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# Carbon Nanotube Fabrication Based on Animal Red Blood Cells

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**Abstract.** Red blood cells of mammals contain both raw carbonaceous material (proteins) and catalyzer precursor (iron atoms of metal-organic hemoglobin molecules) for Carbon nanotube (CNT) fabrication by the chemical vapor deposition method. To demonstrate the possibility of CNT fabrication by using blood as a single raw material, livestock (sheep) blood droplets on silicon substrates were used as samples for pyrolysis in an argon and argon + butane atmosphere at 300; 400; 500; $700^0$ C. Scanning electron microscope (SEM) images, of the product of pyrolysis at 500; $700^0$ C, magnified up to 20000 times, shows dense bushes consisting of nano-size rods. The length of the rods reached 50 μm; widths were around 400 nm and less. The two carbon bands centered at wavenumbers 1340 and 1580 $cm^{-1}$ in the Raman spectra of samples recorded using a low power-incident red laser (638 nm), demonstrates increasing graphitization of carbon atoms with rise of pyrolysis temperature. Both the SEM images and the Raman spectra indicate increasing formation of CNT, with an increase of pyrolysis temperature from 400 to $700^0$ C. No evidence of CNT formation at $300^0$ C was found.

## Introduction

Despite continuous efforts and achievements in Carbon nanotube (CNT) research and application over the last two decades, producing CNTs by a cost-effective technique is still challenging for R&D. The current state of three main methods of CNT production: arc discharge, laser ablation, and chemical vapor deposition (CVD) are characterized sufficiently in review articles of Kumar and Ando [1] and Zhang *et al.* [2]. Although CNT production is possible from many kinds of raw material by the CVD method as described in the review [1], as far as we know, an animal substance like blood was never tried as a single precursor material for CNT production by CVD.

Up to 45% of a mammal's red blood volume consists of red blood cells [3]. A red blood cell (or erythrocyte) is a nucleus-free cell which serves as a rack container for hundreds of millions of hemoglobin metal-protein molecules that each may capture a number of oxygen molecules from air in respiratory organs (lungs or gills). The red blood cells are then carried along a web of blood vessels to release oxygen at a destination tissue. The hemoglobin of most mammals consists of two of α and two of β protein subunits in a tetrahedral arrangement, and each subunit is associated with a non-protein metal-organic prosthetic molecule called Heme. The most common B type of Heme formula is $C_{34}H_{32}O_4N_4Fe$ which contains an iron atom as a bonding center of the surrounding four pyrrole molecules. Iron content in blood varies widely depending on the animal type, and may change according to the physiological state of a given species. For example, a normal range for iron in human blood is 60 μg/dL to170 μg/dL. Red blood cells might be extracted from whole blood by centrifuge separation or using a simpler method: heating with distilled water coagulating the red cell particles, filtering them out, and drying them for future use.

Farm animal blood, in most cases considered to be slaughterhouse waste, is underutilized [4]; this waste contains, in appropriate proportion, both raw material (carbon atoms of hemoglobin proteins) and catalyzer precursor (iron atoms of Heme) for CNT production by CVD. In this work, livestock sheep blood samples were used to demonstrate the possibility of CNT production from blood, using the CVD method.

**Sample Preparation and Measurement Details**

Polysilicon substrates each of 1.5x1.5 $cm^2$ size were cleaned by 15 minutes of ultra-sonication in acetone. A sheep's fresh blood sample (2-3 drops, or less than 0.1 mL) was spread evenly on the surface of the silicon substrate and dried at $50^0$ C for a half hour. The substrate with the dried layer of blood was stored in the furnace of the self-assembled CVD reactor [5]. The main part of the reactor is a horizontal quartz tube (50cm in length with a 1.8 cm inside diameter) furnace encircled in a heating coil. One end of the tube furnace is connected with a gas inlet for argon, butane, and hydrogen gases equipped with corresponding flowmeters, and the other end of the tube is a flame-secure water bubbling gas outlet combined with a thermocouple temperature sensor rod inlet. The substrates with a layer of dried blood samples were placed in the middle of the furnace tube and after 5 minutes purging with 130 sccm flow of argon gas, the temperature inside the furnace was raised gradually, over 30 minutes, to $300^o$ C. The final temperature of $300^o$ C was held within $\pm 5^o$ C during the 30 minutes and then the temperature was gradually decreased back to room temperature. After cooling the blood sample in an argon atmosphere, it was extracted from the furnace and stored in a plastic box. For other blood samples, the pyrolysis was done in same way at final temperatures of 400, 500, and $700^o$ C. In these cases, reaching the higher temperatures of 500 and $700^o$ C took longer, but were within 45-60 minutes. Blood samples also were pyrolyzed at 300, 400, 500, and $700^o$ C under an additional 70 sccm flow of CVD-supporting LPG (butane) gas.

The Raman spectrums of pyrolyzed samples were recorded in the wavenumber range of 800-2000 $cm^{-1}$ with an XploRa (Horiba Jobin-Yvon) Raman spectrometer equipped with an Olympus BX41 microscope. The 50 - fold magnification long focus objective was used**.** The incident laser diode (wavelength 638 nm) power was reduced to 50% for samples pyrolized at 400, 500, $700^o$ C and to 1% for samples pyrolized at $300^o$ C. Scattered photons were counted during 5 s; counting was repeated 20 times and accumulated for the final averaged spectra. For these totally light absorbing charcoal-like black samples the low power laser illumination in combination with multiple spectra accumulation constituted the most optimal Raman data acquisition conditions, because sample vaporization under full power illumination was strong and resulted in noticeable spectra shrinking after each illumination. The clear SEM images of sample surfaces magnified up to 20000 times were taken with a JSM-6510LV (JEOL) electronic microscope combined with an X-Max (Oxford Instruments) EDX (energy dispersive X- ray) spectrometer. EDX spectrums of samples pyrolized at $700^o$ C were taken to clarify elemental composition of different shaped (rectangles and rods) microcrystalline substances observed in SEM images of the samples.

**Results and Discussion**

The SEM images of samples carbonized at $300^0$ C (the first two columns of pictures in Fig. 1) were poor with micro and nano size features, while other columns of pictures in Fig. 1 show increasing numbers of rectangular and rod-shaped microcrystalline structures, with increase of carbonizing temperature. The typical size of the nearly square rectangles was 1μm and less. The rods were 5-10 μm in length, with a width of less than 0.5 μm. At the highest carbonization temperature of $700^0$ C the rods were also observed to resemble bushes of gladioli. A closer view, at 20K magnification, each sword-shaped leaf of a bush consists of thinner rods with a width of 0.3 μm or less (the last column of pictures in Fig. 1). It has to be noted that carbonization in the presence of butane gas resulted in much denser and longer bushes.

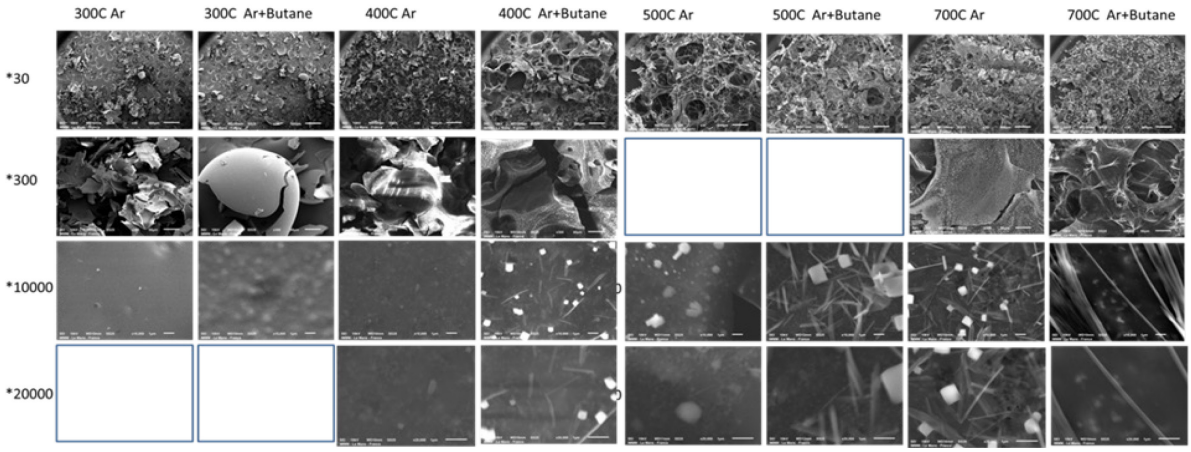


Figure 1. SEM images of the blood drop samples carbonized in an atmosphere of argon (Ar) and a mixture of argon and butane gases (Ar + Butane) at temperatures of 300; 400; 500, and $700^0$ C. The magnifications are shown on the left side of each row of pictures.

The composition of elements of the rectangular and bush-like rod structures was examined with micro EDX in a volume of 1 $\mu m^3$ at a near surface layer of a sample. On a typical SEM image (Fig. 2) of a sample carbonized in a mixed atmosphere of argon and butane gases at a temperature of $700^0$ C, the three points denoted as "Spectre 1, 2, and 3" are positions where the X-ray beam was focused to record EDX spectra of atoms in a one cubic μm volume of underlying material. At the position "Spectre 1," the X-ray beam was focused on the ~ 2 μm size rectangular microcrystalline, which might be difficult to identify at first glance, because of same color background. The elemental composition of the microcrystalline is presented in the second column of Table 1. The positions "Spectre 2 and 3" correspond to a root and middle part of the bush-like microcrystalline structure. The corresponding elemental composition of these sites is shown in the last two columns of Table 1.

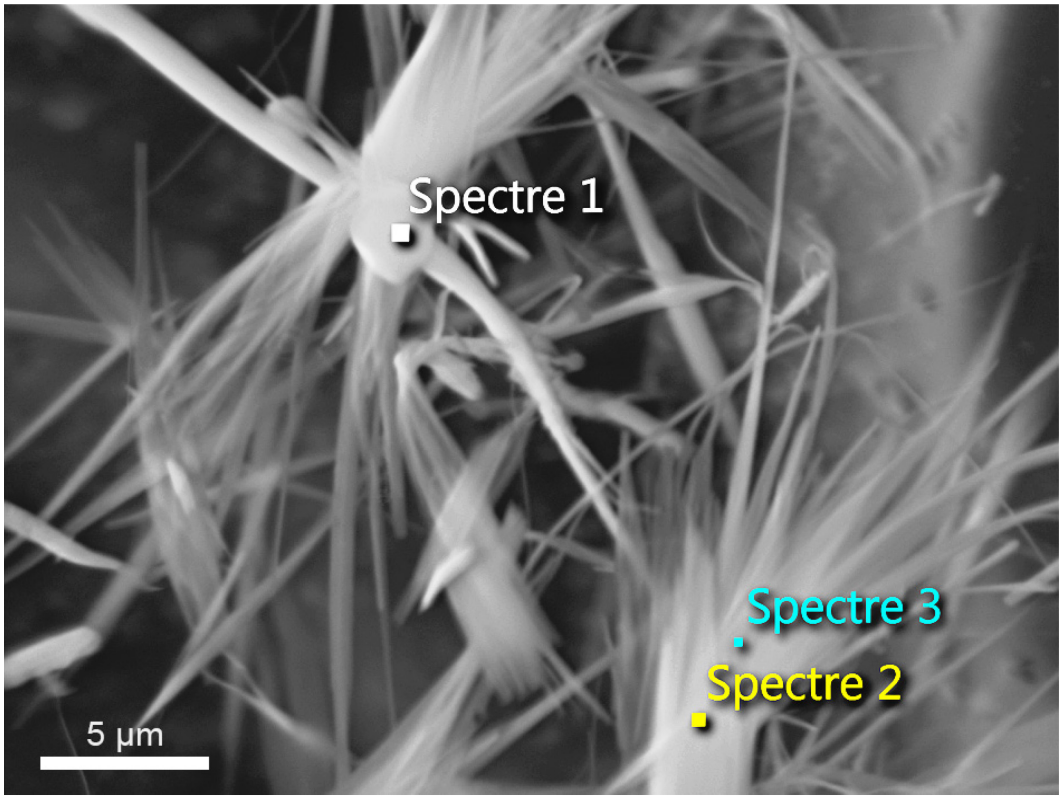


Figure 2. Typical SEM image of a blood drop sample, carbonized in an atmosphere of mixed argon and butane gases, at a temperature of $700^0$ C. The three points denoted as Spectre 1,2, and 3 are positions where EDX spectra were taken to calculate elemental composition of a near surface 1 μm thick layer of the sample.

Table 1. Elemental composition of the sample material at points denoted as Spectre 1, 2, and 3 in Fig.2.

| Elements | Number of atoms (%) at point 1 | Number of atoms (%) at point 2 | Number of atoms (%) at point 3 |
|---|---|---|---|
| C | 0.0 | 80.33 | 81.23 |
| O | 60.94 | 11.57 | 12.19 |
| Na | 22.92 | 2.14 | 1.84 |
| Mg | 0.33 | 0.07 | 0.06 |
| Si | 0.4 | 0.05 | 0.05 |
| P | 1.45 | 0.33 | 0.25 |
| S | 0.21 | 0.06 | 0.04 |
| Cl | 7.28 | 3.16 | 2.09 |
| K | 4.86 | 1.88 | 1.98 |
| Ca | 0.95 | 0.23 | 0.17 |
| Fe | 0.64 | 0.18 | 0.1 |
| Total | 100 | 100 | 100 |

As shown in the second column of Table 1, the sugar-like rectangular microcrystalline structure is carbonless and consists of salts and oxides of inorganic bioactive elements, such as Na, K, Mg, P, Fe, and others, dissolved in blood. The last two columns of Table 1 show that the bush-like microcrystalline structure is a carbon species with trace amounts of inorganics. Considering that each sword-shaped leaf of a bush consists of nano rods at sub μm widths, we suppose that the bushes are a type of multiwalled CNT bundle growing in our particular CVD condition.

The Raman spectrums of SW (single walled)-, DW (double walled)-, and MW (multi walled) - CNT consists of three broad Raman bands centered at wavenumbers: 200 $cm^{-1}$ (the radial breathing vibrational mode of the SW- or DW- tubes); 1340 $cm^{-1}$ (the so called D mode band, related to vibrations of the disordered or defective graphene structure of a CNT wall); and 1590$cm^{-1}$ (the G or graphite mode band corresponding to the stretching vibration of the -CC-bond in a graphene wall plane of a tube) [6].

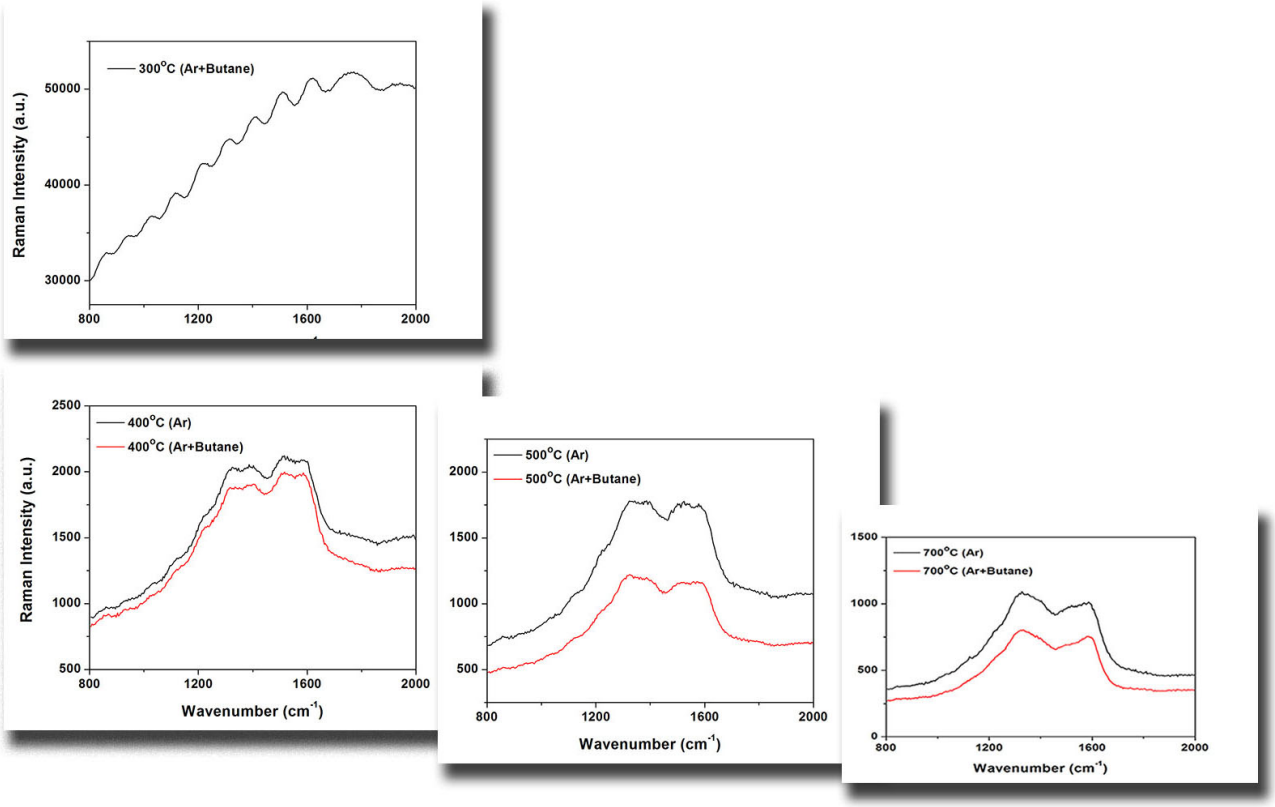


Figure 3. The most intensive Raman spectrums of blood samples after the CVD reaction were carried out at $300^0$ C (upper spectra), $400^0$ C (left in row), $500^0$ C (middle in row), and 700 $^0$C (right in row).

The measured Raman spectrums of our samples are shown in Fig.3. The uppermost, intense spectra, with interference-induced shallow peaks correspond to samples carbonized at $300^0$ C in a mixture of argon and butane gases. The absence of the graphite D and G bands, and presence of very high but featureless fluorescence background in the spectra, indicates that at $300^0$ C, organic molecular species of blood are still not decomposed and carbonized. Therefore temperatures of up to $300^0$ C are insufficient to carbonize blood organics for CNT growth. Comparison of the three spectra in the lower row in Fig.3 shows a decrease of fluorescence background with an increase of CVD temperature from 400 to $700^0$ C, while graphite G and D band peaks are observed with a G/D intensity ratio of bands equal approximately to 1. As shown for each pair of spectra, the fluorescence background is lower if the CVD was carried out with the support of butane gas. The Raman spectrums are demonstrating increasing graphitization of samples with a rise of CVD temperature, while maintaining a G/D ratio at the same low level for different temperatures. This behavior might be explained by the disordering of carbon graphitization by inorganic impurities in the blood.

## Summary

It was shown with EDX, Raman spectra and SEM images of samples, that blood graphitization during CVD occurs at temperatures of 400 $^0$C and above. Whole blood graphitization into the CNT allotrope form is observed at CVD temperature of 700 $^0$C and above. CNT production from blood by CVD might be increased a) if the CVD is performed with supporting carbonaceous gas such as butane; b) with a CVD temperature of 700 $^0$C and higher; c) if the blood is separated from dissolved inorganics before CVD.

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**References**

[1] Mukul Kumar and Yoshinori Ando, Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production, Journal of Nanoscience and Nanotechnology, Vol. 10, 3739–3758, 2010, doi:10.1166/jnn.2010.2939

[2] Qiang Zhang, Jia-Qi Huang, Wei-Zhong Qian, Ying-Ying Zhang, and Fei Wei, The Road for Nanomaterials Industry: A Review of Carbon Nanotube Production, Post-Treatment, and Bulk Applications for Composites and Energy Storage, Small, Volume 9, No. 8, pages 1237–1265, 2013, doi: 10.1002/smll.201203252

[3] https://en.wikipedia.org/wiki/Blood

[4] Clara S.F. Bah, Alaa El-Din A. Bekhit, Alan Carne, and Michelle A. McConnell, Slaughterhouse Blood: An Emerging Source of Bioactive Compounds, Comprehensive Reviews in Food Science and Food Safety, Vol.12, pages 314-331, 2013, doi: 10.1111/1541-4337.12013

[5] R. Galbadrakh, E. Temujin, Tong Young Lee, G. Shilagardi, N. Tuvjargal, B. Battsengel, Carbon Nanotube Production Possibility by Chemical Vapor Deposition and Arc Discharge Methods, Scientific Transactions of the Natl. Univ. of Mongolia, No. 362(17), pages 48-51, 2012 (in Mongolian)

[6] P. Ramesh, T. Okazaki, T. Sugai, J. Kimura, N. Kishi, K. Sato, Y. Ozeki, H. Shinohara, Purification and Characterization of Double-wall Carbon Nanotubes Synthesized by Catalytic Chemical Vapor Deposition on Mesoporous Silica, Chemical Physics Letters 418 (2006) 408–412, doi:10.1016/j.cplett.2005.11.018