

Characterization of Catalyst Effect on Carbon Nanoparticles

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ABSTRACT

Carbon nanoparticles (CNPs) were synthesized using a chemical vapor deposition furnace, acetylene carbon source, and a Ni catalyst at 850 °C. Various sizes (10 nm, 20 nm, and 100 nm) of the Ni catalyst were used for carbon nanoparticle growth. This work demonstrated that the dimensions of the CNPs are dependent on the size of the Ni catalyst. Morphology of the carbon nanoparticles was analyzed using environmental scanning electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and inductively coupled argon plasma atomic emission spectroscopy. It was found that the size of the CNPs decreased with decreasing size of Ni catalyst.

1 INTRODUCTION

Carbon nanoparticles (CNPs), also known as carbon spheres and nanospheres, have been of interest to the nanoscience community since R. Smalley and S. Iijima introduced buckyballs and carbon nanotubes [1, 2]. These spheres of graphene flakes are reported to have diameter sizes ranging from 60-2000 nm [1-8]. They exhibit field emission properties that would be ideal for cathode materials [9], and potentially tribological coatings and lubricant additives [10]. Carbon nanoparticles have also been reported as potential transporters of proteins, nucleic acids, and drug molecules in the nuclear membrane and across the cell membrane [12]. We are interested in the carbon nanoparticles for potential field emission cathodes, as well as to enhance conductivity in conductive inks for antennas. Synthesis of carbon nanoparticles have been performed in many ways, which include: growth from glucose using hydrothermal conditions [3], non-catalytic chemical vapor deposition (CVD) preparation [4], de-oiled asphalt [5], direct pyrolysis of hydrocarbons [6], and recently CVD growth of carbon nanoparticles using Ni catalyst [7]. Following the growth mechanism in [7], we recently reported the growth of carbon nanoparticles on a Si substrate by CVD, for potential electronic devices [8]. In our process, we deposited a Ni catalyst onto a Si substrate. The Ni catalyst were nanoparticles with an average size of 100 nm. The substrate was then placed into a CVD furnace and heated to 850 °C. Nitrogen was flown through the furnace during both the heating up and cooling down, at a mass flow rate of 400 sccm. Acetylene (the carbon source) was flown through the furnace at 850 °C, for 2-3 min, at a rate of 80 sccm. As a result of our growth process, carbon nanoparticles grew on the

Si substrate, with sizes in the range of 500-700 nm. Various growth conditions can affect the size of these carbon nanoparticles. These conditions include (but are not limited to): growth technique, growth time, gases, gas flow rate, catalyst, quantity of catalyst, and catalyst size. Manipulating all of these factors would be an extremely time consuming process. Considering that there is little known about the role of the catalyst in carbon nanoparticle growth, this paper will focus on the effect the catalyst size has on CNPs. If the size of the carbon nanoparticles can be controlled by changing the catalyst size, the fundamental properties can be controlled (e.g., electronic and mechanical properties). The carbon nanoparticles are grown using chemical vapor deposition because it is a simple and cost efficient method of synthesizing carbon nanomaterials. We recently experimented with varying the size of the Ni catalyst. We randomly selected catalyst sizes of 10 nm and 20 nm, along with the 100 nm catalyst that was used in our previous work [8]. Each of the growth experiments had the same growth conditions for each nickel catalyst size: 850 °C growth temperature, flow rate of acetylene and argon was 80:400 respectively, and time of deposition was 2-3 min (dependent on time taken to shut off acetylene gas). According to A. Levesque *et al*, carbon nanoparticles are grown in the following manner: (1) the acetylene gas decomposes into atomic carbon, (2) a wavy 2D structure of graphene flakes are formed, (3) the flakes cluster together in a layered manner around a coaxial (forming a spherical shape) [7]. Reportedly, these 2D flakes are around 4 nm, and they form 3D nanocrystallites that are approximately 2 nm. Furthermore, it is reported that there are some amorphous areas present between the layered flakes. We believe that this is the same growth mechanism that our carbon nanoparticles follow as well, with the exception of a different growth temperature (ours is 850 °C) and size of carbon nanoparticles (which will be seen in the results section of this paper). Characterization of the carbon nanoparticles was performed using the following tools: environmental scanning electron microscopy (ESEM) was used for dimension measurements of the CNPs, Raman spectroscopy of the carbon nanoparticles enabled structural and vibrational analysis, and both X-ray photoelectron spectroscopy (XPS) and inductively coupled argon plasma (ICAP) were used to determine the chemical composition of the carbon nanoparticles. These characterization instruments were useful in showing the morphology of the carbon nanoparticles as the Ni catalyst size was altered.

2 EXPERIMENT DETAILS

2.1 Synthesis of Carbon Nanopearls

A Barnstead International, Model F21135 chemical vapor deposition quartz tube furnace (with a tube diameter of 1.5 in), was used for the synthesis of CNPs. The Ni sizes that were used were as follow: 10 nm, 20 nm, and 100 nm. Previously we reported the use of 100 nm Ni nanoparticles for carbon nanopearl growth [8]. Therefore, we randomly chose two smaller catalyst sizes (10 nm, 20 nm) to determine if controlling the catalyst size would control the carbon nanopearl size. For each experiment, 0.02 g of Ni nanoparticles were placed in an 18 in quartz. The boat was then placed in the CVD furnace and set for a growth temperature of 850 °C for 2-3 minutes. The gases that were used during this process were acetylene and argon. In our previous report [8], we used nitrogen instead of argon. Literature shows that using nitrogen gas results in nitrogen atoms reacting with acetylene to form hydrogen cyanide [11]. Therefore, argon was used for safety and health reasons. The argon continuously flows through the quartz tube furnace while the heating is in process. The acetylene is turned on at 850 °C for 2–3 min, and then it is immediately shut off. Previous experiments have shown that 2-3 min is sufficient time needed to obtain completely spherical CNPs. The argon continuously flows while the furnace cools to room temperature (this enables balanced pressure inside and outside the furnace). The flow rate of the acetylene and argon is the same as in our previous work [8], 80:400 sccm respectively. Following the growth of the carbon nanopearls, the sample is collected from the quartz boat and is prepared for characterization.

2.2 Structure Characterization

The samples were characterized by ESEM (FEI Quanta at 5-10 kV), Raman spectra (Renishaw), XPS (Surface Science Instruments M-Probe spectrometer), and ICAP (Thermo Fisher, 6500 model).

The ESEM samples were prepared by sonicating in methanol until they were no longer agglomerated. A drop of the sample solution was dispersed on a carbon sticky dot and dried under a fume hood. Once the sample was dried, it was placed in the ESEM. Images were taken with a spot size of 4 at 5 keV.

XPS spectra were obtained by compressing a small amount of CNPs and placing onto double sided tape on the sample stage. The chamber pressure was maintained at 10^{-7} Pa, while Al-K α radiation (photon energy 1476.6 eV) was used as the excitation source for the XPS analysis. The samples were subjected to the lowest scan resolution of 4 and a time step of 1 eV. Survey scans were carried out to determine the concentration of impurities.

ICAP metric analysis was performed using acid dissolution sample preparation. A very small amount of CNPs was dissolved in an acidic solution of HCl/HNO₃ (4:1). The solution was maintained at 75 °C in an oven to react for 30 minutes. The sample solution was then diluted in 5% HNO₃ aqueous solution up to at least 5 grams of the total weight. Dilution correction is calculated then entered in instrument software for quantitative analysis. Standards suspended in a 5% HNO₃ aqueous solution were used to calibrate the instrument.

Raman spectroscopy was performed on the CNPs utilizing an excitation wavelength of 532 nm, 5X magnification, and a spot size of 6 μ m. The samples were prepared by dispersing the CNPs onto a silicon or quartz substrate. This substrate had a carbon sticky dot on the surface, which enabled the sample to remain stable.

3 RESULTS

ESEM data was taken for all three carbon nanopearl samples that were synthesized using 10 nm Ni, 20 nm Ni, and 100 nm Ni. Figure 1 shows an image of the carbon nanopearls- synthesized using 10 nm Ni. The sizes of these CNPs range from 200-400 nm. As previously reported [8], the carbon nanopearls are layered on top of each other, similar to a pearl necklace, and are agglomerated. The next ESEM image (Figure 2) was taken of the CNPs that were synthesized using 20 nm Ni. This sample shows a slight increase in the size of the pearls, with a size ranging from 400-500 nm. It appears that switching from a Ni catalyst size of 10 nm to 20 nm increases the overall nanosphere dimension. The last ESEM image was taken of the CNPs grown using the 100 nm Ni. As shown in Figure 3, these nanopearls range from 500-700 nm. The ESEM proves that by changing the size of the Ni catalyst, the dimension of the CNPs can be controlled. This is ideal for applications such as electronic devices, as well as increasing conductivity in conductive inks for fabricating antennas.

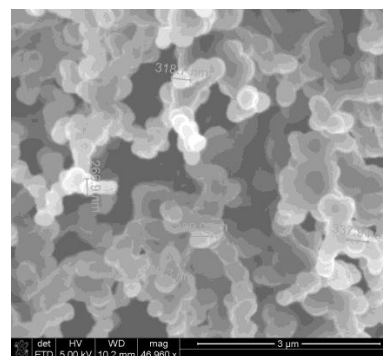


Figure 1: ESEM image of CNPs synthesized using 10 nm Ni catalyst. Size range 200–400 nm.

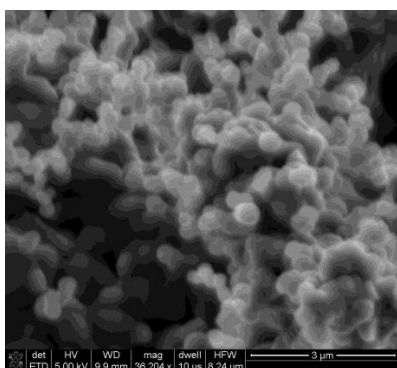


Figure 2: ESEM image of CNPs synthesized using 20 nm Ni catalyst. Size range 400–500 nm.

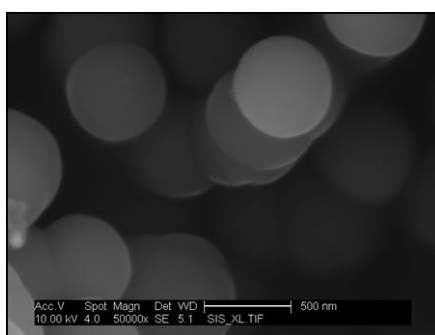


Figure 3: ESEM image of CNPs synthesized using 100 nm Ni catalyst. Size range 500–700 nm.

Raman spectroscopy was performed to characterize the structural, electronic, and vibrational properties of the carbon nanopearls. Figure 4 shows a comparison curve of all three carbon nanopearl samples. In general, graphitic carbon materials can be characterized by two bands in the Raman spectrum: the G-band (in-plane vibrations of sp^2 carbon) between $1580 - 1600 \text{ cm}^{-1}$ and a disorder-induced D-band which appears at $\sim 1350 \text{ cm}^{-1}$ depending on the laser excitation wavelength. The G band is also a result of the C-C bonds stretching [4]. As shown in the spectra, Figure 4, the G band is most intense for the CNPs that were grown using the 100 nm Ni. Observing the CNPs grown using the 20 nm and 10 nm Ni catalyst, the G peak decreases as a function of the catalyst size, respectively. The value of the intensity ratio of D and G bands (I_D/I_G) is indicative of the graphitization degree of carbon material and is used to characterize the order/disorder of the CNPs structure. An increase in I_D/I_G indicates a higher degree of disorder [10]. Therefore, the higher the I_D/I_G ratio, the higher the concentration of amorphous carbons after growth. This is evident in the I_D/I_G values listed in Table 1. The disorder in the carbon structure, shifts in D and G-bands, and width of these bands are evidence of the sample containing both amorphous carbon and CNPs (which can be seen in Figure 2, ESEM image). The

decrease in the G band agrees with the data that was published by J.-Y. Miao *et al* at the Institute of Atomic and Molecular Sciences. J.-Y. *et al* shows that the smaller carbon nanospheres have a less intense G band [9].

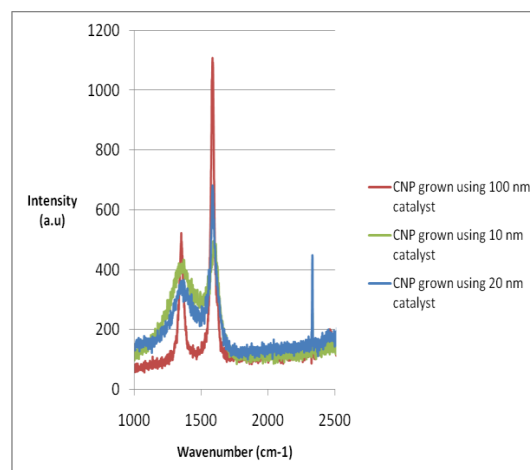


Figure 4: Raman spectroscopy of carbon nanopearls grown using 10 nm, 20 nm, and 100 nm Ni catalyst. Notice the G band intensity is the strongest when the CNPs were grown using 100 nm Ni.

Ni catalyst (nm)	I_D/I_G
100	0.42
20	0.85
10	0.87

XPS was used to determine the chemical composition of the CNPs. Survey scans of each sample batch were performed, more specifically, to determine the concentration of Ni in the sample. Survey scans are illustrated in Figure 5, and the concentration values of Ni as a function of reduction of Ni catalyst size are listed in Table 2. The concentration of Ni decreased with decreasing size of Ni catalyst, and correlates well with results generated from ICAP that are listed in Table 2 as well. XPS measures the elements on surface, while the ICAP separates the carbon from any existing Ni by means of digestion as explained in section 2.2. The size of Ni catalyst plays a significant role in the dimensions of CNPs grown.

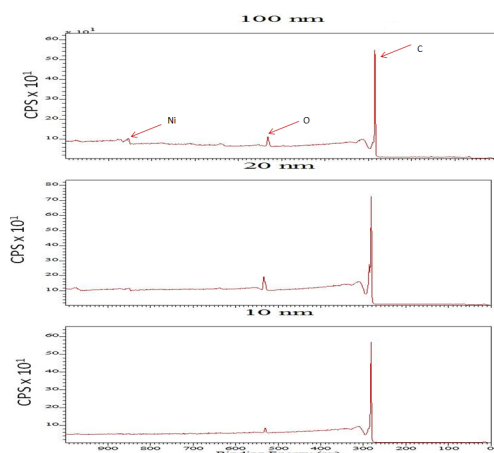


Figure 5: XPS survey spectra of CNPs grown using 100 nm, 20 nm, and 10 nm Ni catalyst.

Ni catalyst size (nm)	XPS: Ni concentration after growth (at%)	ICAP: Ni concentration after growth Avg (%)
100	0.382	16
20	0.291	2.5
10	0.029	0.6

4 CONCLUSION

As we have mentioned, there are many factors that can affect the growth of carbon nanopearls. Due to lack of research on the role the catalyst has in synthesis of carbon nanopearls, we decided to experiment with varying the size of the Ni catalyst. The results from the ESEM showed an increase in diameter of the carbon nanopearls (200 nm-700 nm), as the catalyst size increased. There was a large difference between the size of the catalyst and the carbon nanopearl size (at least 2 orders of magnitude). We believe this to be a result of the large amount of acetylene used in the growth process (80 sccm). However, our experiments show that carbon nanopearls only formed at the acetylene flow rate of 80 sccm. The I_D/I_G ratio, calculated from the Raman spectra, indicated that there was less amorphous carbon as the catalyst size increased. A thorough investigation needs to be done to understand why there is more amorphous present with the smaller carbon nanopearls than in the larger CNPs. Both the XPS and ICAP results demonstrated that there was less Ni remaining in the CNPs as the catalyst size was

decreased. These characterization tools helped to prove that the dimensions of the carbon nanopearls were dependent on the size of the catalyst. As a result, the carbon nanopearls size can be manipulated to fit applications such as field emission cathodes and conductive inks for antennas.

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