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CEMNs Product With Regards

to the Magnetic Field

With Magnetic

Field

10-70

95%

Less Carbon

Impurities

raphene flakes

CEMNs

Without

Magnetic Field

10 - 120

80%

More Carbon

Impuritie

(Graphite Flakes)





Regular Article

Single-step synthesis of carbon encapsulated magnetic nanoparticles in arc plasma and potential biomedical applications



Xiuqi Fang^{a,*}, Xiaoqian Cheng^a, Yuerou Zhang^b, Lijie Grace Zhang^a, Michael Keidar^{a,*}

^a Department of Mechanical & Aerospace Engineering, The George Washington University, Washington DC 20052, USA ^b Physics Science & Engineering Department, Tongji University, Shanghai 200092, China

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1. Introduction

Magnetic Nanoparticles (MNPs) are conceptually single or multi-domain small particles with diameters of about 5-200 nm, and they can be manipulated by an external magnetic field gradient [1]. Once Brown and Neel first introduced MNPs in the 1950s [2,3], a large research field emerged. MNPs have been applied to a variety of fields including: information storage, wastewater treatment, catalyst support and biomedical applications [4–6].

ABSTRACT

A novel highly controllable process of Carbon Encapsulated Magnetic Nanoparticles (CEMNs) synthesis in arc discharge plasma has been developed. In this work, both the size distribution and the purity of the CEMNs have been made more controllable by adding an external magnetic field. It is shown that with the increase of the external magnetic field, the CEMNs get a better separation from the carbon impurities and the size distribution become narrower. This conclusion is valid for Fe. Ni and Fe + Ni CEMNs synthesis. In order to assess biomedical potential of these CEMNs, the cytotoxicity has also been measured for the human breast adenocarcinoma cell line MDA-MB-231. It was concluded that the CEMNs with the concentration in cell of about 0.0001-0.01 ug/ml are not toxic.

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Recently, nanomaterials such as Graphene, Nanotubes and MNPs have been widely used in the biomedical field and yield to great consequences [7–10]. Among all the nanomaterials however, MNPs have caught the most attention because of their unique properties. They can be used in cell labeling[11], drug delivery [12], hyperthermia [13], and Magnetic Resonance Imaging (MRI) [14] due to the following three aspects. First, they are relatively small sized in comparison with cells, viruses and proteins, which means they can get close to the biological entity of interest. Secondly, MNPs could be manipulated by a gradient magnetic field within a certain distance. This allows them to be used as a type of drug delivery system, delivering to a specified targeted area, as well as reducing the overall dosage of the toxic drug needed for

^{*} Corresponding authors.

E-mail addresses: xiuqifang@gwmail.gwu.edu (X. Fang), keidar@gwu.edu (M. Keidar).

treatment. Thirdly, MNPs could be made to resonantly respond to a time varying magnetic field, so the energy could be transferred from the excited area to the MNPs.

Generally, there are two different types of MNPs, namely Metallic MNPs and MNPs with a shell. Due to the stronger magnetic moment, Metallic MNPs are good for some technical applications such as catalyst and drug delivery agent [15]. They are very pyrophoric and reactive to oxidizing agents however, which make Metallic MNPs hard to handle during appropriate biomedical applications without inducing side reactions. In order to protect MNPs, a surface coating (gold, silica, carbon, and transition-metal oxides) can be used. Considering that gold coating is too expensive, and the covalent bonds on silica and the metal oxides are prone to hydrolysis, carbon is left to be the best option [16].

The produced MNPs need to meet 4 major requirements to be considered for a practical application: (1) Uniform (or narrow) size distribution of all particles: (2) Identical shape or morphology: (3) The same crystal structure among different particles and within the same particle (4) Dispersible; When agglomeration occurs, then the nanoparticles could be re-dispersible [17]. To meet these requirement, different methods have been developed to synthesize CEMNs including catalytic chemical vapor condensation, combustion, laser irradiation, spray pyrolysis and arc discharge plasma [18–23]. Most of these synthesis methods provide amorphous carbon shell and a low production rate which is not applicable for practical applications [24]. In comparison, CEMNs synthesized in arc discharge plasma have a relatively higher production rate, and better crystallinity due to the extremely high synthesis temperature^[25]. However, the CEMNs produced using arc discharge plasma generally contains carbon impurities, and have a wide size distribution [26].

Recently, it has been proven that an external magnetic field has influence to the nanomaterial synthesized using arc discharge plasma [27,28]. In this paper, a single-step synthesis and purification of CEMNs in arc discharge plasma has been achieved by applying an external magnetic field during the synthesis procedure. This work is mainly focused on separating the CEMNs and the carbon impurities, as well as achieving narrower CEMNs size distribution during the relatively short synthesis process. Cytotoxicity test of these CEMNs has also been done with human breast adenocarcinoma cell line MDA-MB-231, to assess the potential for the biomedical applications.

2. Experimental setup

The 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). The detailed setup could be found elsewhere. 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. The cathode is a cylindrical rod with a diameter of 13 mm, while the anode is a hollow tube with inner and outer diameters of 3 mm and 5 mm. The fillings in the hollow anode consisted of graphite flakes well mixed with metal powder (Iron Filings from Arbor scientific-fine, and Nickel from Alfa Aesar-300 mesh). The molar ratio for the anode filling is C:Fe = C:Ni = 7:90 and C:Fe:Ni = 7:45:45, respectively.

Fig. 1(a) shows the schematic of the CEMNs synthesis system in an arc discharge plasma. A divider made of stainless steel, was placed between the pair of electrodes and the magnet in order to prevent the magnet from direct exposure to the arc.

The vacuum chamber was pumped to the pressure of about 13 Pa and then high purity helium (of about 99.97% purity) was introduced into the chamber to about 67000 Pa. The arc electrodes were connected to an external DC power source at a fixed arc current of about 40 A. Before the experiment, the two electrodes were placed 2 mm away from each other with a thin copper wire connecting them. When the high current passes through the whole system, the copper wire will instantaneously evaporate due to Joule heating. This exploding wire creates a medium of metallic vapor particles between the two electrodes, which allows the arc to initiate arc discharge. The arc discharge was maintained for about 10 s after it stabilized. The sample was then kept in the chamber for an additional 20 min to cool down to room temperature.

Three different experiments have been done in order to study the size distribution of the CEMNs synthesized under different magnetic fields, namely, no magnetic field, single magnetic field and parallel magnetic field configurations shown in Fig. 1(b)–(d). The magnetic field was formed by neodymium ring magnets from K&J Magnetics, Inc. For the no magnetic field condition, a piece of copper was used as a substrate to collect the synthesized product, which was located 4 cm horizontally away from the center of the arc. For both cases with a single magnet and two magnets, the magnet's surface facing the arc was used as a substrate. The surface



Fig. 1. (a) Schematic of the plasma based carbon encapsulated magnetic nanoparticle synthesis system with the magnetic field. Schematic of the positional relationship between the (b) copper substrate, (c) single and (d) parallel magnetic field and the electrodes.

of the magnets were also placed 4 cm away from the center of the arc.

Hereafter, in order to study the influence of different metal fillings with respect to the size distribution of CEMNs, experiments including Fe, Ni, and Ni mixed with Fe for anode fillings were run. These studies were performed using a single magnetic.

The CEMNs samples were analyzed under SEM (FEI Teneo), RAMAN spectrum (Horiba), and TEM (FEI Talos) and XRD.

3. Results and discussion

3.1. CEMNs characterization

Fig. 2 shows the SEM images of the iron CEMNs with 3 different conditions: (a) no magnetic field. (b) single magnetic field and (c) parallel magnetic field, respectively. The strength of the magnetic field near the anode was measured by a gauss meter (AI Model 100) and was about 0 T, 0.06 T and 0.08 T, respectively. DLS and zeta-potential for these CEMNs were checked with MAL 1151178 NanoZS90, however, the results indicate severe agglomeration of the CEMNs. So, the size distributions of the CEMNs under different magnetic field conditions were measured through a few randomly selected SEM images representing the same sample in different parts. And the data for each type of CEMNs were processed by Image J, which comprised of about 1000 particles in total. From Fig. 2(a) one can see that without the influence of the magnetic field, the spherical CEMNs were mixed with graphite impurities. Approximately 80% of the products are CEMNs according to the SEM results. The CEMNs diameter is between 10 nm to 120 nm with most particles having 20 nm-60 nm in diameter. Fig. 2(b) shows the CEMNs produced under the influence of about 0.06 T magnetic field near the anode. It can be observed that the product is also a mixture of magnetic nanoparticles and carbon nanostructure such as graphene and graphite. Over 95% of the products are CEMNs with the influence of the magnetic field. The diameter of CEMNs is about 10 nm–70 nm and most particles are 30 nm–50 nm in diameter. Fig. 2(c) shows the CEMNs produced under a 0.08 T magnetic field near the anode. This product is more uniform and purer than the previous two products with almost no carbon impurities. (Approximately 98%+) The diameter is between 10 nm and 60 nm and most of the particles have 20 nm–40 nm in diameter.

From the results above one can conclude that applying an external magnetic field results in the shrinking of the CEMNs size distribution. This might be the result of two effects, namely the constriction of the arc discharge plasma by the magnetic field and the acceleration of the CEMNs outside the optimum growth zone [29]. With the confinement of arc discharge plasma by the external magnetic field, the plasma column become more dense and focused compared with the non-magnetic field arc discharge plasma. This leads to an increased plasma density and plasma temperature [30,31]. The second effect is that the temperature inside the growth region is generally higher than the Curie point of most of the magnetic materials during the synthesis procedure. (Curie point for Fe: 770 C, Ni: 627 C) Thus within this region, all the materials are non-magnetic. On the other hand, when the nanoparticles get out of the growth region, the plasma temperature and the nanoparticle temperature decrease significantly. The particles then show ferromagnetic or superferromagnetic behavior depending on the diameter and numbers of domains of these particles [32]. Since



Fig. 2. SEM images of the CEMNs synthesized in (a) no magnetic field, (b) single magnetic field, (c) parallel magnetic field and (d), (e), (f) show the size distributions of each condition.



Fig. 3. SEM images and the size distribution charts processed by Image J for (a) and (b) Fe; (c) and (d) Ni; (e) and (f) Fe + Ni CEMNs with the application of a 0.06 T single magnetic field.

a non-uniform magnetic field has been applied in the considered system, the CEMNs will be pushed towards the higher magnetic field during the nucleation and coagulation processes outside the growth region. This reduces the residence time and leads to the formation of smaller size CEMNs observed in our experiments. After the arc discharge was turned off, the magnet will keep attracting the CEMNs floating in the chamber, which continuously filter the CEMNs from the non-magnetic impurities such as graphite and other carbon allotropes.

In general, one can see from results shown in Fig. 2 that the size distribution and the purity of the CEMNs could be controlled by a magnetic field. Fig. 3 shows the SEM images and the size distributions of Fe, Ni, and Fe + Ni CEMNs synthesized using the same conditions mentioned in Fig. 1(c). The diameter of the CEMNs is

10 nm–70 nm (in case of Fe); 10 nm–90 nm (in case of Ni); 10 nm–90 nm (in case of Fe + Ni). The diversity of the size distributions for these three CEMNs could be sampling limitations. Moreover, Ni and Fe CEMNs growth might not be the same due to the difference in precipitation rates of Ni and Fe atoms and ions in plasma. In addition, the residence time of Ni and Fe CEMNs in the region of the growth is different leading to the different size distributions. In these cases most of the CEMNs have diameter of about 20 nm–50 nm. This analysis indicates that outlined approach can be applied to various anode fillings including nickel and a combination of nickel and iron.

Transmission Electron Microscope (TEM) has been employed to investigate the morphology, chemical composition and crystalline structure of the CEMNs. Fig. 4 (a)–(c) show the TEM



Fig. 4. TEM images for (a) Fe, (b) Ni and (c) Fe + Ni CEMNs, and the insets are the corresponding SAED patterns for each image; HRTEM images for (a) Fe, (b) Ni and (c) Fe + Ni CEMNs, and the insets are the expanded view of the highlighted area for each image respectively.

images of the Fe, Ni, and Fe + Ni CEMNs and their corresponding Selected Area Electron Diffraction (SAED) patterns. Fig. 4(d)–(f) show the High Resolution TEM (HRTEM) of the Fe, Ni, and Fe + Ni CEMNs respectively; with inserts that are the expanded views of the highlighted areas for each image. All the images were taken under 200 kV TEM or HRTEM condition. It can be observed that all of the considered nanoparticles have identical round shapes and every individual particle has a metal core tightly wrapped by a uniform carbon shell. Due to the fact that the uniform carbon shell seals the metal cores, the CEMNs are able to remain stable in the air for months. Majetich has explained this phenomenon in 1995 that both the metal material and carbon are atomized in the plasma due to the extremely high plasma temperature. (over 3000 K) And then they nucleated into clusters. Finally, by phase segregation during the cooling procedure, the carbon coating on the particle exterior is formed [22]. The thicknesses of the shells are different for each type of CEMNs (Fe: 5 nm shell; Ni: 2.5 nm shell; Fe + Ni: 3 nm shell). This is because Fe powder has a smaller mesh than the Ni powder, and the spacing in between the Fe powder allows more graphite powder to fill in. This enables graphite powder to be better mixed with Fe powder, and allows more carbon to be involved in the shell forming procedure. Some of the metal cores for CEMNs are single domain and others share multi-domain such as the Fe + Ni CEMN showing in Fig. 4(c). Both SAED patterns and the expanded view of the highlighted area indicate that each CEMN captured by the HRTEM shares a relatively uniform crystal lattice.



Fig. 5. STEM images for (a) Fe, (e) Ni, (i) Fe + Ni CEMNs and the insets shows the line elemental scan of these CEMNs, respectively; (b)–(d) show the EDX mapping (Fe, Ni and O) for Fe CEMNs, (f), (g), and (h) show the EDX mapping (Fe, Ni and O) for Ni CEMNs and (j), (k), and (l) show the EDX mapping (Fe, Ni and O) for Fe + Ni CEMNs.

After identifying the composition and the crystal lattice of the cores for the CEMNs, an Energy Dispersive X-ray spectroscopy (EDX) equipped with Scanning Transmission Electron Microscope (STEM) has been used for the elemental analysis. Similar to SEM, the STEM scans a very finely focused beam of electrons across the sample. The advantages of the STEM over SEM is enabling the use of other signals such as secondary electrons, scattered beam electrons, characteristic X-rays and electron energy loss. The STEM can also provide an improvement in spatial resolution.

Fig. 5 shows the EDX elemental analysis for Fe, Ni and Fe + Ni CEMNs. Fig. 5(a), (e) and (i) are the STEM images for the CEMNs and the inset images are the corresponding line elemental scans marked by the yellow arrows. Fig. 5(b)-(d) shows the EDX elemental mapping for Fe CEMNs. Fig. 5(f)-(h) are the elemental mappings for Ni CEMNs meanwhile, Fig. 5 (j)–(l) are for Fe + Ni CEMNs. With this result, one can see that the nanoparticles consist of a solid metal core and the shells are doped with oxygen elements on top of the carbon shell. From the line scan it is obvious that the metal line has a curved shape, which represents the spherical structure of the metal core. The relatively flat line for carbon represents the somewhat uniformed carbon shell, which encapsulated the metal core. For the Fe + Ni CEMNs, we can tell from the elemental line scan that the amount of Ni and Fe of each particle contain is relatively the same. This result applies to most of the Fe + Ni CEMNs regardless of the particle size. Although the iron-nickel proportion can be slightly different in each CEMNs, none of the particle was



Fig. 6. XRD pattern of (a) Fe, (b) Ni and (c) Fe + Ni CEMNs.

found containing single elemental core. It is because both Fe and Ni vapor in the plasma arc zone cool down with the same path during the particle forming procedure, which lead to the fact that Fe and Ni exist uniformly in the CEMNs.

Fig. 6 shows the XRD pattern of these three different kinds of CEMNs. All CEMNs have a well-defined crystalline structure. The peak 2θ of about 26.5° corresponds to the (0 0 2) plane of graphite, which indicates the carbon shell consists of a graphite structure. (PDF#41-1487) Fig. 4(a) shows the XRD pattern of the Fe CEMNs. The peak at 2θ of about 44.7° is corresponding to the (1 1 0) plane of Fe which indicates that the Fe CEMNs has a bcc crystal structure of Fe phase. (PDF#06-0696) The other small 20 peaks including 31.17°, 35.68°, 43.3°, 57.4° are corresponding to (206), (119), (0012) and (1115) diffraction lines of Fe₂O₃ phase. (PDF#25-1402) So the metal core of the Fe CEMNs consists of pure Fe and Fe₂O₃, with the Oxygen atoms coming from the rust in the iron fillings. Fig. 4(b) shows the XRD pattern of the Ni CEMNs. The peak at 2θ of about 44.5° and 51.8° are corresponding to the $(1\ 1\ 1)$ and (200) plane of Ni which indicate that the Ni CEMNs has an fcc crystal structure of Ni phase. (PDF#04-0850) The Ni CEMNs do not have any other small peaks, which indicate that the core structure of the CEMNs is pure nickel, and has good crystalline nature. Fig. 4(c) shows the XRD pattern of the Fe + Ni CEMNs. The peak at 20 of about 44.5° and 51.8° are also corresponding to the $(1\ 1\ 1)$ and $(2\ 0\ 0)$ plane of Ni. The other small 2θ peaks including 43.47° and 50.67° are corresponding to (1 1 1) and (2 0 0) diffraction lines of Taenite (Fe,Ni) alloy phase. Taenite is a type of Fe alloy, which contains iron (55%-80%) and nickel (20%-45%). From the XRD pattern for Fe + Ni CEMNs, one can see there are only Ni and Fe, Ni patterns. This indicates that all the iron in the anode filling turns into Taenite, and that the core of the particle is a mixture of Fe, Ni and Ni [33].

In order to test the magnetic property of the CEMNs, a small amount of CEMNs sample and 5 ml methanol were added to a glass bottle. Then, a Fisher scientific Model 150 ultra-sonicator was used to sonicate the solution for about 5 min with amplitude of 50%. As the CEMNs suspension was formed, we placed a magnet next to the glass bottle as shown in Fig. 7 (b).

The dark suspension slowly becomes lighter with the influence of the magnet after 40 s and CEMNs could be observed gathering near the magnet i.e. in the region of a strongest magnetic field. After 200 s of magnetic field influence, it can be observed that all of the CEMNs congregate at the position that the magnet was placed. From this simple experiment, these CEMNs are proven to have ferromagnetic properties that can be attracted and manipulated by a gradient magnetic field. In the mean time, according to the DLS and zeta potential analysis, this phenomenon is also due to the aggregation states of the CEMNs.



Fig. 7. (a) Suspension of the CEMNs with methanol, (b) magnet was placed next to the glass bottle for 40 s (c) magnet was placed next to the glass bottle for 200 s (d) and after the magnet was removed from the glass bottle at 200 s.

3.2. Cytotoxicity test

The human breast adenocarcinoma cell line MDA-MB-231 was used to test the cytotoxicity of these CEMNs. Cells were cultured using Dulbecco's Modified Eagle Medium (DMEM) (Thermo Fisher Scientific, Waltham, MA) supplemented with 10% heat inactivated fetal bovine serum (FBS) (Thermo Fisher Scientific, Waltham, MA) and 1% Penicillin-Streptomycin (Thermo Fisher Scientific, Waltham, MA) at 37 °C with 5% CO₂. At around 80% confluence, cells were detached using 0.25% trypsin-EDTA (Thermo Fisher Scientific, Waltham, MA) and sub-cultured into 96-well plate (Corning, NY) at a concentration of 3000 cells per well. Cells were allowed to incubate for 24 h prior to nanoparticle treatment. Fe, Ni, and Fe + Ni CEMNs synthesized within 24 h were suspended in phosphate buffer saline (PBS) (Lonza, Walkersville, MD) and sonicated using Fisher Scientific Model 150 sonicator at amplitude of 50% for 5 min at room temperature to avoid agglomeration prior to the administration. The sonicated CEMNs solution was then filtered using 70 um cell strainers to dispose the CEMNs clusters, and diluted to the concentrations of 0.0001-100 ug/ml. Right after the CEMNs administration, cells were incubated for 72 h to allow complete nanoparticle uptake and cellular activity.

The viability of MDA-MB-231 cells after 72 h treatment of CEMNs was measured using MTT (3-[4,5-dimethylthiazol-2-yl]-2, 5-diphenyltetrazolium bromide; thiazolyl blue) assay. MTT powder was purchased from Sigma-Aldrich (St. Louis, MO), and dissolved in cell culture media at a concentration of 5 mg/ml. The media with CEMNs was removed from each well and replaced with 100 μ l dissolved MTT solution, and incubated for 3 h at 37 °C with 5% CO₂. At the end of the incubation period the solution was removed, and the converted dye was solubilized with acidic isopropanol (0.04 N HCl in absolute isopropanol). Absorbance of converted dye is measured at a wavelength of 570 nm with background subtraction at 690 nm using Synergy HT Microplate Reader (BioTek, Winooski, VT).

All the data represented are means \pm standard error of the mean of three independent experiments made in three replicates. Statistical significance was determined by student *t*-test. Significance was ascribed at p < 0.05 (*). Fig. 8 shows cytotoxicity of the magnetic nanoparticle with different concentrations. In this study, MTT assay was used to access the cytotoxicity of the three types of CEMNs. All data was normalized to the viability of cells without CEMNs treatment. The figure indicates that the CEMNs exert significant cytotoxicity to MDA-MB-231 cells in dose-dependent manner in the concentration range of 0.0001– $100 \mu g/ml$: cells were barely affected by any type of CEMNs in the range of $0.0001-0.05 \mu g/ml$; at a concentration of $0.1 \mu g/ml$, Fe CEMNs started to show a significant toxic effect; as the concentration increased further, all three types of CEMNs significantly produced cytotoxicity. This study reveals the safe range of concentration for further investigation of CEMNs in other possible applications such as MRI, cell migration control, and drug delivery, etc.

4. Concluding remarks

Based on previous approaches synthesizing CEMNs with arc discharge plasma [23,34,35,36], our group is able to produce uniform spherical CEMNs with clear crystal lattice and less carbon impurities. The size distribution of the CEMNs could also be controlled by applying an external magnetic field. With the influence of a 0.06 T from a single permanent magnet, the average size of CEMNs was found to be 20 nm-60 nm. Using stronger magnetic field of about 0.08 T with two parallel magnets, it was observed that the CEMNs diameter decreases to 10–50 nm. This approach can be applied to Fe, Ni, and Fe + Ni CEMNs synthesis, which offer new possibility for controllable plasma-based synthesis of stable magnetic nanoparticles. It was argued that in magnetically enhanced arc discharge plasma, the reduction of the residence time in the growth region is the key fact for the formation of small sized and more uniform CEMNs. Since nanoparticle is coated with carbon it also provides stability and biocompatibility. In order to assess the potential biomedical application for these CEMNs, the cytotoxicity of CEMNs has also been tested using the Human breast adenocarcinoma cell line MDA-MB-231, and the safe concentration for the CEMNs apply to that cell was found to be $0.0001-0.01 \,\mu g/ml$. This result proves that certain dosage of the CEMNs could be used in biomedical applications including MRI, cell migration control, hyperthermia, and drug delivery.

Cell Toxicity of Magnetic Nanoparticles



Fig. 8. Cytotoxicity of the magnetic nanoparticle with different concentrations.

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