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One-step pyrolytic synthesis and growth mechanism of core–shell type Fe/Fe_3C-graphite nanoparticles-embedded carbon globules

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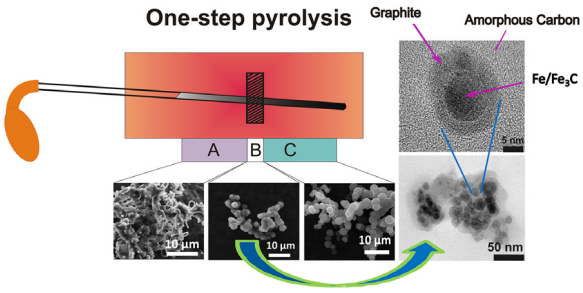
HIGHLIGHTS

- Single-step closed reactor pyrolysis is used to synthesize multifunctional carbon nanostructures.
- The carbon nanostructures were embedded with Fe/Fe_3C-particle surrounded by graphitic shell.
- Low ferrocene concentration facilitates formation of smoother spherical globules than that of high conc.
- At low ferrocene concentration the Fe/Fe_3C particles are smaller and spherical in shape.
- The nucleated Fe-nanoparticles transform to Fe_3C, which then catalyses the formation of graphitic shell and CNTs.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis and detailed characterization of amorphous carbon globules containing Fe/Fe_3C-graphite core–shell type nanoparticles. The samples were synthesized via a low-cost chemical vapour deposition (CVD) method by the single-step pyrolysis of precursors (benzene and ferrocene). The amount of precursors and the reaction temperature were found to control the morphology of the carbon globules, and the shape, size, composition and distribution of Fe/Fe–C based nanoparticles inside the carbon globules. At the CVD tube wall deposition of Fe derived from the decomposed-ferrocene forms Fe_3C particles at high temperature, which are unstable in carbon rich environment and transforms to γ-Fe and carbon-product (graphite). Furthermore, γ-Fe is also unstable at RT and transforms to α-Fe and Fe_3C phases while cooling. A fraction of γ-Fe is, however, kinetically arrested during the cooling process. This leads to the formation of 'Fe/Fe_3C (core)-graphite (shell)' nanoparticles-embedded amorphous carbon globules.

1. Introduction

Carbon-coated magnetic nanoparticles constitute an active area of research, since they find usage in a wide array of applications such as catalysis [1,2], oxygen reduction reaction (ORR) [3], magnetorheology [4], hyperthermia [5], MRI contrast agents [6], magnetic data storage [7,8], microwave absorption [9] and energy conversion and storage [10–14]. Carbon encapsulation of the magnetic nanoparticles provides an inexpensive way to protect the nanoparticles from oxidation [15]. Thus, the nanoparticles can retain their native state for a long duration of time. Furthermore, attention was given to remove the core and synthesize hollow carbon-spheres for ink-fluids and super-capacitor applications [16]. Different approaches have been employed for the synthesis of carbon-coated magnetic nanoparticles, which includes

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solvothermal [17], laser ablation [18], chemical vapour deposition (CVD) [19], ultrasonication [20], detonation [21], arc discharge [22] and pyrolysis [23,24]. Most of these methods require sophisticated instruments and/or expensive precursors [25]. However, pyrolysis is a simple and cost effective method, which presents versatility in the variety of precursors that can be used. Ferrocene is commonly used as nucleation source in the synthesis of these carbon materials, especially, carbon nanotubes. A variety of organic chemicals, solids and household wastes can be used. The encapsulation of carbon on magnetic nanoparticles was attributed to the large size of the core (>50 nm) [26,27]. The smaller magnetic particles (<50 nm) were responsible for nanotube growth [26]. The morphology and other properties can be controlled by changing the growth conditions such as concentration and type of the precursors, furnace design, pyrolysis temperature, etc. [23,28]. In spite of the vast amount of literature available, the mechanism of carbon encapsulation of the magnetic nanoparticles during pyrolysis is not yet well understood.

In this work, we synthesized Fe/Fe_3C nanoparticles embedded carbon globules by a low-cost CVD method via the single-step closed reactor pyrolysis of benzene and ferrocene. A variety of characterizations were undertaken and a growth mechanism has been proposed. All the synthesized materials show core–shell morphology. The variation in concentration of ferrocene played pivotal role in determining the size and distribution of the core Fe/Fe_3C nanoparticles. The surface of the nanoparticles induces graphitization of the amorphous carbon matrix. Our work demonstrates that a selection of certain precursors allows a means to convert toxic and potentially carcinogenic organic wastes (such as benzene) to highly useful carbonaceous products.

Carbon encapsulation is advantageous in various applications. In recent years, catalysts protected by a shell are demonstrated to be better than bare catalyst nanoparticles [29]. Quest for the development of earth abundant metal catalysts and metal-free catalysts has also led researchers to devise low-cost synthesis methods. In this context, synthesis of carbonaceous materials has taken precedence, with an increased interest in their catalytic activity. A great deal of recent studies are being carried out on metal carbide based systems for development of fuel cells [30]. Removal of pollutants from water is another active area of research where such materials are widely used [31,32]. The synthesis method used in our experiment is a versatile modification to the conventional CVD method which greatly reduces the overall cost of the material. It also allows a means to tune the structure and morphology of the core–shell type nanoparticles, thereby increasing the array of applications where it can be utilized. For example, the core–shell Fe/Fe_3C nanoparticles were recently demonstrated to be good microwave absorbing materials as compared to metallic nanoparticles [9].

2. Materials and methods

The detailed synthesis procedure and the specifications of the furnace used for pyrolysis reaction, are similar to our previously reports [23,28]. A mixture of ferrocene and distilled benzene was taken in a quartz tube (length of ∼75 cm and inner diameter of 1 cm). A rubber bladder was attached to the open end of the tube. The tube was then placed in a tube furnace. The furnace was built in-house and temperature calibrated as described in the previous reports [23,28], but with a constant-(high) temperature zone of about 4 cm long. The precursors were positioned at about 10 cm away from this central hot zone, where the temperature was ∼300 °C (while the corresponding temperature of the hot zone was ∼770 °C). The furnace was heated at an average rate of 3 °C min^{-1}. After the final temperature (∼770 °C) reached, the reactor was maintained at that temperature for 2 h. The tube was then cooled down to room temperature. The contents were scraped out from different zones: A, B and C zones (Fig. S1 and Fig. S2 in Supporting Information file and Fig. 1 in Refs. [23,28]), analogous to the positions where the temperature was more than ∼450 and 770 °C. The samples were labelled as 'a', 'b' and 'c'. We repeated experiments taking four different compositions (weights) of ferrocene precursor (15, 30, 45 and 60 mg) in 1 ml distilled benzene, to study the role of precursor concentration on the product morphology. The final products were labelled as FeC-1, FeC-2, FeC-3 and FeC-4, respectively. After the completion of the reaction, we observed that shiny black products were deposited around the inner wall of the quartz tube extending to about 7–10 cm on either side of the hot zone.

The characterization of the synthesized materials was performed by a number of different techniques. The scanning electron microscopy (SEM) images were taken from Cambridge Scanning Electron Microscope. TEM and HRTEM images were obtained using 200 kV (electron energy) in FETEM (JEM 2100F) instrument. The powder X-ray diffraction (XRD) patterns were recorded using "PANalyticalXpert Pro" X-ray diffractometer in the 2θ range of 10°–90° (step size 0.02°). The Mössbauer spectra were measured in transmission geometry (^{57}Co-Rh). 'NORMOS' program was used for the least-squares fitting of the Mössbauer spectra. The magnetic measurements were carried out on PPMS 9T (Quantum Design) instrument.

3. Results and discussion

3.1. Morphology and structure

The SEM images (Fig. 1) of the samples collected from various zones show different morphologies, predominantly, clusters containing globules of ∼1–4 μm in diameter. Comparing the SEM images (for all compositions of ferrocene), the samples collected from the C-zones are more spherical than that from the B-zones, while the samples collected from the A-zones show a few micrometre long wire-like or rod-like structures (maybe partially developed carbon fibres and nanotubes) which evolve from the globules.

Furthermore, the samples prepared using lower weight fractions of ferrocene (i.e., 15 mg and 30 mg) precursor in 1 ml of benzene, show more spherical morphologies than those prepared using higher weight fractions. We have observed smaller diameter globules in the A-zone (especially for the FeC-1 samples (synthesized using lower ferrocene weight of 15 mg)), while those from B- and C-zones have larger diameters. However, for higher concentration of ferrocene the surface distortions of the globules are high (considerably less smooth). Note here that the samples collected from the A-zones have a higher aggregation of the globules when higher precursor (ferrocene) concentration of 60 mg was used (FeC-4), while wire-like structures were seen when moderate precursor (ferrocene) concentrations were used (30 mg (FeC-2) and 45 mg (FeC-3)). This observation emphasizes that an optimum concentration of ferrocene is required for the formation of the wire-like nanostructures.

Two representative images, each, for TEM- and HRTEM are shown in Fig. 2. The TEM images (Fig. 2, left panel) clearly show the core–shell nanostructures embedded in the carbon matrix of the globules. The nano-sized particle cores are surrounded by well defined shells. The spherical core–shell morphology is highly distinct when the samples were synthesized using lower ferrocene concentrations. Interestingly, as the concentration of ferrocene increases, the structure of the core becomes denser and polygonal. For FeC-1 and FeC-2, the average diameter of the core is 5–15 nm, and the size distribution is narrow. In the FeC-3 and (especially) FeC-4 samples, there are some big particles (∼50–75 nm) along with a large number of small sized particles. This observation is