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Original Research Paper

Plasma synthesis of carbon powder with embedded Fe_3C nanoparticles for magnetic separation of biomolecules

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ABSTRACT

In this article we report the synthesis of a carbon powder with embedded magnetic nanoparticles. Precursors, ferrocene and ethylene glycol, were loaded in a quartz combustion tube and pyrolysed by microwave plasma under vacuum conditions. The synthesized powder was similar to graphite in texture, but strongly attracted by magnetic fields. Several analytical techniques were carried out, including X-ray Photoelectron Spectroscopy, Transmission and Scanning Electron microscopies, X-ray Diffraction and BET isotherm. The resulting material is a ramified framework of carbon, similar to activated carbon, with embedded Fe_3C/C core-shell nanoparticles. BET analysis gives a type IV isotherm, common for mesoporous adsorbents. A protocol was developed for the purification of nucleic acids by magnetic separation. The material gives satisfactory results for DNA extraction. It is concluded that due to the non-toxicity nature of the C shells and the outstanding magnetic property of the Fe_3C nanoparticles this absorptive carbonaceous material can be applied in fields of biomedicine or biotechnology.

1. Introduction

Magnetic separation is a process in which a magnetically susceptible material is extracted from a mixture using magnetic force. This technique was first implemented in the extraction of iron and has migrated to nanotechnology [1–3]. Cells or biological molecules can be intentionally attached to a magnetic carrier through physical interactions, and once immobilized in it, they can be separated from a solution and transported to the desired place by fields of external magnets [4]. After the intentional interruption of the interaction between the magnetic carrier and the immobilized molecule, this method of isolation offers the possibility of recovering and then reusing the magnetic carrier.

Now magnetic separation plays an important role in biology, where the benefit is the simplicity it confers to the manipulation of biomolecules [1]. Magnetic separators are applied for time-consuming tasks, for example in the extraction and purification of DNA. DNA extraction is done in a two-step process, involving (i) attaching DNA entities to a magnetic material and (ii) separating out the DNA via a fluid-based magnetic separation device. Specific protocols should be designed to accomplish these two tasks. The magnetic carrier is typically a nanostructured composite specifically intended for such purpose, and consists of a magnetic phase and an absorbent agent [4]. Traditional magnetic materials, like magnetite (Fe_3O_4), are frequently used for that aim. Iron oxide nanoparticles have useful characteristics, among them, good dispersibility, high surface area, and reversible-controllable flocculation [4]. The binding of biomolecules to magnetite is possible through chemical modification of nanoparticle surface by coating it with a biocompatible material [5]. It has been shown that covering magnetite with SiO_2 shells yields surfaces that can be subsequently functionalized, enabling chemical connectivity, or coupling, with other organic molecules [6]. SiO_2 shells also improve the chemical stability of nanoparticles and reduce the toxicity of the magnetic cores [7]. Thereafter, a magnetic core with a protective shell is suitable for the purpose, where the shell has to have affinity to DNA. The Fe_3O_4:SiO_2 core-shell nanostructures achieve this task.

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A much less studied material for magnetic extraction of biomolecules is iron carbide (Fe_3C) [8]. The magnetic properties of carbon encapsulated Fe_3C nanoparticles have been studied in several works [5,9–13]. From these works can be concluded that the Fe_3C/C composites have higher magnetic saturation in comparison with the magnetite/SiO_2 core-shell nanostructures; these also show low toxicity. The Fe_3C/C core-shell nanoparticles can be synthetized by chemical and physical processes [8,11–20]. Different methods have been reported for their synthesis, among them are hydrothermal reaction [20], carbothermal reduction method [17], sol-gel [13], sonochemistry [15], electric plasma discharge [19], detonation [13], pyrolysis [11] and chemical vapor deposition [8]. Disadvantages related to some of the above approaches are the high amount of impurities, formation of unstructured material, low yields, or complicated procedures that need a large amount of time for obtaining the final material or high energy heating sources to achieve high temperatures. Some of the above methods require specialized and expensive equipment, or the use of reducing atmospheres (hydrogen gas) or expensive reactants. Due to the potential uses of these magnetic materials in areas such as ferrofluids, medical imaging, drug targeting and delivery, cancer therapy, separations, and catalysis [6], it is desirable to devise a straightforward method allowing its synthesis in large quantities. In this paper we present a direct and low cost route for the synthesis of Fe_3C/C core–shell composite by a plasma method. The procedure can be scaled for high volume synthesis. The experimental section begins with a description of a microwave plasma reactor in which the direct reaction between ferrocene and ethylene glycol takes place. In the results section there is evidenced that this route generates a composite with embedded Fe_3C/C nanoparticles with characteristics comparable to the methods mentioned above [5,8–14,16,18,20]. We have considered appropriate to include a magnetic extraction of nucleic acids with the use of the synthesized powder. The aim of this work is, therefore, to present the synthesis of magnetic absorptive nanocomposite with a process that can be scaled-up for production at industrial level.

2. Experimental methods

2.1. Reactor description

The low pressure plasma reactor includes a vacuum chamber containing the reactants to be energized to form the plasma. In this implementation the chamber is a fused silica micro-combustion tube (one closed end) from QSI Quartz Scientific, Inc. The dimensions of the combustion tube are: length 300 mm, OD 25 mm and wall thickness 1.5 mm. Fig. 1 shows a photograph of the reactor. It is based on a conventional kitchen microwave oven (Daewoo, 1000-watt output power) that was modified with a 25.4 mm hole at the ceiling wall. An electrical grounded metal chimney was placed at the top to protect the user from leaking microwaves. The combustion tube top-end is the vacuum port. It is connected to a cyclonic separator whose purpose is to trap particles that might flee from the plasma zone. A modified zeolites sorption pump is located downstream; this pump is to preventing the small size particles to reach the principal vacuum system by reducing its kinetic energy through multiple collisions with low temperature surfaces. The system exhibited in Fig. 1 is equipped with an optional turbo molecular pump (75 L s^{-1}). The main pump is a 3.5 CFM vane pump. Great care has been taken to avoid the eluded particles to reach the turbo and mechanic vacuum pumps. We keep away from using membranes as filter because of their tendency to get clogged in short times. The pressure of the system is monitored with a pirani vacuum gauge located at the output of the cyclonic separator. The system components are connected through stainless steel flexible hoses.

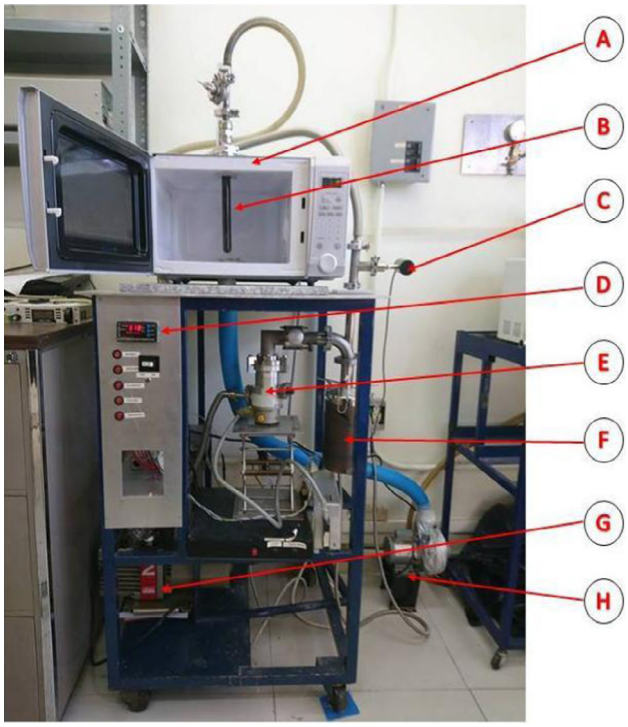

Fig. 1. Photograph of the actual reactor. (A) Microwave oven; (B) micro combustion tube; (C) vacuum gauge; (D) vacuum display; (E) turbo molecular pump; (F) zeolites trap; (G) vane pump; (H) forced air cooling fan. Cyclonic separator is not shown.

2.2. Material preparation

The samples reported in this work were prepared by mixing 1 g of ferrocene with 0.5 ml of ethylene glycol. The mixture was homogenized by stirring and placed in the combustion tube. The reactor was evacuated to a pressure of 1.5 Torr, after that the power was applied for 2 min at 1000 W (nominal). The product was recovered by scraping the tube interior with a plastic spatula. The recovered material was dissolved in alcohol using an ultrasonic bath. The magnetic material was separated from the solution by the use of a rare-earth magnet and the nonmagnetic material was discharged. The final powder was dried at room temperature.

2.3. Material characterization

The powders were observed in a scanning Jeol JSM-5300 microscope with an auxiliary Noran Superdry II Energy Dispersive X-ray microanalysis (EDX) unit. Afterwards, samples were analyzed by X-ray diffraction (XRD) using the Cu K_α line in a Philips diffractometer, model X'pert. Raman measurements performed at 532 nm @ 50mW in an Avantes Instrument. X-ray Photoelectron Spectroscopy (XPS) were carried out in a Specs system with a monochromatic X-ray Al-k source (1486.6 eV) and wide angle analyzer (200 eV pass energy, 1 eV step energy and dwell time 0.1 s). Transmission Electron Micrographs (TEM) were acquired using a Jeol JEM2010 instrument operated at 200 keV. The specific surface area and pore size were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods [21], respectively for N_2 adsorption at 77 K, using a Autosorb-1 from Quanta Chrome Instruments.

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