Journal of Colloid and Interface Science 509 (2018) 414–421

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

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

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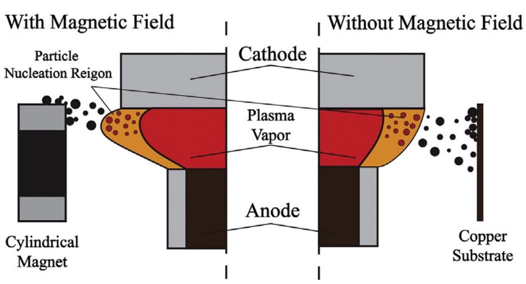
GRAPHICAL ABSTRACT



CEMNs Product With Regards to the Magnetic Field

	With Magnetic Field	Without Magnetic Field
CEMNs Size Distributions (nm)	10- 70	10 - 120
Purity of the CEMNs	95% Less Carbon Impurities (Graphene flakes)	80% More Carbon Impurities (Graphite Flakes)

ARTICLE INFO

Article history:
Received 27 June 2017
Revised 30 August 2017
Accepted 1 September 2017
Available online 7 September 2017

Keywords:
Arc discharge
Synthesis
CEMNs
Biomedical

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.

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].

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

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http://dx.doi.org/10.1016/j.jcis.2017.09.015
0021-9797/

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

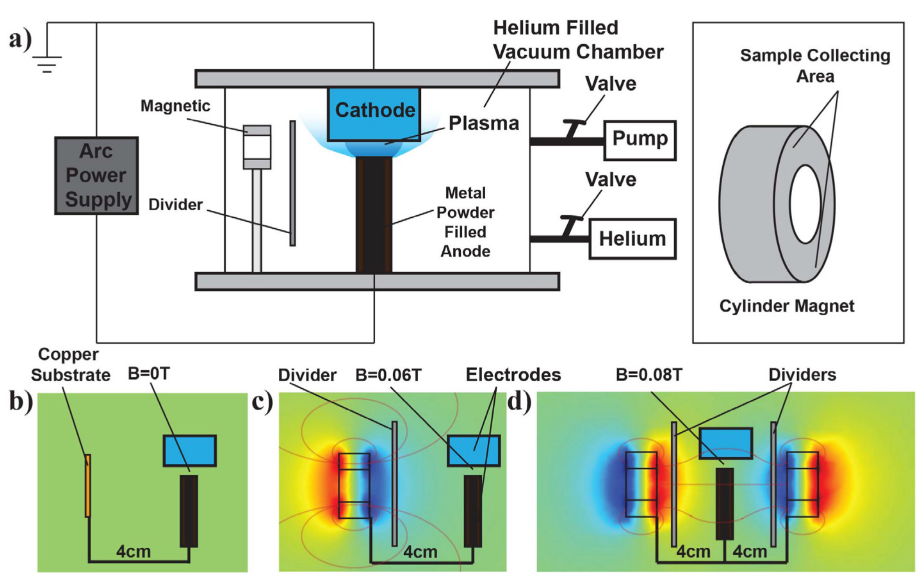

Fig. 1. (a) Schematic of the plasma based carbon encapsulated magnetic nanoparticle synthesis system with the magnetic field. Schematic of the positional relationship between the (b) copper substrate, (c) single and (d) parallel magnetic field and the electrodes.