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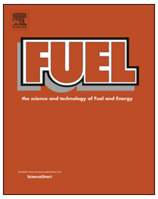

Full Length Article

Application of featured microwave-metal discharge for the fabrication of well-graphitized carbon-encapsulated Fe nanoparticles for enhancing microwave absorption efficiency

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ABSTRACT

Carbon-encapsulated iron nanoparticles (Fe@CNPs) with a high degree of graphitization, good integrity in the graphite shells, and high microwave-absorbing capability were prepared by first dissolving ferrocene into organic solvent and then being carbonized by MW-metal discharges under inert atmosphere. Four different organic solvents (benzene, cyclohexane, paraffin, and anhydrous ethanol) were tested, and well-graphitized Fe@CNPs were formed when using benzene or cyclohexane as the solvent. The use of MW-metal discharges with low-toxic cyclohexane and ferrocene as raw materials provides a new method for the preparation of Fe@CNPs with the merits of simplicity, low environmental impact, and high efficiency. The fabricated Fe@CNPs have excellent microwave-absorbing capability, which is respectively 29, 19.3, and 9.7 times those of carbonyl iron powder, SiC, and carbon nanotubes after 1-min microwave irradiation at 1000 W. The thermal gravimetric analysis demonstrates that the fabricated Fe@CNPs have good thermal stability. Owing to these properties, Fe@CNPs have the potential to shape nanoscale or micron scale high-energy sites for a vast variety of applications in the field of microwave chemistry.

1. Introduction

Since the discovery of fullerene (C60) by British and American scientists in 1985 [1], carbon nanoscience has been developing rapidly. The growing list of new carbon nanomaterials include: carbon nanotubes (CNTs) [2], carbon nanofibers [3], graphene [4], nanodiamonds [5], and carbon nanocomposites [6]. As a special kind of carbon nanomaterial with unique core-shell structure, carbon-encapsulated metal nanoparticles (M@CNPs, M = Fe [7,8], Ni [9–11], Co [12], FeNi [13,14], FeCo [15], FeNiMo [16], etc.) are attracting increasing interests due to their excellent magnetic response, unique chemical and thermal stability, large specific surface area, good biocompatibility, outstanding catalytic activity, and excellent electrical and optical properties [17]. As a result, M@CNPs have been widely studied and applied in magnetic materials [18], magnetic resonance imaging (MRI) [19], battery technology [20–22], catalysis [23–25], energy storage and conversion [26,27], supercapacitors [28], biomedical applications [29], environmental protection [30], and civil engineering [31].

As composite materials, M@CNPs with core–shell structures could have higher microwave-absorbing capability compared with single-component materials, especially when the metal particles are magnetic. Magnetic metallic nanomaterials can effectively dissipate electromagnetic wave via conductive loss and magnetic loss, since they have both relatively high conductivity and high complex permeability. However, the metallic nanomaterials are obviously deficient in dielectric loss. A nanocarbon shell not only protects the inner metallic nanoparticle from oxidation, corrosion, agglomeration, and degradation [32]; but also can make up the deficiency in dielectric loss due to its excellent dielectric characteristics. Therefore, M@CNPs not only can be applied in complex or harsh environments, but also display stronger electromagnetic wave absorption via the collaborative coupling of magnetic metallic core and dielectric carbon shell. As an excellent microwave absorber, M@CNPs are used as electromagnetic interference shielding and absorption materials in civil and military fields, and they also have the potential to promote a variety of microwave-assisted chemical reactions via shaping nanoscale or micron scale high-energy sites (normally termed as “hot spots”).

Traditional methods for preparing M@CNPs include arc discharge, chemical vapor deposition (CVD), pyrolysis, liquid-phase infiltration-carbonization process, and so on. However, these methods have some limitations. For example, the process of arc discharge is complicated and usually accompanied by the generation of many impurities, the

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Table 1
Organic solvents and their properties.

Name	Chemical formula	molecular weight	Dielectric constant	Ferrocene solubility	Density/g cm^{-3}	purity	Melting point	Boiling point	viscosity/mPa s
Benzene	C_6H_6	78.112	2.3	Soluble	0.8765	99.5%	5.5 °C	80.1 °C	0.604
Liquid paraffin	–	–	2.2–4.7	Insoluble	0.87–0.98	IR class	− 24 °C	> 300 °C	4.35–13.92
Anhydrous ethanol	C_2H_6O	46.068	24.3	Slightly soluble	0.7893	99.5%	− 114 °C	78.2 °C	1.074
Cyclohexane	C_6H_{12}	84.16	2	Soluble	0.7739	99.5%	6.5 °C	80.7 °C	0.894

reaction products prepared by CVD are not easy to separate from the catalysts, the pyrolysis method has high requirements for materials and process conditions, and the liquid-phase infiltration-carbonization process has the drawbacks of low yield and high energy consumption [33,34]. Therefore, it is necessary to develop new methods to overcome these limitations.

Here, we put forward a featured method to prepare high-purity M@CNPs via decomposing organometallic compounds by microwave-induced discharges (MID). When metals with sharp edges or tips, or submicroscopic irregularities are subjected to microwave irradiation, intense discharge phenomena (usually electric corona, sparks or arcs) may occur [35–37]. These phenomena have attracted specific attention in recent years, and their profound mechanisms are being unveiled. Owing to the high frequency of microwave radiation, the discharge process is intermittent or "pulsed" in nature, characterized by several discharge cycles in one minute. In each discharge cycle, the electrons are excited and accumulated in the metal tips first, and then escape from metal when they accumulated enough energy in an electromagnetic field, inducing a discharging process with the instant release of energy, shaping the local hot spots. After that, the electrons relax back to their original state and prepare for the next discharging process, while the hot spots are cooled by the surrounding medium at a lower temperature. Thus, the discharging process produces intense heating and plasma effects followed by a cooling process [35]. This special mode of discharging is very suitable for the preparation of high-purity well-graphitized M@CNPs. It can provide sufficient energy to break down the organometallic compounds into elemental metal atoms and carbon species. During the subsequent cooling process, metal/carbon core/shell structures are formed as the carbon species form graphite shells. Owing to the lack of sustained high temperature, the generation of long CNTs byproduct can be effectively reduced, leading to the fabrication of high-purity M@CNPs. Chen et al. [37] have investigated the discharge phenomena of metal-solvent mixtures under microwave irradiation, and found that the discharge process was often accompanied by the decomposition of solvents and the formation of graphite materials, which laid the foundation for preparing M@CNPs by microwave-metal (MW-metal) discharges in organic solvents. If we can find the suitable combination of organometallic compound and organic solvent (termed as "organometallic-solvent system") and optimize the discharge process therein, it is possible to develop a simple, environment-friendly, and highly efficient method for preparing M@CNPs.

In this paper, carbon-encapsulated iron nanoparticles (Fe@CNPs, for short) were fabricated by utilizing MW-metal discharges in different organometallic-solvent systems. Ferrocene was chosen as the suitable organometallic compound since it is low-toxic and soluble in many organic solvents. Nickel wires were used to induce the discharges, with an attempt to judge whether the metal wires can be the metal source since Ni has a relative low melting point (1453 °C). Four different solvents, namely benzene, cyclohexane, liquid paraffin, and anhydrous ethanol were tested to deduce the formation mechanisms and find relatively low-toxic solvents and effective preparation method. The fabricated Fe@CNPs were characterized comprehensively by SEM-EDS, TEM, HRTEM, XRD, and Raman spectroscopy analyses. The microwave-absorbing capability and thermal stability of the prepared Fe@CNPs were also tested, and their potential applications in microwave chemistry were discussed.

2. Experimental section

2.1. Materials

Ferrocene ($FeC_{10}H_{10}$, 98% purity, Aladdin Industrial Corporation) was selected as the metal source. Nickel wires (diameter: 1 mm, length: 3–6 mm, Shanghai Shen Long High Temperature Line Co. Ltd.) were used to trigger microwave discharges. Argon (99.999% purity) was used as the protective gas in all experiments. In order to investigate the effect of different raw materials on the preparation of Fe@CNPs under MW-metal discharges and identify the less toxic candidates, four organic solvents were tested (Table 1). In addition, CNTs (> 96% purity), carbonyl iron powder (> 99.5% purity), and green SiC powder (> 98% purity), were used to compare with the prepared Fe@CNPs samples in their microwave-absorbing capability. All of them were purchased from Aladdin Industrial Corporation.

2.2. Preparation of Fe@CNPs

The synthesis of Fe@CNPs was performed in a customized quartz reactor (i.d. = 90 mm, o.d. = 100 mm, height = 120 mm) in a custom-designed industrial microwave oven that has an adjustable microwave output power of 0–4000 W and operates at the frequency of 2.45 GHz (Fig. 1). In each experiment, 0.6 g ferrocene and 9 g organic solvent (ferrocene: organic solvent = 1:15) were mixed together in a small quartz tube (i.d. = 30 mm, o.d. = 35 mm, height = 60 mm), and then subjected to ultrasonic dispersion for 10 min for even mixing. After that, nickel wires (2 g) were added into the quartz tube, which was then held fixed in the quartz reactor by adding some quartz sand. The quartz reactor, tube, and sand all have excellent microwave-transparent properties.

In each experiment, argon flow entered the quartz reactor ten minutes before the reaction at a flow rate of 200 mL/min in order to exclude the air inside. Then, the microwave output power and irradiation time were set at 1800 W and 5 min, respectively. After reaction, the reactor was naturally cooled down to ambient temperature under an inert atmosphere. The Fe@CNPs were obtained by removing nickel wires from the solid products.

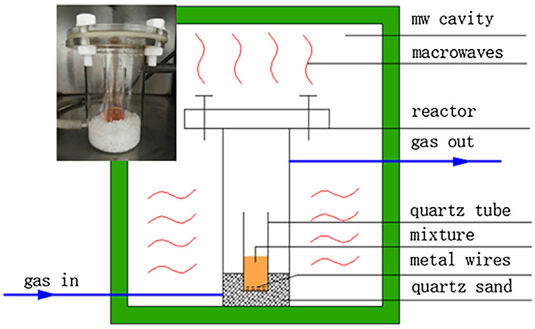

Fig. 1. Schematic of the experimental device.