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Synthesis of carbon nanotubes and iron oxide nanoparticles in MW plasma torch with $Fe(CO)_5$ in gas feed

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ABSTRACT

The MW plasma torch (2.45 GHz) in the mixture of $CH_4/H_2/Ar$ (42/430/1540 sccm) with added $Fe(CO)_5$vapors was used for the synthesis of iron oxide nanoparticles and carbon nanotubes. The particles with well-defined facets consisting of Fe_3O_4 and γ-Fe_2O_3 and self-assembled into long chains were produced at the power of 360 W. At higher power of 440–460 W the deposit contained significant amount of multi-walled carbon nanotubes covered by iron oxide nanoparticles. The diameter of CNTs was 8–20 nm. The particles had Fe_3O_4 and/or α-Fe_2O_3 cores of spherical shape covered by a thin layer of carbon.

1. Introduction

Recently, atmospheric pressure discharges became studied by some research groups for synthesis of carbon nanotubes (CNTs) and iron-based nanoparticles (NPs) because of their relatively simple set-up without expensive vacuum systems. Some publications deal with the synthesis of CNTs using dc plasma arc jet or torch ignited in flow gas between two electrodes [1,2]. Generally, these methods produce soot with certain portion of unaligned single and multi-walled CNTs. The experiments with microwave (MW) torches are focused on the floating catalyst approach using ferrocene or iron pentacarbonyl ($Fe(CO)_5$) [3,4]. Nanocrystalline Fe_2O_3particles have been prepared in gas phase at atmospheric pressure by employing an oxygen microwave (MW) plasma jet with vaporized $Fe(CO)_5$[5]. Microwave plasma torch at atmospheric pressure has been successfully used for the synthesis of supported carbon nanotubes (CNTs) using Fe thin film catalytic layer [6–8]. In this paper, the torch with added $Fe(CO)_5$vapors was tested for production of both, CNTs and iron-based NPs.

2. Experiment

The synthesis of iron-based NPs and CNTs was carried out in microwave plasma torch at atmospheric pressure operating at the frequency of 2.45 GHz. MW power was transmitted by a waveguide through a coaxial line to a hollow nozzle electrode. The coaxial line and the electrode were constructed for a dual gas flow allowing separate delivery of two gas mixtures into the central and outer part of the torch. The mixture of H_2 and CH_4 was added by a set of holes at the nozzle perimeter, i.e. into the outer torch part. The central hole of the nozzle accommodated flow of Ar mixed with $Fe(CO)_5$ vapors. The Ar flow rate was regulated by two electronic flowmeters. Its smaller portion flew above liquid $Fe(CO)_5$ pulling its vapors through the nozzle. The typical flow rate conditions were 1540 sccm of Ar, 5 sccm of Ar over $Fe(CO)_5$, 42 sccm of CH_4 and 430 sccm of H_2. The MW power ranged from 360 to 480 W. Two indicative experiments carried out at 360 and 460 W are referred in the text as #1 and #2, respectively. In the experiment #3, H_2 flow rate and power were 360 sccm and 440 W,

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respectively, whereas the other conditions remain the same. The powder was synthesized in the whole volume of the quartz tube but the product was captured on a silicon substrate facing the torch at the distance far from the active plasma zone, 100–130 mm from the nozzle.

X-ray powder diffraction was carried out with X'Pert Pro MPD device (PANanalytical B.V., Almelo, the Netherlands) using Co K α radiation and interpreted by means of the HighScore Plus software [9] with commercial databases [10,11]. Transmission electron microscopy (TEM) was carried out with the Phillips microscope CM12 (tungsten cathode) using a 120 kV electron beam. Copper grids coated with a carbon support film were used to prepare the samples. The sample powder was dispersed in ethanol, the suspension was treated in an ultrasonic bath for 10 min, and then the copper grid was dipped into it. Raman spectroscopy was performed using Renishaw inVia Raman microscope. The laser wavelength and power were 632.8 nm and 50 mW, respectively.

3. Results and discussion

The synthesis of materials from the $CH_4/H_2/Fe(CO)_5/Ar$ mixture in MW plasma torch was influenced by several external parameters such as MW power, concentrations of reactive gases, gas flow rates and the position of substrate on which the products were collected. During our preliminary experiments we concentrated on the set of conditions described in the previous section, in which the MW power was the only variable. However, the increase of power can influence several internal parameters of the synthesis. Among others, it prolongs the torch length, increases gas temperature and the temperature of quartz tube walls.

Synthesis at low power (360–400 W) yielded grey or black powder composed mostly of iron-based nanoparticles exhibiting magnetic properties. The SEM micrograph of a deposit #1 is shown in Fig. 1. The as-deposited nanoparticles were aggregated into chains without the application of an external magnetic field. The chains of the NPs were observed even after the preparation of the sample for the TEM observation involving 10 min of ultrasonication (see Fig. 2). Iron-based NPs self-assembled into the chains were observed also by other authors. Knipping et al. [12] and Huelser et al. [13] observed long chains of ferromagnetic NPs formed when the particle diameters were above 15 nm. The particles were composed of iron bcc core surrounded by a thin oxide layer. Shorter and more dendritic chains were found by Huber et al. [14] for bcc iron particles with the diameters below 15 nm exhibiting superparamagnetic behavior.

The chain-agglomerated particles synthesized by MW torch consisted of iron oxides. The Raman spectroscopy and X-ray powder diffraction did not reveal the presence of iron bcc or iron carbides (see Fig. 3). The diffraction peaks could be assigned either to cubic magnetite Fe_3O_4(JCPDS No. 85-2355) or maghemite γ-Fe_2O_3 (JCPDS No. 39-1346 and JCPDS No. 25-1402 for cubic maghemite-C and tetragonal maghemite-Q, respectively). The diffraction analysis alone cannot distinguish between these two types because of their structural similarity. However, the presence of maghemite is confirmed by two weak peaks at 27.7° and 30.5° corresponding to reflections (2,1,0) and (2,1,1), respectively, that are not found in the diffraction pattern of magnetite. Most of the particles had hexagonal, crystalline form (see the inset of Fig. 2). The average diameter of the particles, as determined by the measurement of their area and spherical shape approximation, was 80 nm.

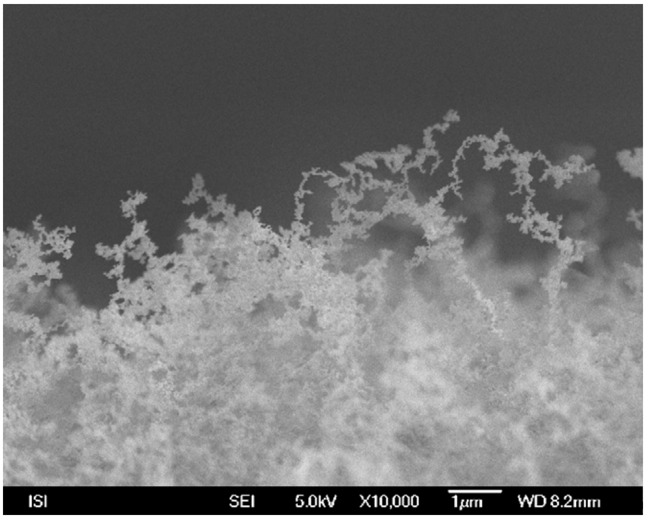

Fig. 1. SEM micrograph of sample #1, i.e. the iron oxide particles forming self-assembled chains synthesized at MW power of 360 W. The flow rates of methane, hydrogen, argon and argon over liquid $Fe(CO)_5$ were 42, 430, 1540 and 5 sccm, respectively.

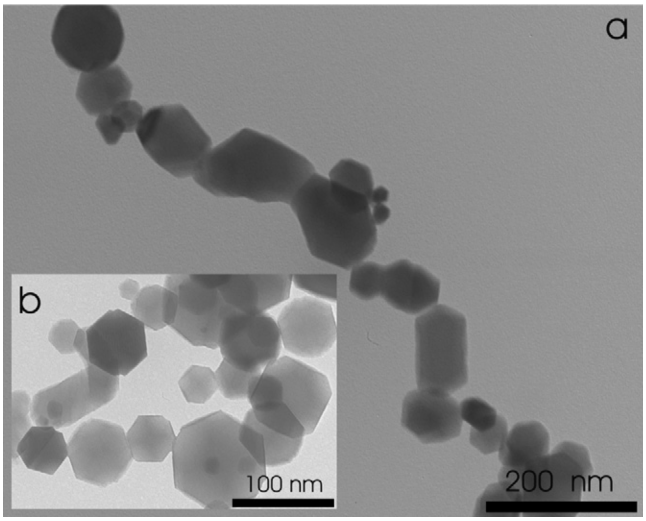

Fig. 2. TEM micrographs of sample #1 demonstrating (a) formation of self-assembled chains composed of iron oxide NPS and (b) well-defined facets of most of the particles. For the deposition conditions see caption of Fig. 1.

The deposit synthesized at higher powers 460–480 W contained significant amount of multi-walled carbon nanotubes (MWNTs) with the diameter 8–20 nm. They were densely covered by iron-based NPs. It can be seen from Fig. 4 in which true-secondary and backscattered electron SEM images of the sample #2 deposited at 460 W are compared. The particles are visualized as bright spots in the backscattered image due much higher atomic number of iron compared to carbon. The appearance of the particles differed from the well-faceted particles synthesized at lower power (360–400 W). They were more spherical with clear distinction of heavier, i.e. darker, particle core and thin surface layer composed of lighter elements (see Fig. 5). According to Raman spectroscopy, X-ray and electron diffractions the deposit did not contained iron or iron carbides, only iron oxides. Therefore, it is assumed that the particle core is composed of iron oxide encapsulated by thin carbon layer. This assumption is further supported by the fact that the sample is also composed of CNTs as seen from Figs. 4 and 5.

The presence of CNTs in the deposit formed at the power of 460–480 W is probably caused by prolonged residence time of catalytic particles in the zone of high temperature required for CNT synthesis. The increased residence time was the result of prolonged torch length as compared to the low power conditions 360–400 W. The gas temperature approximated from the rotational structure of