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Selective graphene covering of monodispersed magnetic nanoparticles

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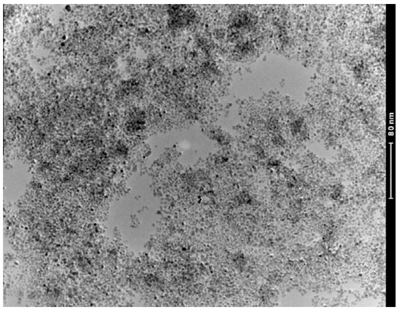
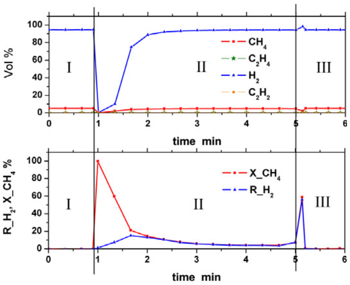
HIGHLIGHTS

- Stable and biocompatible core-shell graphene-coated magnetic nanoparticles.
- Small and narrow distribution body-centered-cubic-Co/Fe nanoparticles.
- Growth process control for selectively covered nanoparticles.
- Wide characterization of the nanoparticles.
- Mechanism of nanoparticles formation and covering.

GRAPHICAL ABSTRACT





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ABSTRACT

Core-shell few layer-graphene-coated metal nanoparticles (GCMNP) were synthesized by methane catalytic chemical vapor deposition (CVD). The GCMNPs of cobalt and iron dispersed on an alumina support catalyze themselves the decomposition of methane, which is the source of carbon.

Different synthesis operating conditions were investigated to achieve a good control of the coverage of GCMNPs and to understand the mechanism of GCMNP (particularly with respect to their size) and carbon coverage formation. Moreover, the reactor outlet gas was continuously monitored on-line during the catalyst activity. Several techniques were utilized to characterize the catalyst and the reaction products and to correlate their properties with the reactor operating conditions.

The reaction yield was monitored to produce small body-centered-cubic-Co/Fe nanoparticles (4.1 nm mean diameter) with a very narrow size distribution, selectively covered by two graphene layers.

1. Introduction

The attention to the process parameters in the preparation of stable magnetic nanoparticles (MNPs), to obtain a quality controlled product, is of particular importance in view of the exploitation of their properties [1–3] in the different fields in which they can be used, including catalytic, environmental, biological, biomedical and electronic.

Much attention has been addressed to the synthesis of MNPs [1–3] and different strategies have been developed to preserve their stability against agglomeration or precipitation and oxidation phenomena, involving polymers [4–6], silica [7,8], precious metals [9,10] and carbon-coated NPs (CMNPs) [11–19].

The carbon covering has many advantages over other coatings, such as much higher chemical and thermal stability, having also the possibility to be easily functionalized. It has been reported [3,19,20] that CMNPs are biocompatible materials, but the mechanism of such hybrid magnetic nanostructures cytotoxicity is still not fully explored. More recently, it has been concluded [21,22], that a great caution should be devoted to physicochemical features

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of the CMNPs and further preclinical studies are needed before their use.

Different carbon coating strategies have been developed. Carbon-encapsulated metal or metal carbide nanocrystallites have been generated by the Kratschmer arc-discharge process already in 1995 [11]. Since then, many studies have shown that in the presence of metal nanoparticles (Co, Fe, Ni, Cr, Au, etc), graphitized carbon structures, such as carbon nanotubes and carbon onions, are formed under arc-discharge, laser ablation, and electron irradiation [12–15]. Gedanken and co-workers reported a sonochemical procedure that leads to air-stable cobalt nanoparticles [16]. Johnson et al. describe a simple method to prepare carbon-coated magnetic Fe and Fe3C nanoparticles by direct pyrolysis of iron stearate at 900 °C under an argon atmosphere [17]. Moreover, carbon-coated nanoparticles are usually in the metallic state, and thus have a higher magnetic moment than the corresponding oxides [1].

Chemical Vapor Deposition (CVD) technique offers the advantage of being the easiest to scale up towards an economically viable production [19–25].

In particular, He et al. [24] demonstrated for the first time the feasibility of synthesizing carbon-encapsulated nanoparticles free of byproducts, such as carbon nanotubes/nanofibers, carbon nanoparticles and amorphous carbon, and agglomeration, which would limit the potential applications of the NPs. He et al. prepared NPs with a mean diameter of 15 nm, with a standard deviation of 3 nm, via CVD over a Ni/Al catalyst. Seo et al. [19] obtained stable magnetic nanoparticles by impregnating high-surface-area silica powder in methanol with iron and cobalt species. Carbon coating of the metal-loaded silica was obtained by flowing a 100% methane stream in a CVD chamber. They found, for their body-centered-cubic-NPs of 7 nm diameter the highest saturation magnetization obtained for nanocrystal, and despite the smaller size a lower value for the 4 nm NPs, likely due to the presence of a mixed body-centered-cubic-FeCo and face-centered-cubic-Co phases. The nanoparticles were tested as advanced magnetic resonance and near-infrared imaging agents and, more recently, for few-cells enrichment and detection [26].

On the other hand, little or no attention has been focused on the synthetic process in which the products, having identified the catalyst and carbon source, strongly depend by operating conditions chosen. The selective coating of nanoparticles, is still, an aspect to analyze and optimize. In fact, the presence of carbon in the samples, other than the nanoparticles coating, (e.g., coming from an homogeneous decomposition) would decrease the magnetic performances and constitutes an impurity in view of the successive applications. For example, feeding a pure hydrocarbon flow makes it very difficult to obtain a satisfactory reaction yield and/or controlled nanoparticle coverage and carbon selectivity. Little attention has been devoted to investigating the influence of the support on the characteristics of the prepared materials. In addition, insight into the formation mechanism is key to controlling the synthesis process.

Identification of the parameters that determine the size of the nanoparticles and their distribution for Co/Fe on Al_2O_3 has not been explored.

Herein, we report the preparation of stable core-shell graphene-coated magnetic nanoparticles (GCMNPs) via catalytic chemical vapor deposition (CCVD) of methane at atmospheric pressure. Alumina, which is a very good support catalyst due to its narrow and small size porosity and the coupling effect with the metal active phase, was used as the support for the Co and Fe [27]. The prepared nanoparticles (~4.1 nm in diameter) possess a very narrow size distribution and are by-product free.

Particular attention has been devoted to studying the effects of the reactor operating conditions on the reaction yield and quality of the produced materials. Therefore, feed gas composition, total flow rate, catalyst mass, metal catalyst weight, and catalyst pretreatment were varied in the CCVD runs. In addition, the inlet and outlet reactor concentrations of the reactants and products, respectively, were monitored continuously with specific gas analyzers to obtain a quantitative description of the synthesis process.

To perform the growth experiments, a vertical arrangement has been chosen for the reactor because it does not suffer from the longitudinal diffusive limitations along the reactor axes in typical CVD horizontal furnaces [27,28]. During CVD synthesis at atmospheric pressure and a typical temperature (700–900 °C), the rate-limiting step is typically the diffusion through the boundary layer. Under these conditions, the mass transfer rate, which depends on the diffusion coefficient that is inversely proportional to the pressure, is disfavored, and the reaction kinetics, which depend exponentially on the temperature, are favored. Therefore, the reactor geometry can affect the results of the synthesis. To partially solve this problem, we have chosen to work with a vertically arranged reactor to avoid the boundary layer variation along the surface of the catalyst bed, as would be typical in a horizontal CVD chamber.

To characterize the catalyst and the reaction products and to correlate their properties with the operating conditions, various techniques were employed as follows: transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman spectroscopy, thermogravimetric analysis (TG-DTG) coupled with a quadrupole mass detector, X-ray diffraction analysis, inductively coupled plasma mass spectrometry (ICP-MS), dynamic light scattering (DLS), and N_2 adsorption–desorption at 77 K.

2. Materials and methods

The Co, Fe catalyst (50 wt.% of each metal) was prepared by wet impregnation of gibbsite (γ-Al(OH)$_3$) powder [27,29] with cobalt acetate and iron acetate solutions followed by drying at 80 °C for 3 h.

CCVD was performed in a continuous flow microreactor fed by a methane–hydrogen gas mixture. The microreactor was a quartz tube (16 mm internal diameter, 300 mm in length), and the catalyst (particle sizes in the range 38–53 μm, sieved prior to synthesis) was loaded onto a sintered support [27,29]. An external coaxial quartz tube (35 mm internal diameter) allowed the reactant stream to be preheated. The temperature of catalyst bed was measured with a K thermocouple located inside a third internal coaxial quartz tube (4 mm internal diameter). The reactor was heated by an electrical oven whose temperature was controlled by a temperature programmer-controller (Eurotherm 2408). Cylinder gases (99.998 pure methane and 99.9990 pure hydrogen) were mixed to obtain the methane/hydrogen stream that was fed into the reactor. A constant flow rate of each gas was provided by mass flow controllers. The experimental plant for the synthesis was equipped with on-line analyzers (Uras 26, ABB) that permit the alternating monitoring of the inlet and outlet reactor concentrations of the reactants (methane (CH_4) and hydrogen (H_2)) and products (acetylene (C_2H_2), ethylene (C_2H_4), and hydrogen (H_2)) continuously during the reaction via a bypass valve.

The typical procedure for preparing GCMNP particles includes (1a) feeding the reacting gas to the analyzers to verify the steady state inlet concentration. (1b) N_2 is fed to the reactor by another feed line to pre-treat the catalyst. (2) The pre-treatment nitrogen flow was stopped using the bypass valve, and the reacting gas stream was started to feed the reactor. (3a) After 5 min, the reacting gas stream was stopped, and nitrogen was fed to the reactor. Next, (3b) the reacting gas is fed to the analyzers. (4) The reactor was extracted from the furnace and allowed to cool under ambient temperature conditions. (5) Chemical attack, with a diluted HF solution (15 vol.%) for 3 h, followed by centrifugation and washing, in distilled water, under filtration.