

# SYNTHESIS OF CARBON ENCAPSULATED IRON NANOPARTICLES BY CARBONIZATION OF STARCH WITH IRON AS CATALYST

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## 1. Introduction

Since the first report about carbon encapsulated metal nanomaterials by Ruoff et al. [1], metal filled nanocapsules with unique microstructures and particular properties have been widely studied because of their potential applications in magnetic recording media, magnetic resonance imaging and bio-engineering[2-4]. Nanoscale magnetic particles usually exhibit unique features and specific properties such as superparamagnetism and quantum tunneling of magnetization [5]. However, the high surface to volume ratio of metal nanoparticles leads to their rapid oxidation, which results in antiferromagnetic oxide surface shells formed around metal nanoparticles that influence significantly the magnetic behavior of these particles. In this case, an efficient oxidation resistant coating such as carbon shells would be required [6]. Moreover, the carbon coatings can endow these magnetic particles with the biocompatibility and stability in many organic and inorganic media [7]. Up to now, a number of techniques including arc discharge, laser/electron irradiation, chemical vapor deposition (CVD) [8-9] have been used to produce carbon encapsulated nanomaterials (termed as CEN). However, these techniques are apparently not suitable for mass production of CEN. In the present study, we report a novel catalytic method to prepare carbon encapsulated Fe nanoparticles with starch as the carbon source, which was achieved by carbonizing a mixture of starch and iron oxide particles in hydrogen flow under mild conditions.

## 2. Experimental

In our experiments, starch bought from Shenyang Lianbang Chemical Company was used as carbon source for making carbon encapsulated iron nanomaterials. For each run, starch (2.00g) was added into 5.0 ml de-ionized water to make a paste. The paste was then fully mixed with the ultra fine hydroxide made from precipitation of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.10g) and 0.1 mol/L NaOH with a molar ratio of oxyhydrogen ion to metal ion being 3:1. Furthermore, the mixture was baked for 2 h at 100 °C. Finally, the dried materials were mechanically crushed into fine powder in a mortar. All chemicals used in the study were in AR grade.

The experiment set-up for preparing CEN consisted of a quartz reactor tube (I.D. 30 mm and 600 mm in length) and a horizontal furnace with a temperature control system. The fine powder described above was put in a quartz boat, then placed into the middle of quartz tube reactor that was fixed in furnace, and the hydrogen gas was introduced

into the reactor at a flowing rate of 20 cm<sup>3</sup>/min. The system was then ramped at 5 °C/min to reaction temperature (typically 900 °C) and held at the final temperature for 4h before cooling back to room temperature in nitrogen gas. A large amount of fiber-like black material was formed in the quartz boat.

Samples for TEM (JEM 2000EX, operated at 100 kV) study were prepared by dispersing a small amount of fiber-like black materials in ethanol with mild sonication for 5 min. Drops of the dispersion were placed onto a copper micro-grid covered with carbon film for examination.

### 3. Results and Discussion

The TEM images show that the monodisperse metal nanoparticles encapsulated in the quasi-spherical carbon structures were prepared, of which two typical ones are shown in Fig. 1. The size distribution of these encapsulated nanoparticles is in a range of 20-110 nm, which centers at 50-60 nm. As can be seen in Fig. 1B, these Fe nanoparticles have a ball-like core-shell structure, and are completely encapsulated by the uniform wrapping shell or carbon coatings. In general, the morphology of the iron filled nanoparticles obtained by heating starch is similar to those obtained by other methods.[9] It is interesting to note that empty carbon capsules are also occasionally observed, which are found to be attached on the CENs, as shown in Fig. 2. Energy dispersive X-ray analysis (EDX) of the CEN samples revealed that in addition to a little phosphor, the dominant elements in the carbon encapsulated nanoparticles are carbon and iron, of which the typical EDX spectrum is shown in Fig. 3.

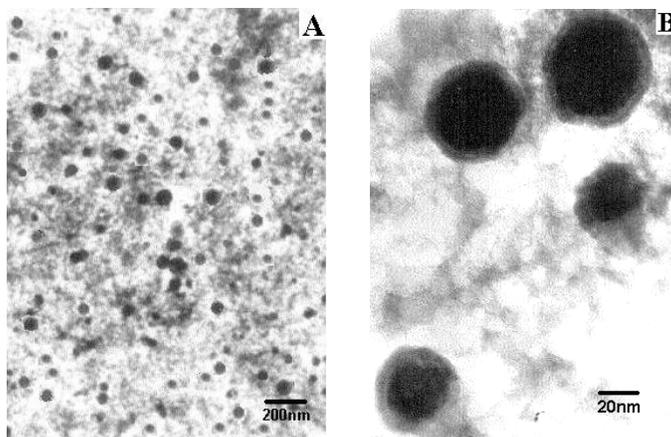


Fig. 1 TEM images of carbon encapsulated Fe nanoparticles obtained by carbonizing mixture of starch and iron oxide

The samples were further examined using XRD (RINT-2000 diffractometer, Rigaku, Cu K $\alpha$ ), which reveals that the graphitization of the carbon layers outside the iron particles is obvious, as can be seen in Fig. 4. It is clear that catalytic graphitization reactions take place during the preparation process of CENs, which must be related to the iron particles formed in-situ, and this is evidenced by a series of comparative experiment. When pure starch was heated under the same conditions, little graphite is

observed in the XRD pattern. In fact, the phenomenon of catalytic graphitization is well known [10]. Several typical peaks corresponding to single phases of iron ( $\alpha$ -Fe and  $\gamma$ -Fe) can be clearly seen in the XRD pattern shown in Fig. 4, which clearly demonstrates that iron species formed is reduced in-situ by hydrogen during the carbonization process. The iron particles formed in-situ would act as catalyst to speed up the transformation of carbon released from the decomposition of starch into graphitic one. In other words, the iron particles formed in-situ has played a key role in the formation of carbon encapsulated nanoparticles. The phosphor derived from starch (see the EDX spectrum in Fig. 3) might also play a similar role, as the role played by sulfur [11], in promoting the formation of graphitic layers around the nanoparticles.

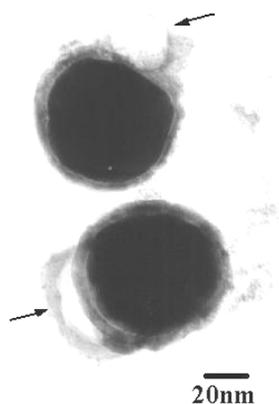


Fig. 2 TEM image of hollow carbon capsules grown on the carbon encapsulated nanoparticles based on starch

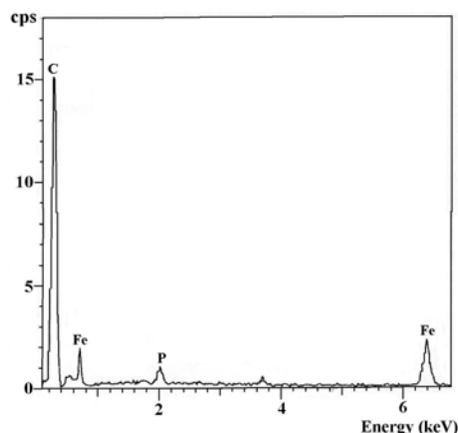


Fig. 3 EDX spectrum of carbon encapsulated Fe nanoparticles

The carbon encapsulated iron nanoparticles reported here were obtained by carbonizing a mixture of starch and iron hydroxide in hydrogen at 900 °C for 4h, of which the formation mechanism is not clear at the moment. An attempt has been made to figure out the mechanism involved in the process. As mentioned above, little graphitic

carbon was formed when pure starch was carbonized under the heating conditions. It was also found that little CENs were obtained when the carbonization was conducted in flowing argon instead of in hydrogen. With all these information in mind, it is easy for one to speculate that the iron species formed in-situ has acted as catalyst for the growth of the graphitic carbon layers formed around the CENs, though the detailed scheme involved is not known. More work is needed to clarify the formation mechanism of starch-derived carbon encapsulated nanoparticles, and the work is still in progress.

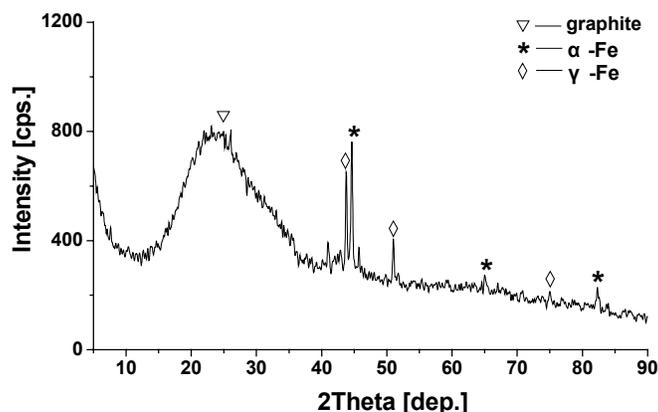


Fig. 4 XRD pattern of carbon encapsulated Fe nanomaterials

For the preparation of carbon encapsulated nanomaterials, different carbon sources such as graphite [12], petrochemicals [13] and organometallic compounds [14] have been tested before. In our case, starch is adapted as a carbon precursor to prepare carbon encapsulated iron nanomaterials under mild conditions, to our knowledge, which has never been reported in literature. Starch is a cheap and non-toxic biomaterial. Once being heated, starch would decompose, resulting in a large amount of small molecules and carbonaceous species. The preliminary results presented here lead one to believe that starch is another ideal biomaterial for making carbon nanocapsules, though the mechanism involved in the process differs greatly from the scheme in the case of protein type biomaterial (ferritin) [15]. Zhukhman et al have ascribed particular thermal effects to structural changes taking place in starch [16]. It has been found that between 200 °C and 220 °C constitutional water in starch would be removed. The evolution of volatile carbon-containing species (CO, CO<sub>2</sub> and organic compounds) starts suddenly at 270 °C and continues up to 310 °C. As the temperature further increases up to 600 °C, the decomposition of starch is basically finished, at such a low temperature no graphitization reactions would take place. Obviously, for the carbon encapsulated iron nanomaterials reported in the present study, the graphitization of carbon must be promoted or catalyzed by the iron particles formed in-situ during the carbonization step. In other words, the formation process of carbon coating nanoparticles is a metal-mediated graphitization process, in which carbon species released from decomposition of starch would deposit on the surface of nanosized Fe particles and re-crystallize to form graphitic carbon layers. It should be noted that there is no clear-cut explanation for the formation mechanism of carbon encapsulated nanoparticles at the moment, which should be clarified simply because a better understanding of the mechanism involved in

the preparation step will surely help to control the quality of carbon encapsulated nanomaterials. The work is now in progress.

#### 4. Conclusions

In summary, carbon-coated iron nanoparticles with well-developed quasi-spherical shape has been prepared with starch as carbon source. This is a new and efficient approach for the mass production of nanocage structures under mild conditions, which needs to be further explored for preparing various carbon coated metal nanomaterials. Also more work is needed to optimize the preparation conditions and to clarify the formation mechanism of the carbon coated nanoparticles derived from starch.

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