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Review Article

Stable Room-Temperature Magnetic Carbon/Graphite: From Discovery to Bionanotechnological Applications

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Abstract

Almost two decades ago, we reported - and patented - by the first time on a simple chemical route aiming to synthetize stable room-temperature magnetic bulk carbon/graphite. We obtained the experimental confirmation that its magnetism originates from defects in the structure (and not from ferromagnetic impurities) from direct measurement of the local magnetic field using ^{13}C nuclear magnetic resonance associated to the numerical results obtained from DFT (*Density-Functional theory*) calculations. We have also developed the chemical synthesis route to obtain nanofluid magnetic carbon/graphite. In this short review of our own work, we briefly show these findings as well as the main physical and chemical properties of this material and recent results aiming biotechnological and medical applications. From theoretical calculation, we have analyzed its possible use as a contrast, for example, in the MPI (*Magnetic Particle Imaging*) technique. Finally, we show here the potential of this material to be used as a drug carrier to reach different targets like those associated with cancer, diabetes and Alzheimer by using what we have called MAGUS® (*Magnetic Graphite Universal System*).

Keywords: Magnetic carbon; Drug carriers; Magnetic particle imaging

Introduction

Over the last twenty-five years, the survey for macroscopic magnetic ordering phenomena in organic materials has been one of the most exciting and interesting subjects in both Physics and Chemistry. Achieving striking properties in macroscopic stable room-temperature bulk magnetic carbon/graphite (MG) could open an enormous number of novel applications. The possibility of nanostructured magnetic materials of this type has increasingly attracted the interest of the scientific community, not only because of their physical and chemical properties but mainly because of their potential applications in high-tech devices. Thus, obtaining macroscopic quantities of MG has been of fundamental and general interest. Throughout the past two and half decades, the work done in this subject by Makarova et al. [1], Esquinazi et al. [2], among many others is plenty of strong experimental and theoretical results showing the Physics and Chemistry of MG samples. This novel and inexpensive chemical route we have reported in 2005 and 2006 [3,4], allows to obtain macroscopic quantities of MG samples and it consists of a controlled chemical etching on the graphite structure, performed by a *redox* reaction in a closed system between pure carbon/graphite and copper oxide (CuO). X-ray diffraction measurements suggest that this MG could be represented by the coexistence of a matrix of pristine graphite and a foamy-like carbon/graphitic structure compressed along the *c*-axis. At T = 300K, the saturation magnetic moment, the coercive field and the remnant magnetization are 0.25emu/g, 350Oe and 0.04emu/g, respectively. In addition to that phase transition at 300K, we have also observed a low-temperature anomaly in the dependence of the zero-field-cooled magnetization in MG with an average granular size L of about 10nm.

We have attributed it to the manifestation of the size effects below the quantum temperature $T_L \alpha \hbar^2/L^2$ and is well fitted by a periodic function proportional to the bulk magnetization and the thermal de Broglie wavelength [5]. Related to that behavior, we have proposed a theoretical interpretation for both intragranular and intergranular contributions based, respectively, on super-exchange interaction between defects induced localized spins in a single grain and proximity mediated interaction between grains through the barriers created by thin layers of non-magnetic carbon/graphite [5]. We obtained the experimental confirmation that magnetism in MG originates from defects in the structure (and not from ferromagnetic impurities of any type) from direct measurement of the local magnetic field using ^{13}C nuclear magnetic resonance associated to the numerical results obtained from DFT (*Density-Functional Theory*) calculations. These experiments allowed us, for the first time, to directly evaluate the local hyperfine magnetic field in MG samples corroborating the intrinsic nature of the magnetism. A comparison of the experimental hyperfine fields to DFT calculations showed reasonable agreement, supporting the view that magnetism originates from various defects in the material structure [6].

As we all know, potential nano-systems for uses in biological, biotechnological and medical applications are the so-called nanofluids defined as fluids containing suspended solid nanoparticles with different sizes. A most recognizable class of magnetically controllable nanofluid simultaneously exhibiting both fluid and magnetic properties is the ferrofluid. This consists of a suspended colloidal fluid of nanosized iron oxide (Fe_3O_4 or g-Fe_2O_3) particles frequently called SPIO (*Superparamagnetic Iron Oxides*). These are a class of Magnetic Resonance Imaging (MRI) contrast agents composed of nanoparticles of iron oxide crystals coated in carbohydrates. Instead of SPIO and aiming for applications of MG in medicine and other biotechnology related areas, we have developed the chemical synthesis route of Nanofluid Magnetic Graphite (NFMG)[7]. We have obtained it from previously synthesized MG samples by stabilizing the aqueous fluid suspension with an addition of an active cationic surfactant. The structural analysis of NFMG (with average particle size of about 10nm) confirmed its stability in aqueous solution. By measuring the magnetization as a function of temperature and applied magnetic field in both MG and NFMG samples, we observed the typical ferromagnetic behavior. The comparative study unambiguously demonstrated that, after the chemical treatment, both MG and NFMG as well as all its suspensions (prepared with acetone, CTAB and water) exhibit a stable net magnetization at room temperature. Studying these samples of NFMG we have also observed unusual magnetic properties at low temperatures [8]. There, the measured magnetization exhibits an anomaly that we have attributed to the manifestation of quantum size effects below 50K, the quantum temperature T_L, mentioned before. It also exhibits pronounced temperature oscillations above T_L attributed to manifestation of the hard-sphere type of pair correlations between ferromagnetic particles in the nanofluid above that temperature. Since the magnetic behavior of NFMG is important for possible biological, biotechnological and medical applications of MG, we have also studied its stability issues and the structure-sensitive magnetic properties. All samples where with an average particle size of the order of 10nm. The obtained highvalues of the Zeta potential (reaching 40.5mV, 41.7mV and 42.3mV for pH levels equal to 6, 7 and 8, respectively) indicated a good stability of the dispersed solution. A rather strong reactivity between nanofluid ingredients and the cationic surfactant was evidenced by using DRIFT (*Diffuse Reflectance Infrared Fourier Transform*) spectroscopy. The measured hysteresis curves confirm a robust ferromagnetic behavior of all NFMG samples at room temperature. The observed structure of sensitive temperature oscillations of the magnetization is interpreted as a strongly coherent thermomagnetic response of the nanofluid which is important for its applications in biology, biotechnology and medicine [9,10].

A first possible question arising here is if this NFMG could be used as a contrast, for example, for using in the so-called MPI (*Magnetic Particle Imaging*) technique. We have already answered this question [11]. The image quality using the NFMG is comparable or even better than for superparamagnetic nanofluids. It shows more edged and less blurred results. This may be attributed to the existence of a remnant magnetization of the ferromagnetic particles. However, due to the currently low saturation magnetization of the NFMG the generation of a strong MPI signal will only be possible in the future when high concentrations will be obtainable.

A second possible question is if MG could be used as a drug carrier. We have also answered this question. We have developed a new magnetic bio-hybrid system for potential application in drug delivery from the assembly of the biopolymer alginate and MG nanoparticles [12]. The drug *Ibuprofen*® (IBU) intercalated in a Mg-Al Layered Double Hydroxide (LDH) was chosen as a model of Drug Delivery System (DDS) to be incorporated as a third component of the magnetic bio nanocomposite DDS. The IBU was incorporated either as the pure drug or as the LDH-IBU intercalation compound and processed as beads or films for application as drug release systems. The presence of MG nanoparticles improved the physical and mechanical properties of the resulting bio nanocomposites, decreasing the speed of drug delivery due to the protective effect as a physical barrier against water absorption into the beads. The control on the release rate was specially improved when the drug was incorporated as the LDH-IBU intercalation compound, being this fact attributed to the additional physical barrier afforded by the inorganic layered host solid. These bio nanocomposite systems could be also stimulated by an external magnetic field, enhancing the levels of the released IBU, which would be advantageous in order to modulate the dose of released drug when required. This new magnetic DDS could be used for immobilization of other drugs and enzymes, but also as wound dressings or as scaffolds in tissue engineering, as they could be also processed as foams, for uses in controlled drug delivery.

Finally, since the development of a new and efficient drug delivery system is as important as the discovery of a novel active

molecule, we have built the unprecedented particle named MAGUS®, an acronym for *Magnetic Graphite Universal System*. We have assembled an innovative and promising system composed by a biocompatible nanostructured MG particle coupled with different molecules *simultaneously*. In the worldwide, infections contribute significantly to the emergence of cancer. Approximately twenty-three percent of cancers are a result of infections, in developing countries. Taking that into consideration, initially we successfully assembled the system by using anticancer antibody and two new metabolites – antimicrobial and anticancer peptides - targeting to fight gastric cancer and *Helicobacter pylori* infection at the same time**.** Before using the anticancer peptides, we have efficaciously verified the concept and well-functioning of this complex carrier by using the nanostructured biocompatible MG functionalized with different anticancer antibodies and an anticancer drug commercially available. At present moment, we are functionalizing the nanostructured biocompatible MG with radioactive particles of Iodine-131 for thyroid cancer treatment, and the corresponding anticancer antibodies. It is important to highlight that, through the use of the interaction antigen-antibody and the possibility of magnetically directing the magnetic functionalized MG by using an external magnetic field, we are giving to our drug delivery system a *double way* to reach just the target, i.e. the cancer, and not the healthy cells. In short, we are giving specificity to the delivery system through our MAGUS as a pioneering way to treat cancer. Something that conventional drugs and other treatments do not have at all. Now, we are testing MAGUS® to fight diabetes and Alzheimer disease following similar methodologies.

In conclusion, the magnetic carbon/graphite we synthesize by the first time by following an unprecedent simple chemical route, appears as a very promising way to achieve different valuable goals mainly in biotechnology and medicine areas.

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Conflict of Interest

We declare that do not exist any financial or interest conflicts.

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