Mass Production of Graphene and Magnetic Nanoparticle in Arc Discharge Plasma and Their Protential Biomedical Applications

X. Fang[*], A. Shashurin[**] and M. Keidar[***]

[*]The George Washington University, SEAS-SEH
Room 3100, 800 22nd St NW, Washington, DC USA, xiuqifang@gwmail.gwu.edu
[**]Purdue University, west lafayette, IN, USA, ashashur@purdue.edu
[***]The George Washington University,Washington DC, USA, keidar@gwu.edu

ABSTRACT

Nowadays, a more efficient and environmental friendly method to synthesize Graphene Platelet Networks (GPNs) and Carbon Encapsulated Magnetic Nanoparticles (CEMNs) is highly requested in the world. Potential biomedical usage of these materials such as promoting the nerve cell to grow and targeting drug delivery has caught a lot of researchers' attention. Proposed here method offers a single-step direct approach to synthesize GPNs on any substrate made by different material that could be able to resist 800C and pure CEMNs with identical shape and less impurities.

Keywords: GPNs, CEMNs, plasma

1 INTRODUCTION

Nanomaterial, such as 0D Fullerenes, 1D nanotubes, 2D graphene and 3D spherical nanoparticles has caught a large number of researchers' attention. GPNs, as a flake network consist of single layer carbon atomic sheet, is the first 2-dimensional (2D) novel material available to the world.[1] With the combination of superior elasticity, mechanical stiffness, high electrical and thermal conductivity,[2] it is being studied for a wide range of applications such as flexible electronics, high-frequency transistors, energy storage, tissue enhancement additives, and biochemical applications. MNs, as a spherical magnetic nanostructure, are made of different magnetic materials and their alloys.[3] Due to its specific magnetic properties, MNs have been used in divergent field such as biosensing applications, targeted drug delivery, Magnetic Resonance Imaging (MRI), Magnetic detections and Magnetic Particle Imaging (MPI).

Currently, several approaches have been used to synthesize GPNs, including mechanical and chemical exfoliation, chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), epitaxial growth, free-standing flakes microwave synthesis, laser ablation and arc discharge plasma.[4] As for MNs, different synthesis method such as microemulsions, sol-gel synthesis, sonochemical reactions, hydrothermal reactions and flow injection synthesis have been widely applied.

Research Question: Among all these mechanical and chemical methods listed above, a variety of short comes such as low production efficiency; toxic by product and expensive synthesis procedure could be listed. Is there a more efficient and cheaper way to provide these nanomaterials in bulk?

Motivation: The motivation for this research is to provide a environmental friendly, more efficient and cheaper way to synthesize GPNs and CEMNs in bulk for biomedical applications using arc discharge plasma.The first objective is to use a pure carbon source to synthesize graphene without inducing any by-products and metal impurities. The second objective for this work is to control the size and carbon impurities of the CEMNs during the synthesis procedure.

2 METHODS

The GPNs and CEMNs were synthesized in a stainless steel cylindrical vacuum chamber with a total volume of 4500 cm^3 (27 cm in length and 14.5 cm in diameter). Detailed setup could be found in the previous paper.[5] A pair of electrodes, a cathode and anode, is installed along the vertical axis of the chamber. Both electrodes are made of POCO EDM-3 graphite. Figure 1a shows the schematic of the GPNs synthesis system. The cathode is 12mm and the anode is 3mm in diameter, which was placed 4~5mm away from each other. The substrate made of different material was 50mm away from the center of the electrodes. The whole system was pumped down to 10^{-2}torr and the substrate was heated up to about 800 k before the arc was generated. During the experiment, the arc was sustained by a welding machine and the arc current and arc voltage was kept 70A and 30V measured by an oscilloscope.

Figure 1b shows the schematic of the CEMNs synthesis system. The cathode is 12mm in diameter while the anode is a hollow tube with inner and outer diameters of 3mm and 5mm, respectively. The fillings in the anode hollow consisted of graphite flake well mixed with metal powder (Iron Filings from Arbor scientific, Nickel from Alfa Aesar). The molar ratio for the anode filling is C: Fe = C: Ni =7:90 and C: Fe: Ni = 7: 45: 45. This experiment is processed in a 500 Torr helium environment. A divider made of stainless steel was placed in between the electrodes

and the magnet in order to prevent the substrate from direct contact with the arc discharge. Before the experiment, the two electrodes were placed 2mm away from each other. The arc was sustained by the same welding machine and the arc current and arc voltage was kept 30A and 30V, respectively.

Synthesized sample collected on both the substrate and the magnetic were then characterized and analyzed under SEM (FEI Teneo), RAMAN spectrum (Horiba), and TEM (FEI Talos) and AFM.

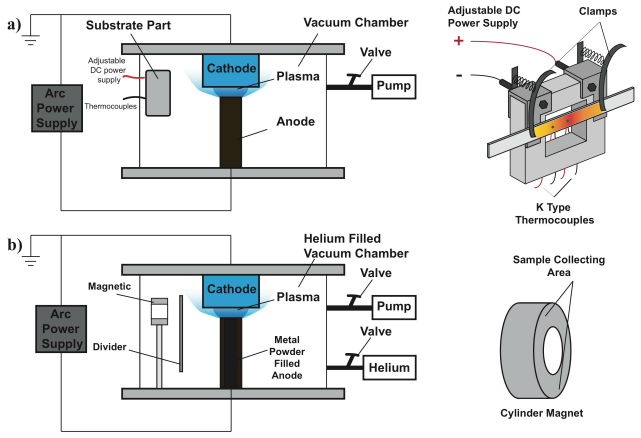

Figure 1.a) Schematic of the GPNs synthesis system and the inset figure shows the heating substrate part. b) Schematic of the plasma based CNs synthesis system with the magnetic field and the inset figure shows the position that the MNs were collected.

3 RESULTS

The heated area of the GPNs substrate was covered with dark structure uniformly. Figure 2 shows the SEM image, RAMAN spectrum and AFM height measurement for the GPNs substrate. From the SEM image, one could see flakes structures with an average diameter of 300 nm were densely packed on the surface of the substrate. RAMAN spectrum shows 3 feature peaks for graphene, namely D peak G peak and G' peak. I(G')/I(G)=0.8 indicates that about 3~ 4 layered GPNs were synthesized all over the heated substrate area. AFM image shows that the height of the GPNs is around 100nm.

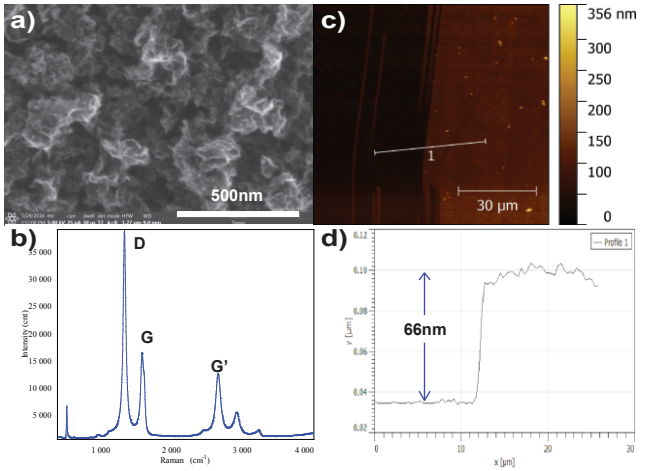

Figure 2. a) SEM image for GPNs on a silicon substrate. b) RAMAN spectrum for the GPNs c) AFM and d) height measurement for the GPNs

Figure 3 shows the SEM images for Fe, Ni and Fe+Ni MNs and their size distributions. Overall, all three different MNs shows the same spherical features with a size distribution of 10~90nm and the majority of the nanoparticles are 30~50nm in diameter.

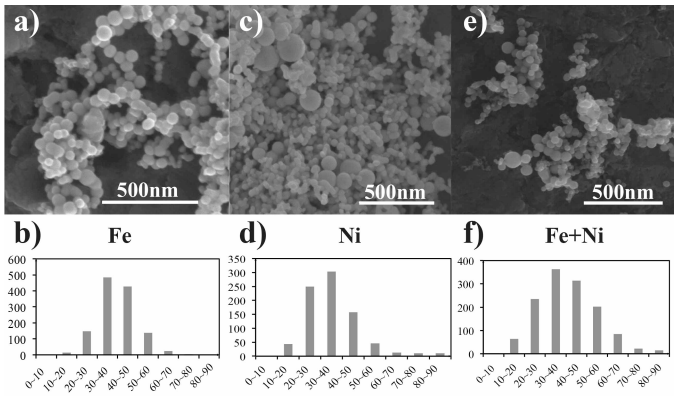

Figure 3. a) Fe MNs and b) its size distribution; c) Ni MNs and d) its size distribution; e) Fe+Ni MNs and f) its size distribution

Figure 4 shows the TEM images for Fe, Ni, Fe+Ni MNs with their Fast Fourier Transform. And the selected area crystal line images were also presented here to show the perfect metallic structure for these MNs. In the TEM images, one could see that the spherical metal structures were covered with thin carbon surface. It is because graphite powder was added to the anode fillings.

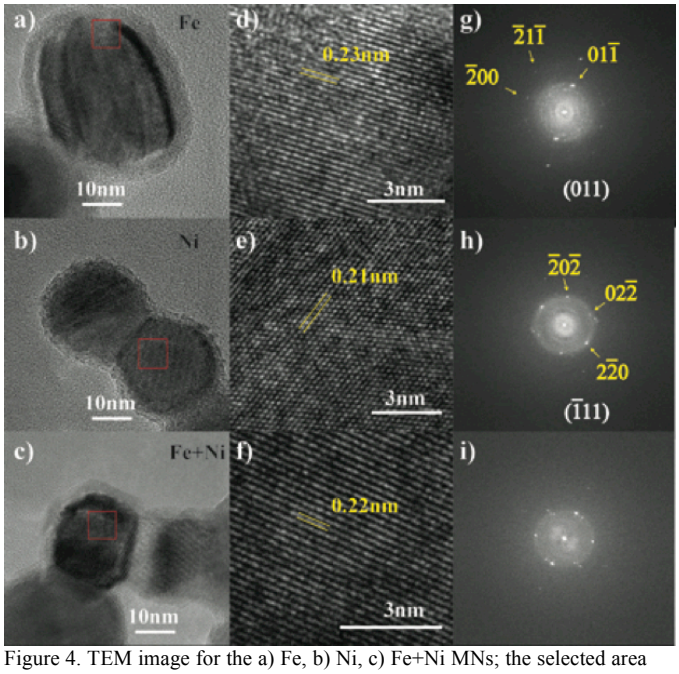

Figure 4. TEM image for the a) Fe, b) Ni, c) Fe+Ni MNs; the selected area crystal line images for d) Fe, e) Ni, f) Fe+Ni MNs and the FFT for g) Fe, h) Ni, i) Fe+Ni MNs

As for the carbon encapsulated shell in these CEMNs, there are several theories to explain this. Most of the theories are developed from the mechanism about the formation of the catalyst involved with the carbon nanotube synthesis. In 1995, Majetich et al suggested a theory that both the metal material and carbon are atomized in the plasma, then they nucleated into clusters. Finally, by phase segregation during the cooling procedure, the carbon coating on the particle exterior is formed. Figure 5 shows the formation process of the CEMNs by phase segregation during the cooling of the plasma synthesis procedure.

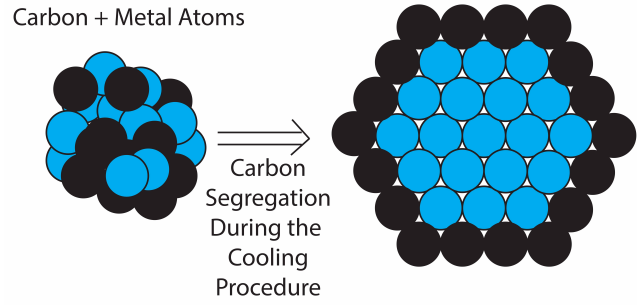

Figure 5.formation process of the CEMNs by phase segregation during the cooling of the plasma synthesis procedure

After the CEMNs were collected from the surface of the magnet, by scraping them off with a razor blade, methanol was added to the CEMNs in a glass bottle. Fisher scientific Model 150 ultra-sonicator was used to sonicate the solution for about 5 minutes with amplitude of 50. As the CEMNs suspension is formed, we placed a magnet next to the glass bottle as shown in Fig. 6 b).

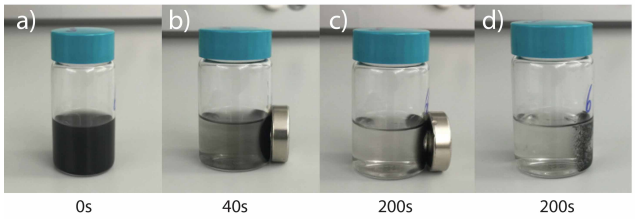

Figure 6.a) suspension of the CEMNs with methanol, b) magnet was placed next to the glass bottle for 40s c) magnet was placed next to the glass bottle for 200s d) and after the magnet was removed from the glass bottle at 200s

CEMNs are small magnets, and they can be manipulated by an external magnetic field gradient because of Coulomb's law. Due to this "action at a distance", CEMNs could be applied for target drug delivery including anticancer drugs, or a cohort of radionuclide atoms. The applications of CEMNs is to reduce the dosage and by providing a more efficient and localized targeting of the drug. The CEMNs could be used as a hyperthermia agent, which was made to resonantly respond and deliver toxic amounts of thermal energy to targeted bodies due to a time-varying magnetic field. Thus it is very important to test the cytotoxicity of the CEMNs in different cell lines.

Human breast adenocarcinoma cell line MDA-MB-231 was used to test the cytotoxicity of magnetic nanoparticles (MNPs). The viability of MDA-MB-231 cells after 72 hr treatment of MNPs was measured using MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide; thiazolyl blue) assay.

In this study, MTT assay was used to access the cytotoxicity of the three types of MNPs. All data was normalized to the viability of cells without MNP treatment. The figure indicates that the MNPs exert significant cytotoxicity to MDA-MB-231 cells in dose-dependent manner in the concentration range of 0.0001 – 100 ug/ml: cells were barely affected by any type of MNPs in the range of 0.0001 - 0.05 ug/ml; at a concentration of 0.1 ug/ml, Fe NPs started to show a significant toxic effect; as the concentration increased further, all three types of MNPs significantly produced cytotoxicity. This study reveals the safe range of concentration for further investigation of MNP in other possible applications.

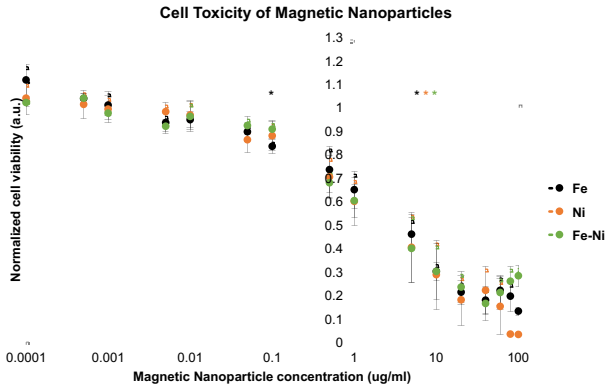

Fig. 6. Cytotoxicity of the magnetic nanoparticle with different concentrations

4 CONCLUSIONS

Graphene Platelet Networks (GPNs) were successfully synthesized on different substrate materials (including Si, Mo, and ceramic etc.), which are capable to withstand the synthesis temperature of about 800C.Good quality and high purification of CEMNs was synthesized using magnetic enhanced arc discharge plasma. It is also proved that the size distribution of the CEMNs could be controlled by the strength of the magnetic field. The cytotoxicity test of the magnetic nanoparticle has been done with Human breast adenocarcinoma cell line MDA-MB-231. An optimal concentration of CEMNs to apply to that cell was found to be 0.0001 – 100 ug/ml.

REFERENCES

[1] Novoselov, Konstantin S., et al. “a roadmap for graphene” Nature 490.7419 (2012).

[2] Geim, Andre K., and Konstantin S. Novoselov. "The rise of graphene."Nature materials 6.3 (2007).

[3] R, AI-Jishi.,et al. “lattice dynamical model for alkali-metal-graphite intercalation compounds.”Physical Review B26, 4523 (1982).

[4] W. Choi., et al. “synthesis of graphene and its applications: a review.” Critical Reviews in Solid State and Materials Sciences 35, 52-71 (2010).

[5] A. Shashurin.,et al. “Voltage-current characteristics of anodic arc producing carbon nanotubes.”Journal of Applied Physics 104, 63311 (2008).

[6] F. Ding, A. Rosén, K. Bolton, Molecular dynamics study of the catalyst particle size dependence on carbon nanotube growth. *The Journal of chemical physics* **121**, 2775-2779 (2004).

[7] J. H. J. Scott, S. A. Majetich, Morphology, structure, and growth of nanoparticles produced in a carbon arc. *Physical Review B* **52**, 12564 (1995).

[8] R. Asmatulu, M. A. Zalich, R. O. Claus, J. S. Riffle, Synthesis, characterization and targeting of biodegradable magnetic nanocomposite particles by external magnetic fields. *Journal of Magnetism and Magnetic Materials* **292**, 108-119 (2005).