTs) on the fiber surface. This procedure greatly improves the overall surface area without changing the size of the biosensor. CNTs can be utilized to develop high-performance biosensors by increasing surface area exposure to biomolecules. CNTs can also easily adsorb both organic and inorganic elements and are capable of advocating as a proper mediator to prepare biosensors with improved specific areas. Recently, chemical vapor deposition (CVD) has taken center stage regarding the development of CNT composites. The CVD technique grows radial CNTs on carbon fibers which can then be used to develop microelectrodes.

Breakthroughs have been made to prepare and use CNT-containing electrodes to detect NADH and hydrogen peroxide. However, full advantages of CNTs have not yet been realized. Arvinteet et al. (2009) reported a

modification of the single-walled carbon nanotube (SWNT) method for preparing a biosensor with a mediator. The SWNT acts as a sensor to spot NADH and hydrogen peroxide. Electropolymerization converts CNT composites to CNT-carbon modified film electrodes [3]. In glucose oxidase and uricase immobilization, modified electrodes are used as platforms to sense glucose and uric acid [4].

Silk has attracted research interest for many years because of its excellent mechanical, physical, and environment-obliging properties. These advantages far surpass the attributes of synthetic materials. Silk fibers have a wide range of applications. Silk is composed of a filament core protein, termed fibroin and this can be used to apply in scaffolding cell-based tissue engineering [5]. Silk fibers are also employed as sutures in biomedical applications [6], while fibroin is used in biotechnological materials and in biomedical applications [7]. Silk products have been developed for external skin preparations including wound dressing, masks, carbonized cocoons as gas adsorbents, and hazardous substance decomposers. Applications of carbonized silk materials can also be found in other fields such as fuel cell production, capacitors, and electromagnetic shields. Furthermore, ongoing research is investigating silk synthesis to become carbon fiber. Khan et al. synthesized carbon fibers (CFs) from natural biopolymers and *Bombyx mori* silk fibroin at 800°C to improve mechanical properties such as increasing tensile strength and elongation at break [8], while Deng et al. [1] determined that carbon fiber made of silk fiber as a platform of microbial biosensor had the ability to detect toxic substrates.

The extraordinary mechanical properties of CNTs have generated enormous research interest. However, CNTs still have limited applications because of their size, despite the fact that they have many unique properties. Another problem arises in separating CNTs from the substrate. Consequently, CNTs have been mainly used as additives to improve the

properties of certain composites such as ceramics, resin, and composite reinforcement. Despite recent popularity in using CNTs on material composites, even dissemination has proved to be difficult. Therefore, synthesis of CNTs onto CFs has now become an interesting research area.

The synthesis of CNTs into CFs has been shown to improve mechanical properties. Typically, CNT synthesis consists of the deposition of a thin film of catalyst on a suitable substrate like silica or alumina using advanced technologies of electron beam evaporation, sputtering, or high vacuum. Various methods utilized to achieve CNT synthesis include arc-discharge, laser vaporization, catalyst pyrolysis, chemical vapor deposition (CVD) [9][10][11][12] and plasma enhanced chemical vapor deposition (PECVD) approaches. CVD has become the most suitable method for large-scale production of CNTs because it is low cost and provides high purity, whereas arc-discharge and laser techniques are unaffordable. Therefore, the CVD method is widely used to grow CNTs on CFs [13][14][15][16]. CNTs can be created from natural materials such as cotton [17] and bamboo [18].

Although a large amount of research has been conducted regarding silk applications, there is still no updated report concerning CNT synthesis on CF from natural silk carbon fiber through chemical vapor deposition to improve material properties in biomedical engineering for the use of humans. However, the properties of native silks make them suitable alternative and sustainable materials together with plant fibers for engineering composites as the main focus of this study. This research presents an initial report concerning the development of new materials by the synthesis of multi-wall carbon nanotube grafts on a carbon fiber substrate made from silkworm cocoons.

2. Experimental

2.1. CF treatment prior to CNT growth

Silkworm cocoons were purchased from Queen Sirikit Sericulture Center in Khon Kaen, Thailand. The fibers were boiled in sodium carbonate solution at a concentration of 0.02 molar at 100°C for 30 minutes and then washed with distilled water at 27°C. Next, the silk fibers were dried at 70°C for 4 hours before surface coating with a catalyst by infusion in 50 ml of well-suspended ethanol solution containing 3 wt% of ferrocene ($C_{10}H_{10}Fe$) (98%, Sigma-Aldrich) for 2 hours at room temperature. Then, the catalyst-coated fibers were taken out from the solution and dried at room temperature in a convection-flow fume hood overnight before carbonization. Thermal treatment was used to remove carbonized agents on the surface of the silk fibers at 250°C for 3 hours in a furnace.

2.2. CF/CNT growth process

Synthesis of CNTs was performed in a CVD reactor with ferrocene catalyst particles dispensed on the silk fiber surface. The CVD system consisted of a horizontal tubular furnace and a 50 mm diameter ceramic tube. The first step was to place the silk fibers in the ceramic bowl. After that, the silk fibers were pressed to the middle zone of the CVD furnace and purged for 20 minutes with nitrogen gas. Then, release hydrogen at flow rate of 150 ml/min to set temperature of the furnace chamber to 500°C for 3 hours, before adjusting to 700°C to initiate the carbonization process for 30 minutes.

Carbon fibers were created from the silk fibers. Then, acetylene gas was used to grow CNTs on the CF surface for 5, 10, 15 and 20 minutes with hydrogen and nitrogen gases at a furnace temperature at 850°C. Feeding rates were set at 100, 150 and 350 sccm for acetylene, hydrogen, and nitrogen respectively. During the final CNT

growth process, the reactive gases were removed from the furnace by purging with nitrogen. A schematic diagram of the CVD unit is shown in Figure 1.

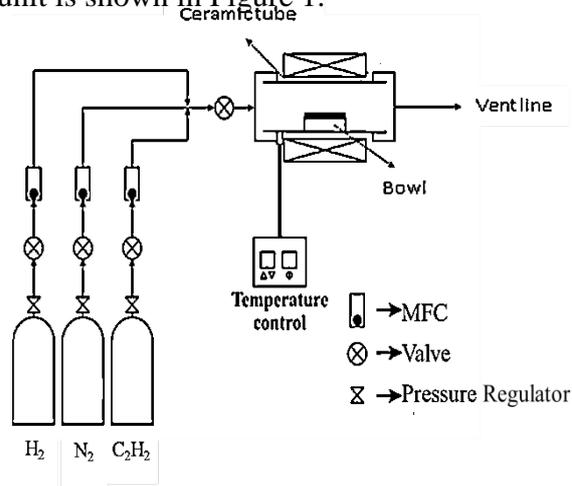


Figure 1 Schematic diagram of the CVD unit

2.3. Characterization techniques

Micrographs of CNT-grafted carbon fibers were achieved by a scanning electron microscope (SEM; LEO-1455, USA). Transmission electron microscopy (TEM) was used to identify the structure of the CNTs (FEI Tecnai G20, Netherlands) operating at 200 kV of accelerating voltage. Specimens were prepared by ultrasonic dispersion of slightly ground samples in a 40% ethanol-water solution. A drop of suspension was applied on the carbon-coated copper grids. Defects and graphitic nature of the fibers were studied by a Raman spectroscope (Bruker Ram II, Germany).

3. Results and discussions

Silk fibers before and after iron-catalyst coating are shown in Figures 2a and 2b. The diameter of the silk fiber before coating varied from 5 to 10 μm . After coating with catalyst, the silk fiber increased in diameter varying from 6 to 12 μm . Many large catalyst particles were visible on the surface of the silk fiber and some clusters formed due to the non-uniform coating of catalyst particles. Figure 2b shows the clusters of iron particles. Thermogravimetric

analysis (TGA) is a method used to ascertain catalyst contents as well as other carbon impurities present as soot [19]. Results of TGA for silk fibers and catalyst-coated silk fibers were conducted under nitrogen atmosphere from room temperature to 700°C and are shown in Figure 3. The lower curve (a) indicates the degradation of a silk fiber while the upper curve (b) represents a catalyst-coated silk fiber. At 650°C, the char yield of the catalyst-coated fiber was 3% higher than the uncoated fiber due to the weight of the coated catalyst which was not degraded at this temperature [10]. The CVD technique provides an iron catalytic conversion phase on the surface of nucleation centers. In Figure 2, the fiber surface appeared to be retracted and contained small pores. These characteristics found on the surface were caused by hydrogen and ethylene gases which strongly reduce oxidized catalysts to release the oxygen's local metallic particles that etched the surface of the carbon fibers into deep pits [10].

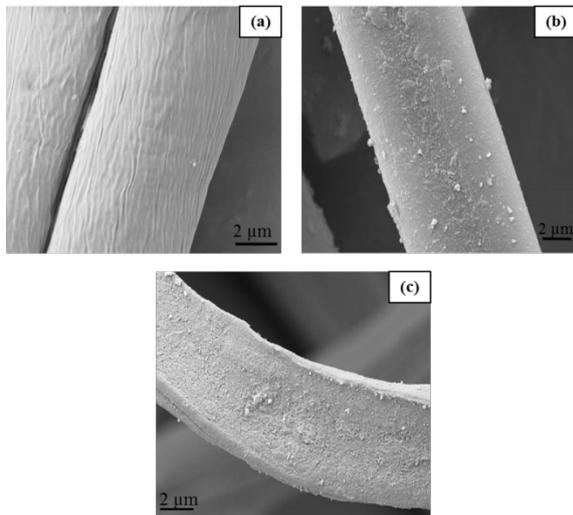


Figure 2 SEM images (a) silk fiber with a diameter of 7 μm, (b) silk fiber coated iron catalyst with a diameter of 7 μm, (c) carbon fiber from silk

Carbon fibers were prepared from silk fibers through the CVD process. Iron

catalyst particles were diffused into the carbon fiber substrate before growing CNTs on the carbon fibers. Figure 4 a-d demonstrates SEM micrographs showing CNTs grown on CFs at The CNTs began to grow on the peeled edge of the CF as shown in Figure 2a.

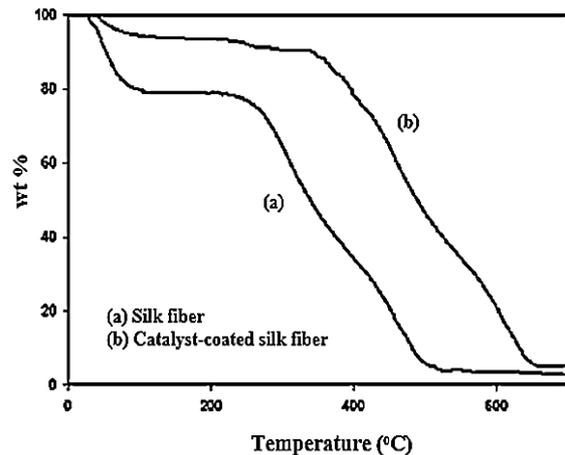


Figure 3 TGA curve of catalyst-coated silk fiber

Amounts of CNTs were small, appearing only on some parts of the surface. The CNTs grew well in high density areas of iron catalytic nanoparticles leading to a positive alignment of CNTs on the substrate [11]. Estimated lengths of the nanotubes varied between 2 and 100 μm. Observation was carried out after the growth of multi-walled nanotubes (MWCNTs) at different times of ethylene gas feed. CNT growth increased with increasing time of acetylene feed from 10, 15, and 20 minutes, respectively as shown in Figure 4 b-d. The highest growth was at 20 minutes. Alignment and diameter of CNTs may be determined by the size of catalytic particles. CNTs appeared to be more tangled as the time increased. Alignment of CNTs on CF substrates occurs because of a nucleation process catalyzed by iron on the site of an active surface. The remaining iron catalyst on

the CFs had potential to synthesize MWNTs continually.

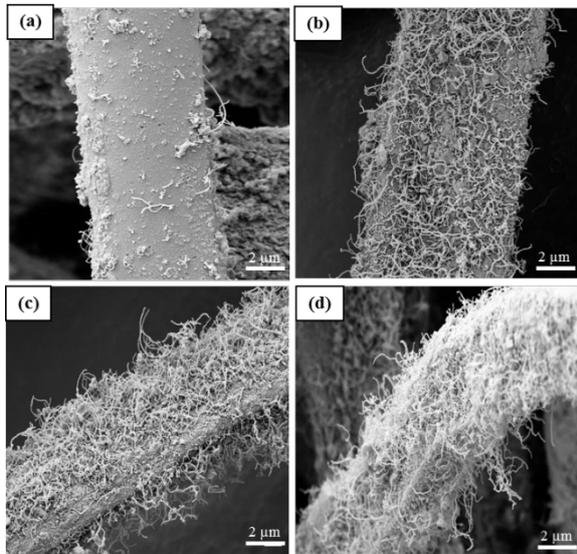


Figure 4 SEM micrographs of CNTs grown on carbon fiber using acetylene gas at 850°C for (a) 5, (b) 10, (c) 15, and (d) 20 minutes

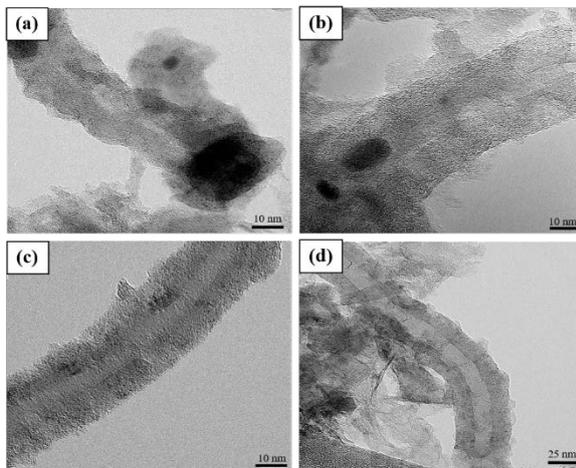


Figure 5 TEM images of carbon nanotubes grown on carbon fibers using acetylene gas at 850°C (a) 5, (b) 10, (c) 15, and (d) 20 minutes

Figure 5 shows carbon nanotubes growing on carbon fibers from 5 to 20 minutes using acetylene as a source of gas at 850°C. Figure 5 a-d shows TEM images of a single nanotube which confirms that the prepared CNTs were multi-

walled. There were many layers on the MWCNT walls which were 8-10 nm thick. The diameter of the nanotubes ranged from 25-30 nm. Carbon nanotube site density and length increased with growth time up to 5 minutes when using acetylene gas. After increasing growth time, the only outcome was enhancement of carbon nanotube site density. As time increased, active catalyzed particles as well as nanotube density also increased. During synthesis, the catalyst particles rotated because of uneven growth speed on the sides of the particles. The shape of a nickel catalyst particle is irregular and diameter of the MWCNTs ranged from 10 to 30 nm as shown in Figure 5a.

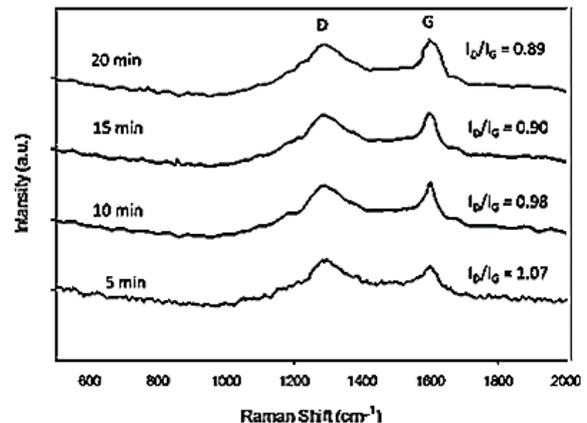


Figure 6 Raman spectra of MWCNTs

Figure 6 shows a collection of Raman spectra of MWCNTs. The graphite band (G band) is the Raman band which appeared in the 1500-1605 cm^{-1} of the first region. The disorder band or D band appeared in the 1250-1450 cm^{-1} region. Figure 6 confirms the characteristics of the prepared MWCNTs. In addition, when MWCNT growth appeared, the intensity ratio (I_D/I_G) decreased, proving that the as-prepared MWCNTs were highly graphitized.

4. Conclusion

A MWCNT/CF composite was successfully synthesized by decomposition of an acetylene-hydrogen mixture using iron

catalyst at 850°C on silk fiber substrate. The MWCNTs had a diameter of about 20 nm. Raman spectra proved that the as-prepared MWCNTs were highly graphitized. This composite could be a very useful substrate for metal oxide modifications.

5. Reference

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