Encapsulation of Iron Carbide in Carbon Nanocapsules

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Whiskers of iron carbide encased in carbon shells have been prepared from iron(II) phthalocyanine. Solid FePc is oxygenated and then thermally treated under H_2 flow. With proper control of conditions, Fe_3C free from metallic iron can be synthesized. The product was characterized with the help of Mössbauer effect spectroscopy, X-ray diffraction, X-ray absorption, and transmission electron microscopy. The iron carbide whiskers range in length from 300 to 500 nm, and their widths are approximately 100 nm. The carbon coating is uniform and about 2.7 nm wide.

Introduction

Various types of carbon arc discharge generators are being used for the formation of fullerenes, metallofullerenes, and other carbonaceous materials. The discovery of the presence of LaC_2 and YC_2 encapsulated in carbon shells, among other carbonaceous materials, in the carbon arc, elicited great interest.[1,2] The procedure was soon adapted for production of carbon-coated nanocrystallites of magnetic carbides and metals such as rare-earths and iron group metals (Fe, Co, Ni), which were isolated from other carbonaceous material using a magnetic field.[3–6] The carbon shells are airtight and protect the encaged metals and carbides from the ambient atmosphere. Such carbon-coated magnetic particles have potential for a variety of industrial applications.

Here we report a novel procedure for preparation of iron carbide (cementite) nanocrystallites encapsulated in thin carbon shells. The method involves oxygenation of solid iron(II) phthalocyanine (FePc), followed by thermal treatment at relatively low temperatures, in hydrogen. The reaction is presumably catalyzed by radicals. This procedure can be adapted for the preparation of any other carbide starting with the appropriate metal porphin-based compound.

Experimental Section

Batches of commercially available FePc (Aldrich Co) were oxygenated at 180 °C in a flow of O_2/N_2 mixtures with 40–60% O_2 for 6–10 days. The oxygenated FePc was heated under H_2 flow for 1 to 20 h at 300–400 °C.

Caution: Oxygenation of FePc at 180 °C under a flow of pure O_2 results in an explosion.

X-ray absorption experiments were done at the National Synchotron Light Source, Brookhaven National Laboratory. The beam line was configured with Si (220) monochromator crystals and a rhodium-coated postmonochromator mirror for focusing and harmonic rejection. The cutoff energy of the mirror was set for 12 keV. The measurements were done at room temperature.

Transmission electron microscopy experiments were performed at NIST using a JEOL 3010 (300 kV) TEM. The microscope is equipped with a windowless Ge energy-dispersive X-ray spectroscopy (EDS) detector.

Mössbauer effect measurements were done using a conventional spectrometer with constant acceleration and in conjunction with a multichannel analyzer. The γ-ray source, ^{57}Co diffused in a rhodium matrix, was kept at room temperature. The velocity scale was calibrated using metallic iron foil. Chemical shifts are expressed relative to α-Fe.

An X-ray powder diffractometer with Co Kα radiation (the range of scanning in 2θ was 3–140° with the rate of $^1/_4$°/min) was used in the present work.

Results and Discussion

Different techniques were used to characterize the product formed by sequential thermal treatment of FePc in O_2 and H_2 flow.

Mössbauer Effect Studies. The Mössbauer spectrum is shown in Figure 1. The magnetic species formed, which constitutes 90% of the total area, has

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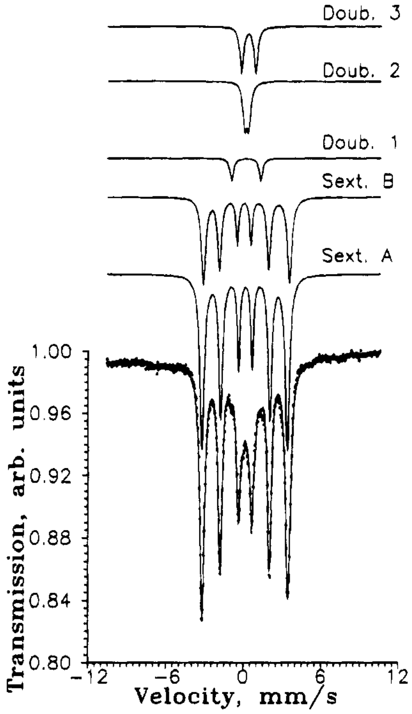

Figure 1. Mössbauer spectrum at room temperature of Fe_3C obtained from FePc.

Mössbauer parameters very similar to those reported for iron carbide, Fe_3C (cementite),[7-9] as well as for samples synthesized in our laboratory by thermal treatment of iron oxide at 550 °C under a flow of a mixture of CO and H_2 (3:7 volume ratio).[7] The iron in Fe_3C occupies two different lattice sites in the ratio 2:1, and the spectra were computer analyzed accordingly. The internal magnetic fields for the two lattice sites in the compound obtained from FePc are 204 and 205 kOe, respectively, with practically the same chemical shift (relative to α-Fe) of 0.18 mm/s for both sites at room temperature (Figure 1). Samples of Fe_3C prepared from iron oxide yield internal magnetic fields of 207 and 209 kOe and chemical shifts of approximately 0.18 mm/s. These values correspond fairly well with those reported in the literature,[7-9] for example, Caer et al.[8] observe 206 and 208 kOe with a chemical shift of 0.18 mm/s. The lower values of internal magnetic fields observed for Fe_3C whiskers obtained from FePc may be related to their size, the widths being about 100 nm, as discussed later.

A careful examination of the Mössbauer spectrum (Figure 1), as well as results from other runs, indicates the absence of significant amounts of metallic Fe and Fe_3O_4. If the duration of thermal treatment in H_2 is prolonged or if the temperature is raised, then the yield of metallic Fe increases considerably, e.g., 8 h of thermal treatment in H_2 at 450 °C.

X-ray Diffraction. X-ray diffraction (Figure 2) again shows that the product exhibits peaks which correspond to those of the ASTM standard Fe_3C. The background is considerably enhanced due to diffuse scattering from the carbonaceous material present in our preparation.

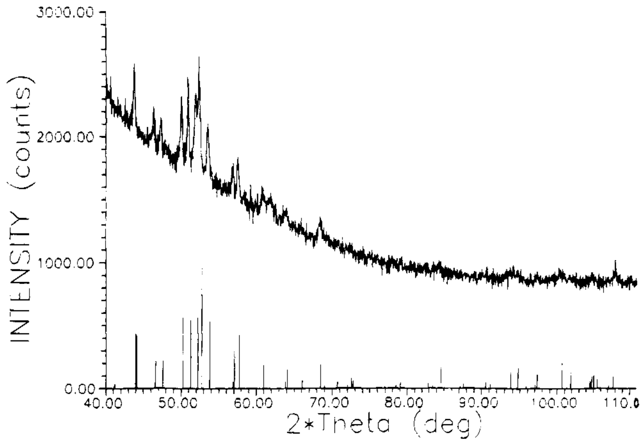

Figure 2. X-ray diffractogram of Fe_3C obtained from FePc with a bar diagram of ASTM standard for Fe_3C.

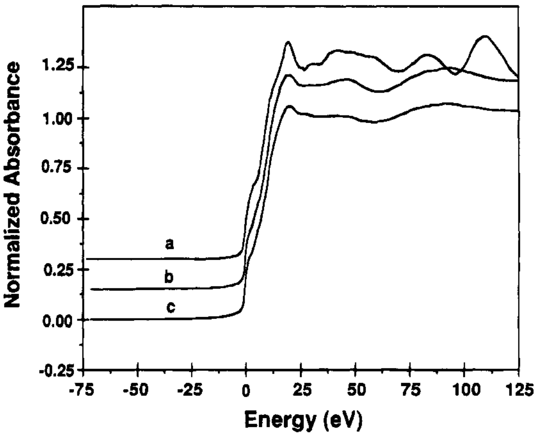

Figure 3. XANES plots for (a) iron foil, (b) Fe_3C synthesized from Fe_2O_3 by conventional procedure, and (c) Fe_3C obtained from FePc.

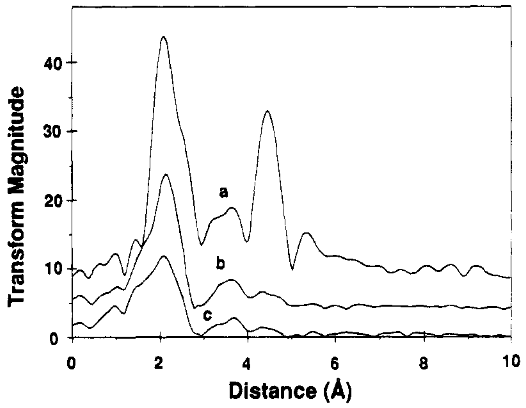

Figure 4. Plots of radial structure functions (FT of EXAFS data) of (a) iron foil, (b) Fe_3C synthesized from Fe_2O_3 by conventional procedure, and (c) Fe_3C obtained from FePc.

X-ray Absorption Spectral Measurements. The X-ray absorption near-edge spectra (XANES) for an iron foil (plot a), standard Fe_3C (plot b), and the product obtained from FePc (plot c) are shown in Figure 3. The spectrum for our preparation (c) is very similar to that of Fe_3C (b) and decidedly different than that of metallic iron (a). The radial structure functions, i.e., Fourier transforms of the EXAFS data, as shown in Figure 4, again tell us that (c) is similar to (b). These observations along with X-ray diffraction pattern clearly indicate the identity of the synthesized product as Fe_3C, with possible substitution of some of the carbons by nitrogen

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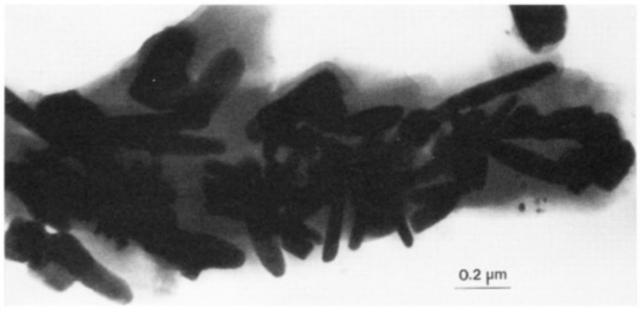

Figure 5. Transmission electron microscopy image of Fe_3C obtained from FePc.

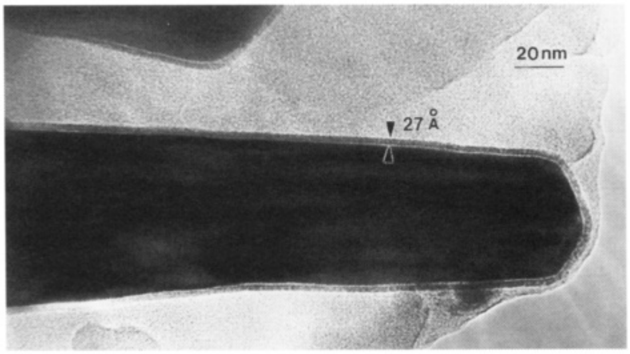

Figure 6. High magnification transmission electron microscopic image of a Fe_3C whisker (obtained from FePc), which is coated with carbon.

atoms as discussed below.

Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDS). The TEM images (Figure 5) show that the Fe_3C formed from FePc has whisker-type structure. The length of the whiskers range between 300 and 500 nm. The ratio of length to width is approximately 4. These whiskers are mostly embedded in a carbonaceous matrix and tend to distribute as clusters (Figure 5). A high-magnification TEM image (Figure 6) shows that the whiskers are covered by a uniform layer of carbon which is about 2.7 nm thick.

EDS analysis indicates the presence of a few atomic percents of nitrogen in Fe_3C formed from FePc. This is consistent with results of chemical analysis, which show presence of nitrogen at the level of 5−7 at. %. This should not be surprising in view of the fact that the core of phthalocyanine is FeN_4. The question regarding the exact location of nitrogen atoms is still open. A careful analysis of Mössbauer spectra indicate the absence of any known Fe−N phase (e.g., nitrides of various composition) in our material.

EDS analysis also indicates that there is some oxygen associated with the carbonaceous matrix.

Conclusion

Phthalocyanines and other porphin-based compounds permit oxygen diffusion between the layers of molecules either when heated in the presence of O_2 or even at room temperature.[10] When the oxygenated material is thermally treated under H_2 flow, pyrolysis occurs, presumably involving radicals. If the conditions are appropriate, the end product is Fe_3C whiskers coated with a fairly uniform layer of carbon. The material was characterized with the help of Mössbauer spectroscopy, X-ray diffraction, EXAFS, and TEM. If the treatment in H_2 is prolonged or at a higher temperature, metallic iron is the main product.

Commercially available transition metal phthalocyanines have varying amounts of O_2,[10] as seen for FePc by Mössbauer spectroscopy.[11] Therefore, the compounds obtained earlier by thermal treatment at approximately 600 °C under argon flow of "partially" oxygenated MePc (Me = Fe, Co, Mn, and Ni)[12] can now be identified as carbides. This is supported by the magnetization versus magnetic field hysteresis loops, and the Mössbauer spectra of the ^{57}Co-labeled compound. Carbon-coated compounds were not known then, and the modified properties misled the authors. When the metal phthalocyanines are well oxygenated and hydrogen is substituted for argon, carbides are formed at much lower temperatures (300−400 °C).

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