

Effect of oxidation and heat treatment on the morphology and electronic structure of carbon-encapsulated iron carbide nanoparticles

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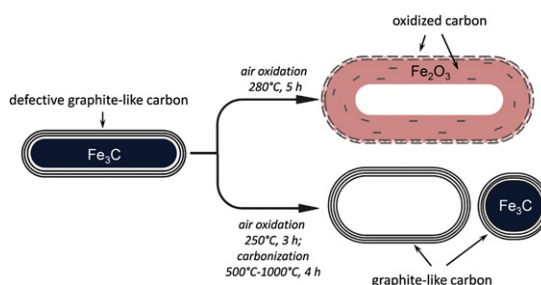
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HIGHLIGHTS

- ▶ Fe₃C@C nanoparticles produced by co-carbonization of ferrocene and aromatic oil.
- ▶ X-ray spectroscopy study of Fe₃C@C nanoparticles after oxidation and heat treatment.
- ▶ Thermal oxidation of CENPs yields hollow Fe₂O₃/CO_x nanoparticles.
- ▶ Annealing of Fe₂O₃/CO_x produces graphite-like carbon capsules filled with Fe₃C.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon-encapsulated iron carbide nanoparticles have been produced by co-carbonization of a mixture of an aromatic heavy oil and ferrocene at 450 °C under autogenous pressure. Transformations of the morphology and electronic structure of nanoparticles induced by air oxidation and subsequent heat treatment in a nitrogen atmosphere were examined using transmission electron microscopy, X-ray diffraction, near edge X-ray absorption fine structure spectroscopy, and X-ray emission spectroscopy. It was found that hollow nanoparticles, composed of iron oxides and oxidized carbon, were developed with thermal air oxidation of the initial product at 280 °C for 5 h. The mild oxidation of the product (250 °C for 3 h) followed by the carbonization at 500–550 °C yielded the hollow nanoparticles containing iron carbide/oxides and defective graphite-like carbon. The further annealing of nanoparticles at 1000 °C produced carbon nanocapsules with highly graphitized carbon walls and partially filled by spherical iron carbide nanoparticles.

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1. Introduction

Iron-containing nanoparticles attract much attention owing to their unique magnetic and chemical properties [1,2]. Nanoparticles composed of metallic iron, iron oxide or iron carbide offer high potential for magnetic resonance imaging, hyperthermia therapy, drug delivery, and magnetic recording [3–5]. These nanoparticles

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also can be used as catalysts for the Fischer–Tropsch process, synthesis of carbon nanotubes, and in organic aqueous oxidation [6–9]. However, oxidation of iron and iron carbide nanoparticles at ambient conditions restricts their practical applications in many fields. Encapsulation of nanoparticles in chemically inert shells could help in resolving of this problem. Carbon shells protect the iron-containing nanoparticles against oxidation, prevent their spontaneous agglomeration and modify the properties. Because of high electrical conductivity of carbon shells these composite nanoparticles may be used as anodes for lithium ion batteries [10]. Furthermore, it was demonstrated that iron and iron oxide nanoparticles inside carbon possess high catalytic activity and selectivity as well as remarkable stability [11,12]. Carbon-encapsulated magnetic nanoparticles seem to be useful for environmental and biomedical applications, for example, as sorbents for removal of heavy metal ions from aqueous solutions [13,14]. Moreover, coating of iron-containing nanoparticles with inert shells makes these nanoparticles less toxic [15].

Recently, the effective method for large-scale synthesis of carbon-encapsulated iron carbide nanoparticles by co-carbonization of Chinese aromatic heavy oil and ferrocene under autogenous pressure has been developed [16–18]. Observed reconstruction of the produced nanoparticles in the enlarged hollow iron oxide nanocapsules with air oxidation was attributed to the nanoscale Kirkendall effect [19–21]. The role of carbon in this transformation is still unclear. It was suggested that carbon layers moderate the interdiffusion rates of air oxygen and core metal that controls oxidation process of the nanoparticles [19].

Detailed study of morphology and electronic structure of carbon-encapsulated iron-containing nanoparticle is great importance to control their functional properties. Characterization of carbon-coated metal nanoparticles is a not trivial task because common methods are often not efficient. For example, X-ray diffraction (XRD) has limitations when studying the small-size nanoparticles and nanoparticles with low crystallinity. Methods of soft X-ray spectroscopy, which are sensitive to local chemical bonding of atoms, can be used for examination of nano-sized objects. Unfortunately, a number of works devoted to the analysis of the electronic structure of ferromagnetic metal nanoparticles encapsulated in carbon shells is very limited [22].

The present work aimed to explore the modifications of the morphology and electronic structure of carbon-encapsulated iron carbide nanoparticles with air oxidation and carbonization at different temperatures. The morphology of nanoparticles is examined by transmission electron microscopy (TEM), while the phase composition and the electronic structure of material at different stages of the transformation are determined using XRD, X-ray emission spectroscopy (XES), and near edge X-ray absorption fine structure spectroscopy (NEXAFS). XES and NEXAFS are complementary methods probing the partial density of occupied and empty states, respectively.

2. Experimental

The carbon-encapsulated iron carbide nanoparticles were produced following to procedure described elsewhere [17]. A mixture of a Chinese aromatic heavy oil, mainly containing 2- and 3-ring aromatic compounds with alkyl substituents (15 g) and ferrocene (50 g) was introduced into a 300 ml autoclave and heated up to 450 °C under autogenous pressure with the final value of ca. 11 MPa. The system was maintained at the final temperature for 30 min, and then cooled to room temperature naturally. The obtained product was repeatedly extracted with pyridine in order to completely remove the unreacted oil and small molecular species, and the pyridine insoluble fraction was regarded as the

desired product (sample 1). The sample 1 was heated in air at 280 °C for 5 h, and denoted as sample 2. The sample 1 oxidized in air at 250 °C for 3 h and then heat treated at 500 °C for 1.5 h and 550 °C for 1.5 h in nitrogen atmosphere was labeled as sample 3. The sample 4 was produced by annealing of the sample 3 at 1000 °C for 1 h under nitrogen atmosphere.

The morphologies of nanoparticles in the produced samples were observed by TEM on a JEM-2010 microscope with 200 kV accelerating voltage and 1.8 Å point resolution. The samples for TEM examination were prepared by ultrasonic dispersion of powder suspended in ethanol on colloidal carbon substrate. XRD measurements were carried out with a Rigaku D/max-2500B2+/PCX system using Cu K α -radiation ($\lambda = 1.5406$ Å) over the range of 5–90° (2θ) at room temperature.

Powdered samples of natural graphite, commercially available Fe₂O₃ (>98% purity) and Fe₃C (~90% purity) were used as reference samples for the NEXAFS and XES measurements. The investigated and reference samples were applied to the scratched copper substrates attached to a holder in the chamber of X-ray spectrometer. The NEXAFS experiments were performed at the Russian–German beamline at Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using the MUSTANG experimental station. NEXAFS spectra near C K- and Fe L-edges were acquired at the photon energy of 280–350 eV and 705–720 eV, respectively, in the total-electron yield mode. The spectra were normalized to the primary photon current from a gold-covered grid recorded simultaneously. The monochromatization of the incident radiation in the carbon and iron absorption region was ~80 and ~200 meV (full width at a half maximum), respectively. During the experiment, the pressure in the chamber was ~10⁻⁷ Pa. XES C K α -spectra were recorded on a laboratory spectrometer “Stearat” using a crystal-analyzer of ammonium biphthalate (NH₄AP). Reflection efficiency of the NH₄AP crystal reveals strong variations when energy of X-ray radiation is close to the K-edge absorption of carbon and the recorded spectrum should be corrected using a procedure described elsewhere [23]. The deposited samples were cooled down to liquid nitrogen temperature in the vacuum chamber of an X-ray tube operating with copper anode ($U = 4$ kV, $I = 0.8$ A). Determination of the X-ray band energy was accurate within ± 0.15 eV with spectral resolution of ~0.5 eV.

3. Results and discussion

TEM images of the samples 1–4 are presented in Fig. 1. The co-carbonization of a mixture of aromatic heavy oil and ferrocene taken in a ratio of 3:1 produced iron-containing rods covered by graphite-like shells and embedded into carbon matrix (Fig. 1a). The particles size varies from 100 to 250 nm in the length and from 20 to 50 nm in the outer diameter, average thickness of surrounding carbon layers is ~5 nm. XRD pattern of the sample 1 (Fig. 2a) showed a broad asymmetric peak at $2\theta = 25.6^\circ$ assigned to diffraction from the (002) planes of hexagonal graphite structure. The distance between graphite layers derived from the peak position is found to be ~3.45 Å. The larger interlayer spacing as compared to graphite indicates lower ordering of the hosting carbon layers. According to the XRD data the metallic cores are mainly composed of the cementite Fe₃C with an admixture of body-centered cubic (bcc) phase of iron (α -Fe).

Oxidation of sample 1 in air at 280 °C for 5 h yielded hollow nanoparticles with a length varied from 50 to 400 nm, outer diameter ranged within 40–80 nm, and average wall thickness of 15 nm (Fig. 1b). As compared to the initial material, these nanoparticles are larger in size and have the thicker walls with the stronger TEM image contrast. This observation along with emptying of the nanoparticle interior implies that core iron atoms migrated

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