Ellipsoidal Carbon Capsules Encapsulated Magnetite Nanorods

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A novel ellipsoidal carbon capsules, with submicrometer sized Fe_3O_4 nanorods inside, were fabricated by in situ carbonization–reduction process from sandwich α-Fe_2O_3@Air@ polypyrrole ellipsoidal spheres in vacuum at 823 K.

Since the discovery of carbon nanotubes[1] in 1991, there has been a worldwide interest on hollow carbon products owing to their applications in broad areas of science and technology.[2] Encapsulating second phase inside carbon hollow structures has been particularly focused on because carbon shell can immunize the encapsulated species against environmental degradation effects while retaining their intrinsic properties.[3] Accordingly, magnetic elements or compound-encapsulated capsules are important materials of information technologies and biomedicines.[4] The preparation of magnetic encapsulation core–shell capsules includes two routes: one-step and two-steps. The former, such as various modified pyrolysis techniques from complex compounds or organic–inorganic composites, is simultaneous preparation of carbon shell and magnetic core.[5] The later involves the coating or filling of magnetic species into hollow structures.[6] Up till now, although a number of carbon capsules have been reported, nonspherical hollow capsules have received much less attention. Previously, we reported the fabrication and characterization of sandwich Fe_2O_3@Air@polypyrrole ellipsoidal particles.[7] Based on that work, novel ellipsoidal hollow carbon nanocapsules with movable magnetic cores have been successfully fabricated by in situ carbonization–reduction process in vacuum.

In a typical fabrication of Fe_3O_4@Air@C capsules, the ellipsoidal α-Fe_2O_3@Air@PPy core/shell precursor particles were firstly prepared as previous report.[7] The pre-synthesized α-Fe_2O_3@Air@PPy capsules were placed in a quartz tube, then vacuum sealed and heated at a heating rate of 1 K/min. After 3 h of carbonization at 823 K, the quartz tube was cooled to room temperature on standing. Magnetic capsules were obtained after opening the sealed tube.

Fe_3O_4@Air@C capsules are shown in TEM image (Figure 1c). They inversely replicate the shape of the template particles (Figure 1a). And they have uniform ellipsoidal morphology with the narrow size distribution (See, Support Information, Figure SI1).[13] Because the hollow cavity of capsules provides enough space, submicrometer size of Fe_3O_4 nanorods with 450–120 nm length–width are encapsulated movably inside the capsules. The average diameter of carbonized nanocapsules is about 730/ 360 nm. Their carbon wall thickness is easily controllable because the polypyrrole wall thickness of the α-Fe_2O_3@Air@PPy template capsules has been realized between 20 to 60 nm.[7] Therefore, the thickness of carbon wall after the carbonizaation
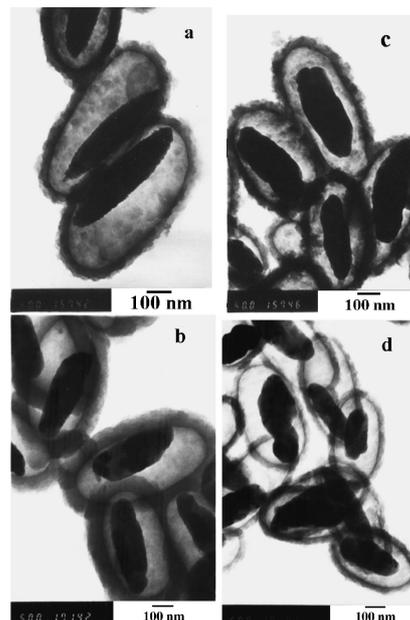
Figure 1. TEM images of α-Fe_2O_3@Air@PPy (a) and Fe_3O_4@Air@C capsules with the 55 (b), 25 (c), and 15 (d) nm thickness carbon shell.

is in the range of 15 to 55 nm. Figures 1b and 1d display another two types of Fe_3O_4@Air@C capsules with different wall thickness, respectively.

During the in situ carbonization–reduction process, compact carbon wall structures were formed via the carbonization of polypyrrole accompanied by dehydrogenation, denitrogenation, and aromatization. Most of the gaseous by-products in the decomposition of the PPy wall once were identified to be such as CH_4 and HCN.[8] Although the mechanism is not clear, these gases may provide a reduced atmosphere, making the hematite (α-Fe_2O_3) cores being synchronously reduced to magnetite phase (Fe_3O_4).

X-ray diffraction patterns (XRD) are used to register the phase transformation of cores from hematite (α-Fe_2O_3) to magnetite (Fe_3O_4). They were recorded on a MAC Science MXP 18 AHF X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.54056$ Å). In Figure 2a, all sharp peaks can be indexed to hematite phase while those in Figure 2b mark well with magnetite (Fe_3O_4). It confirms that pure Fe_3O_4 nanorod cores can be obtained through this route. Considering the carbon content in Fe_3O_4@Air@C product, the broad peak at 26.2° belonging to carbon in XRD pattern is not observed clearly enough in Figure 2b. However, the Raman spectrum of the carbonized Fe_3O_4@Air@C product exhibits two distinct peaks at 1586
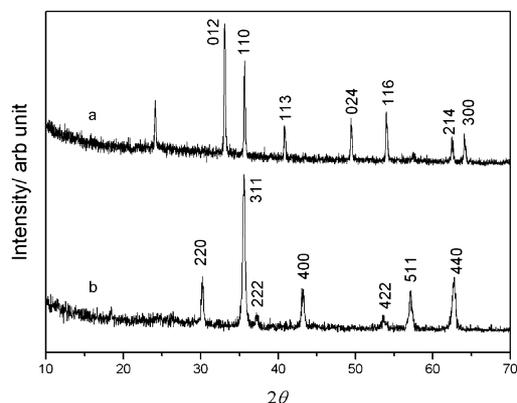
Figure 2. XRD patterns for α-Fe_2O_3@Air@PPy (a) and Fe_3O_4@Air@C (b) particles.
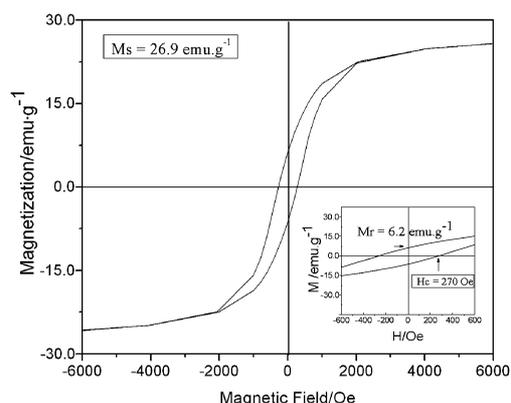
Figure 3. Magnetic hysteresis loops of Fe_3O_4@Air@C spheres.

and $1352\,cm^{-1}$ (See Figure SI2).[11] The band at $1586\,cm^{-1}$ (G band) is assigned to the E_{2g} vibration of graphitic carbon with the sp^2 electronic configuration. On the other hand, the peak at $1352\,cm^{-1}$ (D band) is attributable to the A_{1g} mode of diamond-like carbon with the sp^3 configuration.[9] The relative intensity (I_D/I_G) of Fe_3O_4@Air@C capsules is 0.88. Furthermore, 320, 513, and $672\,cm^{-1}$ peaks are attributable to Fe_3O_4 nanorod cores (see inset in Figure SI2).[13]

The magnetic property, which is primarily due to Fe_3O_4 nanorods encapsulated in the carbon cavity, has been measured in $300\,K$ using a superconducting quantum interference device (SQUID) magnetometer. The saturation magnetization for Fe_3O_4@Air@C spheres is evaluated to be $26.92\,emu/g$ at about $6000\,Oe$ in Figure 3. The values of the coercive force and residual magnetization are evaluated to be $270\,Oe$ and $6.15\,emu/g$ (see inset in Figure 3), respectively. Considering the iron oxide content in the carbon capsules, the coercive force for this sample is large. It is known that the coercive force is $500–800\,Oe$ for bulk magnetite particle. The coercivity of Fe_3O_4@Air@C capsule is lower than the bulk one because the H_c is strongly dependent on the particle size and domain characteristics of magnetic particles. However, the capsules show larger H_c than nanoparticles because its particle size is larger than $100\,nm$, critical size of the single domain for the Fe_3O_4 particle. Neverthe-

less, the coercivity of Fe_3O_4@Air@C capsule is large compared with the spherical magnetite and magnetite microcrystalline octahedrons.[10,11] In magnetic particles of nanometer size, magnetic anisotropy strongly affects the shape of the hysteresis loop and the coercivity.[12] Therefore, the increased magnetic anisotropy in nonspherical submicrometer sizeed rod shape magnetocrystallinity is attributable to the large coercivity.

The significance for the fabrication of ellipsoidal carbon capsules with magnetic rods inside from the sandwich α-Fe_2O_3@Air@PPy template is the in situ carbonization–reduction process. Because of the synchronous process of carbonization of polymer wall and the reduction of hematite cores, no additional reducing regent was needed during the reducing process of hematite cores, leaving to the Fe_3O_4@Air@C capsules without byproducts. It is a convenient route to obtain magnetic carbon capsules without further purifying.

In summary, uniform ellipsoidal Fe_3O_4@Air@C capsules, with movable submicrometer sizeed Fe_3O_4 rod cores inside, were fabricated by in situ carbonization–reduction process in vacuum at $823\,K$. The wall thickness of Fe_3O_4@Air@C capsules can be controlled between 15 and $55\,nm$. It was found that Fe_3O_4@Air@C capsules were ferromagnetic at room temperature, which indicates that they may have important potential applications in biomolecular delivery or electromagnetic nanodevices, such as anisotropic colloidal particle assembly under exterior magnetic field.

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13　Supporting Information is available electronically on the CSJ-Journal Website, http://www.csj.jp/journals/chem-lett/index.html.