Fast and Controllable Synthesis of Core−Shell Fe₃O₄−C Nanoparticles by Aerosol CVD

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ABSTRACT: A method for simple and fast (30−60 s) synthesis of spherical “Fe₃O₄ core−carbon shell” structures by atmospheric pressure aerosol pyrolysis of benzoic acid in dimethylformamide solutions containing dispersed Fe₃O₄ nanoparticles is described. It has been experimentally shown that it is possible to control both the size of the core−shell particles and the size of Fe₃O₄ grains and their amount in the particle core by the variation of benzoic acid concentration in solution and using pre-stabilized by mannitol iron oxide nanoparticles. It has been found that particles with an average size of 250−350 nm are formed at the concentration of benzoic acid in the range 0.5−1 mol/L. At a concentration of about 1 mol/L, preliminary stabilization of iron oxide nanoparticles by mannitol with a size of about 180 nm is performed.

INTRODUCTION

The technological importance of iron oxide nanosystems in view of different technological end-uses leads to the development of new synthesis methods.⁸⁻¹⁴ In this letter, we report a new method for the synthesis of core−shell structures based on Fe₃O₄ nanoparticles and carbon, which can be considered as promising materials for various applications in industry and medicine.⁸⁻¹⁰ Among other iron oxides, magnetite (Fe₃O₄) is more stable and has higher magnetic characteristics. It can be used, for example, in medicine in diagnostic systems (MRI), targeted delivery, protein immobilization, biolabels, and so forth. Existing methods for the preparation of nanomaterials with a “Fe₃O₄ core−carbon shell” structure are usually time consuming and difficult to implement. They can provide high productivity of the material with required characteristics and composition only in rare cases.

The aerosol-assisted chemical vapor deposition (AACVD) can be considered as an attractive method for the fast formation of different nanomaterials including core−shell nanostructures in the “iron oxide−carbon” system. In this case, one can use solutions of carbon-containing reagents required for the “carbon shell” formation with dispersed Fe₃O₄ particles as initial substances. The main advantages of this approach compared to other methods are simplicity of the synthesis procedure and required equipment, as well as significantly lower reagent consumption. Variations of process parameters allow to smoothly and predictably change the structural characteristics of the obtained particles. However, there are only a few papers dedicated to the study of principal possibility to synthesize carbon nanoparticles using this method⁹ and to fill porous carbon nanospheres with metal oxide particles.¹¹

The AACVD method has not been used for the synthesis of the “Fe₃O₄ core−C shell” nanostructures. The aim of this work was to study the influence of the main technological parameters of the aerosol chemical deposition process on the composition and structure of the formed nanoparticles with a “Fe₃O₄ core−carbon shell” structure.

RESULTS AND DISCUSSION

The AACVD process was carried out in a vertical flow reactor with “hot walls” (see Experimental section). To obtain powdered nanomaterials with a “Fe₃O₄ core−carbon shell” particle structure, a solution of benzoic acid in dimethylformamide (DMF) containing Fe₃O₄ nanoparticles dispersed in it was used. Magnetite nanoparticles were preliminarily synthesized in accordance with the method described in ref 11, with and without the use of mannitol as a stabilizer. Then, the aqueous solution base was replaced by a solution of benzoic acid in DMF. Unstabilized iron oxide nanoparticles form agglomerates of about 100 nm in size before the base is replaced. The use of mannitol allows to obtain particles in aqueous medium with an average size of about 10 nm.¹² When the medium is replaced from aqueous to solution of benzoic acid in DMF, mannitol is dissolved and Fe₃O₄ nanoparticles are also subjected to agglomeration, however, with a lower intensity comparing to water because DMF acts as a stabilizer.¹³ The concentration of the benzoic acid solution
in DMF was 1 mol/L (in several experiments it was different and this is highlighted in the text). The content of iron oxide nanoparticles in solutions was about 1 mg/mL.

The temperature along the reactor was set at 750 °C. The residence time of the reagents in the reaction (heated) zone was controlled in the range of 20−60 s by changing the carrier gas flow rate in the range of 0.3−1 L/min.

To establish the time required for the formation of carbon in the “iron oxide–benzoic acid solution in the DMF” system, we studied the IR spectra (Figure 1, spectra were vertically shifted for better visualization) of synthesized composite powders and carbon-containing powders obtained by the AACVD method from a solution of benzoic acid in DMF. It was found that the intensities of the absorption bands corresponding to vibrations of C−H, fragments (Table 1) decrease in the IR spectra when the residence time of the reagents in the reaction zone is increased and therefore a more complete decomposition of the carbon-containing reagent occurs.

![Figure 1](image1)

**Figure 1.** IR spectra of powders obtained at different times: (a) composite and (b) carbon-containing.

| \( \nu \), cm\(^{-1} \) | vibration type          |
|---------------------|-------------------------|
| 680−890             | C−C\text{bend} ring; C=O\text{bend} |
| 1120                | C−H\text{bend}          |
| 1590                | C−C\text{stretch} ring  |
| 1750                | C=O\text{stretch}       |
| 2780−3200           | C−H\text{methyl} ring   |

The results of EDX-analysis of the particles obtained in the reaction system “iron oxide–benzoic acid solution in DMF” with a residence time of about 40 s showed that particles contained iron, oxygen, and carbon. Figure 2 shows the scanning electron microscopy (SEM) image and the data of EDX analysis of the single particle in accordance with the marked profile line.

According to X-ray photoelectron spectroscopy (XPS), the composition of iron oxide in the obtained particles corresponds to Fe\(_3\)O\(_4\) (see Experimental section). Figure 3 shows the images of the synthesized particles obtained with the use of transmission electron microscopy (TEM). The size of the particles was in the range 200−600 nm, and more than 80% of them had a size in the range 300−400 nm (Figure 3a,c). As one can see from the high-resolution TEM (HR-TEM) image (Figure 3d) of the synthesized particles, there is a lighter shell and a dark core inside usually consisting of several 80−100 nm grains (Figure 3b). This fact allowed us to suggest that the compositions of the shell and the inner core are different. The image of the substance forming the shell with a thickness of about 2−2.5 nm (Figure 3d) did not contain clearly visible atomic planes. This is evidence of its amorphous structure, and a lighter color probably indicates that it consists of lighter atoms compared to the core. The results of electron diffraction (Figure 3d) showed that the sample contains iron oxide with the structure of magnetite.\(^{15}\) HR-TEM allowed to estimate the value of an interplanar spacing of 4.86 Å (Figure 3d), which corresponds to the (111) planes in the Fe\(_3\)O\(_4\) phase.\(^{16,17}\) Comparing the data of EDX-analysis, XPS, and TEM, one can conclude that the synthesized particles have a “Fe\(_3\)O\(_4\) core−C shell” structure.

The scheme shown in Figure 4 illustrates the mechanism of Fe\(_3\)O\(_4\)−C nanoparticle formation in the system “iron oxide−benzoic acid solution in DMF”. An aerosol particle generated with the use of an ultrasonic nebulizer contains several Fe\(_3\)O\(_4\)
nanoparticles surrounded by benzoic acid molecules. When aerosol particles are introduced into the reactor, the solvent is evaporated from the surface of the aerosol particle and a solid layer of carbon-containing substances are gradually formed. Then, it is subjected to pyrolysis with the formation of a carbon shell. It is the most probably that carbon in the system participates not only in the formation of the particle shell, but also in the binding of Fe₃O₄ grains to each other.

Particles with an average size of about 250 nm are formed when the benzoic acid concentration is lowered to 0.5 mol/L (Figure 5a). The use of pre-stabilized mannitol Fe₃O₄ nanoparticles allows to reduce the average size of the formed core−shell particles to about 180 nm with a more narrow size distribution (Figure 5b). Because of the lower tendency of the iron oxide particles to agglomerate in DMF, smaller grains are formed (Figure 5c). It is possible also, that mannitol in the solution can play the role as an additional carbon-containing reagent in the system. It can be converted into sugars (mannose and galactose) which then are transformed to carbon because of pyrolysis at a higher temperature.¹⁸

### CONCLUSIONS

A method for “Fe₃O₄−shell C core” spherical structure synthesis by the pyrolysis of aerosols of a solution of benzoic acid in DMF with dispersed Fe₃O₄ nanoparticles has been developed. It was experimentally shown that by changing the concentration, it is possible to control the size of the formed particles. A decrease in the particle size and the number of Fe₃O₄ grains in the core, as well as the formation time, is possible in the case of preliminary stabilization of iron oxide nanoparticles by mannitol, which is also an additional carbon-containing component in the system. Detailed step-by-step explanation of this process will be featured in an upcoming publication. Further research activities on the proposed method will be aimed at studying the sorption ability of particles, magnetic characteristics, and at increasing the synthesis rate and yield of the final product.

### EXPERIMENTAL SECTION

**Nanoparticle Formation.** powdered nanomaterials with the “Fe₃O₄ core−C shell” structure were obtained by the AACVD in the experimental setup shown in Figure 6. The liquid reagents from reservoir 1, where they were transferred to aerosol form with the use of piezoelectric nebulizer, were transported into the reaction zone by argon used as a carrier gas. “Hot wall” vertical reactor 3 is equipped with heating elements that allow setting different temperatures in the reactor sections. Single-crystal silicon substrates were placed on the inner surface of nickel cylinder 4, which together with electrode 5 works as an electrostatic filter for collecting of the synthesized products.

**Materials Characterization.** Size and structure analysis of the nanoparticles was carried out according to the SEM images (SUPRA 55VP). Statistical analysis of particle size characteristics was carried out by processing SEM images using the Digimizer software package in at least 200 measurements. The
The test sample is 3.6 at. %, O corresponding to the iron oxide (II, III). Binding energies of $530.31$ and $710.58$ eV correspond to the iron and oxygen in magnetite. The Fe $2p_{3/2}$ 710.58 eV peak has no satellites, which is typical, unlike other iron oxides, for Fe$_3$O$_4$. \cite{19, 20}

**REFERENCES**

1. Mantovan, R.; Lamperti, A.; Georgieva, M.; Tallarida, G.; Fanciulli, M. CVD Synthesis of polycrystalline magnetite thin films: structural, magnetic and magnetotransport properties. *J. Phys. D: Appl. Phys.* 2010, 43, 065002.

2. Warwick, M. E. A.; Kaunisto, K.; Barreca, D.; Carraro, G.; Gasparotto, A.; Maccato, C.; Salviati, G.; Tallarida, M.; Das, C.; Fesno, F.; Korte, D.; Stanger, U.; Franko, M.; Schmeisser, D. Surface functionalization of nanostructured Fe$_3$O$_4$ particles: core-shell composites. *J. Phys. D: Appl. Phys.* 2013, 5, 7130–7138.

3. Wang, S.; Huang, F.; Zhang, M.; Kong, X.; Zi, Z.; Liu, Q. Fe$_3$O$_4$/C core-shell carbon hybrid materials: from design to light-activated lithium-ion battery anode. *Nanoenergy* 2017, 8676, 2018, 8676–8684.

4. Wang, C.; Zhong, H.; Wu, W.; Pan, C.; Wei, X.; Zhou, G.; Yang, F. Fe$_3$O$_4$/C core-shell carbon hybrid materials as magnetically separable adsorbents for the removal of dibenzothiophene in fuels. *ACS Omega* 2017, 2, 127, 155603.

5. Wang, S.; Huang, F.; Zhang, M.; Kong, X.; Li, J. One-pot synthesis of in-situ carbon-coated Fe$_3$O$_4$ as a long-life lithium-ion battery anode. *NanoTechnology* 2017, 28, 155603.

6. Liu, M.; Jin, H.; Uchaker, E.; Xie, Z.; Wang, Y.; Cao, G.; Hou, S.; Li, J. One-pot synthesis of in-situ carbon-coated Fe$_3$O$_4$ as a long-life lithium-ion battery anode. *NanoTechnology* 2017, 28, 155603.

7. Wang, S.; Huang, F.; Zhang, M.; Kong, X.; Zi, Z.; Liu, Q. Fe$_3$O$_4$/carbon chain-like core/shell composites: synthesis and microwave absorption properties. *Integr. Ferroelectr.* 2018, 190, 76–84.

8. Huang, Y.-K.; Su, C.-H.; Chen, J.-Y.; Chang, C.-T.; Tsai, Y.-H.; Syu, S.-F.; Tseng, T.-T.; Yeh, C.-S. Fabrication of silica-coated hollow carbon nanospheres encapsulating Fe$_3$O$_4$ for magnetical and MR imaging guided NIR light triggering hyperthermia and ultrasound imaging. *ACS Appl. Mater. Interfaces* 2016, 8, 14470–14480.

9. Kaskela, A.; Nasibulin, A. G.; Timmermans, M. Y.; Aitchison, B.; Papadimitratos, A.; Tian, Y.; Zhu, Z.; Jiang, H.; Brown, D. P.;
(10) Ardekani, S. R.; Aghdam, A. S. R.; Nazari, M.; Bayat, A.; Yazdani, E.; Saievar-Iranizad, E. A Comprehensive review on ultrasonic spray pyrolysis technique: mechanism, main parameters and applications in condensed matter. *J. Anal. Appl. Pyrolysis* 2019, 141, 104631.

(11) Atkinson, J. D.; Fortunato, M. E.; Dastgheib, S. A.; Rostam-Abadi, M.; Rood, M. J.; Suslick, K. S. Synthesis and characterization of iron-impregnated porous carbon spheres prepared by ultrasonic spray pyrolysis. *Carbon* 2011, 49, 587–598.

(12) Tyurikova, I. A.; Demidov, A. I. Synthesis of water-based Fe₃O₄ magnetic nanoparticles, stabilized by oleic acid and mannitol. *Inorg. Mater.* 2017, 53, 413–418.

(13) Azuma, R.; Nakamichi, S.; Kimura, J.; Yano, H.; Kawasaki, H.; Suzuki, T.; Kondo, R.; Kanda, Y.; Shimizu, K.-i.; Kato, K.; Obora, Y. Solution synthesis of N,N-dimethylformamide-stabilized iron-oxide nanoparticles as an efficient and recyclable catalyst for alkene hydrosilylation. *ChemCatChem* 2018, 10, 2378–2382.

(14) Stepanian, S. G.; Reva, I. D.; Radchenko, E. D.; Sheina, G. G. Infrared spectra of benzoic acid monomers and dimers in argon matrix. *Vib. Spectrosc.* 1996, 11, 123–133.

(15) Lafuente, B.; Downs, R. T.; Yang, H.; Stone, N. The power of databases: the RRUFF project. In *Highlights in mineralogical crystallography*; Armbruster, T.; Danisi, R. M., Eds.; Walter de Gruyter GmbH, 2016; pp 1–29.

(16) Rudman, R. Handbook of X-rays, for diffraction, emission, absorption, and microscopy. *J. Chem. Educ.* 1968, 45, 443–444.

(17) Tsurin, V. A.; Yermakov, A. Y.; Uimin, M. A.; Mysik, A. A.; Shchegoleva, N. N.; Gaviko, V. S.; Maikov, V. V. Synthesis, structure, and magnetic properties of iron and nickel nanoparticles encapsulated into carbon. *Phys. Solid State* 2014, 56, 287–301.

(18) Anastasakis, K.; Ross, A. B.; Jones, J. M. Pyrolysis behaviour of the main carbohydrates of brown macro-algae. *Fuel* 2011, 90, 598–607.

(19) Yamashita, T.; Hayes, P. Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials. *Appl. Surf. Sci.* 2008, 254, 2441–2449.

(20) Muhler, M.; Schütze, J.; Wesemann, M.; Rayment, T.; Dent, A.; Schlögl, R.; Ertl, G. The nature of the iron oxide-based catalyst for dehydrogenation of ethylbenzene to styrene. I. Solid-state chemistry and bulk characterization. *J. Catal.* 1990, 126, 339–360.