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SYNTHESIS AND PERFORMANCE OF BIOCOMPATIBLE CORE- SHELL CARBON- IRON MAGNETIC NANOPARTICLES FROM STARCH

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A novel method was introduced to synthesize biocompatible carbon-encapsulated magnetic iron nanoparticles, in which starch both functioned as precursor and as stabilizer for iron nanoparticles. The structure, size distribution, phase composition, magnetic properties and oxidation resistance of the as-obtained particles were investigated by transmission electron microscopy, X-ray diffraction, vibrating sample magnetometry and differential scanning calorimetry. Results show that the carbon-coated iron nanoparticles are spherical particles with a diameter of 20-40 nm feature well-constructed core/shell structures with an iron core inside and an onion skin carbon layer outside, carbon layers can protect inner iron core from been oxidized, the hysteresis curves show that with the increase of iron content the saturation magnetization, remanence magnetization andintrinsic coercive force increasing. While the ratio of remanence to saturation magnetization (Mr/Ms)of all the sample less than 0.25, implying that they are super-paramagnetic at room temperature.

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Keywords：Carbon；Carbon coated nanoparticles；Starch coating method

1. Introduction

Carbon-encapsulated metal nanoparticles, or carbon –coated metal nanoparticles was first synthesized by Ruoff[1]. They are new type of composite materials have a core - shell structure with a metal or metal carbide core and carbon or graphite outer layer [2] , Due to confined within a small range by carbon layer these nanoparticles exhibit new quantum performance，electrical properties, optical properties, magnetic properties [3,4]. So these nanoparticles have a potential valuable use in the xerographic[5], hyperchromic magnetic resonance imaging contrast agents and agents [6], where the biological performance is particularly noteworthy，such as magnetic targeting drug delivery and the magnetic hyperthermia heating agent[7]. Although there a variety of means to produce carbon coated materials, but they all have a same shortcomings, for instance low yield and high cost. So far, low-cost high-yield produce carbon coated metal nanoparticles still is a huge challenge, which limit widespread use of carbon-coated metal particles.

In this paper, we employed simple starch coating method to synthesize carbon-coated iron nanoparticles, it is a new method to prepare carbon coated nanoparticles. In first step, prepare iron nitrate starch complex by sol-gel method, then thermal decompose it under hydrogen atmosphere, finally synthesis of carbon-coated iron nanoparticle. Starch in which both as the carbon source and as the iron nanoparticles stabilizer. Compared with other methods, this method can be a lot of preparation with low cost.

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2. Experimental

2.1 Procedure and precursors

Fe $(NO_3)_3 \cdot 9H_2O$, starch powders and ammonia were used as starting materials. Dissolved starch in ammonia solution, mixed it with Fe $(NO_3)_3 \cdot 9H_2O$ in ethanol solution under agitation. Then yellow brown viscous suspension was obtained,

$$Fe(NO_3)_3 + 3NH_3 \bullet H_2O \rightarrow Fe(OH)_3 + 3NH_4NO_3$$

And the brown substances is $Fe(OH)_3$. After vacuum filtration the samples were put into a evaporating dish and dried it at 100 ^oC for 24h in a oven,

$$2Fe(OH)_3 \xrightarrow{heat} Fe_2O_3 + 3H_2O$$

iron oxide starch precursor was prepared.

2.1.2 carbonization

Then the precursor was placed in the tube furnace for coal carbonization. Carbonization process was under the atmosphere of hydrogen, and the N_2 as pretreatment gas for 30min, hydrogen flow rate 35mL / min. Carbonization temperature curve: 10 ^oC / min, from room temperature to 300 ^oC. Then to 800 ^oC with the increase rate of 5 ^oC / min, and keep in 800 ^oC for 4 h. Natural cooled to room temperature. A black powder-like substance was obtained, these powder are the final products.

2.1.3 The iron content calculation:

$$\text{Iron conent} = \frac{(\text{mass of } Fe(NO_3)_3 \bullet 9H_2O) * \frac{56}{404}}{\text{mass of starch} * \frac{72}{162}}$$

2.2 Characterization

A X-ray diffraction(XRD) with Cu（Kα） radiation was used at room temperature to identify the phase and the crystal structure .The micro-structure of carbon-coated iron nanoparticles was observed by using transmission electron microscope (TEM)(JEM-2010 HR) operating at 200Kv. Magnetic properties at room temperature of the products were characterized by a vibrating sample magnetometer (VSM), at magnetic field of -12-+12KOe. Q600 DSC / TGA simultaneous, TA companies in the United States was employed to test DSC / TGA .Test conduction: weight between 1.5-2.0 mg, carrier gas is air, heating rate 20 ^oC / min, from room temperature to 800 ^oC.

3. Results and discussion

3.1. Structural and morphology of carbon-coated iron nanoparticles

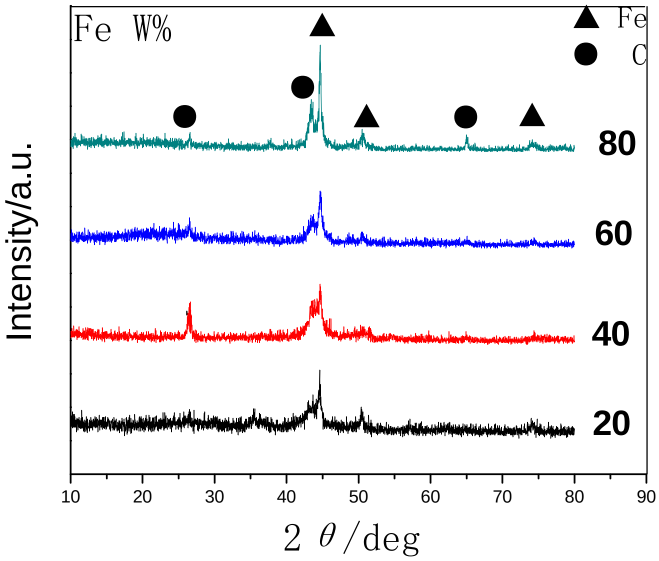

Fig.1. XRD patterns of different content iron carbon-coated iron nanoparticles.

Fig.1 is XRD patterns of different content iron carbon-coated iron nanoparticles, (iron content in the sample are 20%, 40%, 60%, 80% respectively) what can be seen from the diagram, the products only have carbon and iron peaks， and no peaks for iron carbide and oxide could be detected, indicating carbon-coated iron nanoparticles did not contain iron oxides and carbides. We found there are not obvious diffraction peaks in the sample of 20% iron content (carbon content 80%) carbon-coated iron anoparticles, this is due to amorphous carbon in the samples. It is obviously that all the samples have the diffraction peak of iron. and with the increase of iron content the diffraction intensity increased, the sample of 80% iron content with the strongest (110), (200), (211) diffraction peak (PDF card 06-0696). At the same time we can see that the carbon-coated iron nanoparticles of carbon content of 40% of with a strong carbon peaks, which shows that the sample contains crystalline carbon.

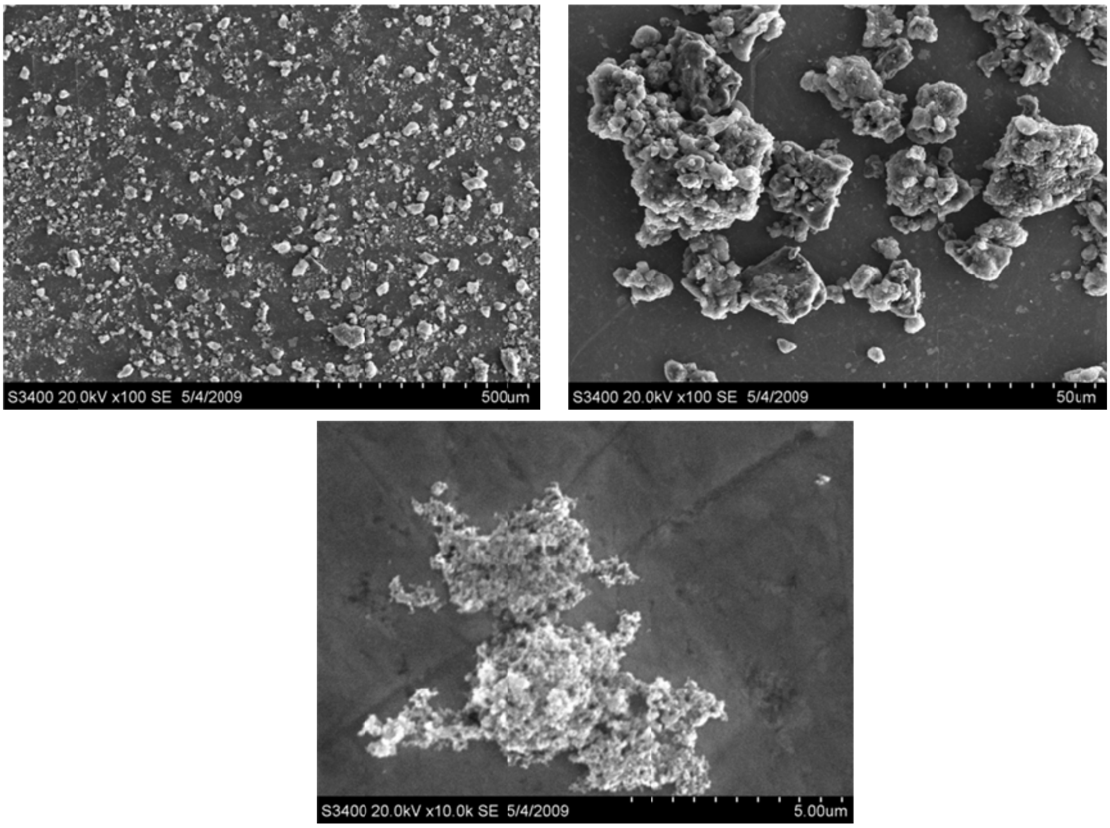

Fig.2 SEM images of carbon coated iron nanoparticles

Soluble starch is amylose, molecular formula is $(C_6H_{10}O_5)$ n, in the iron / starch gel, The starch powder as a dividers, separate iron oxide nanoparticles, and in the heating process it prevent the aggregation of iron nanoparticles effectively. Heated to about 300 ^{o}C, starch start decomposed, and finally generated the different types of carbon graphite [12,13] . Under the iron catalystic, these graphite-like materials final formed lamellar graphite and coated on the surface of iron nanoparticles.

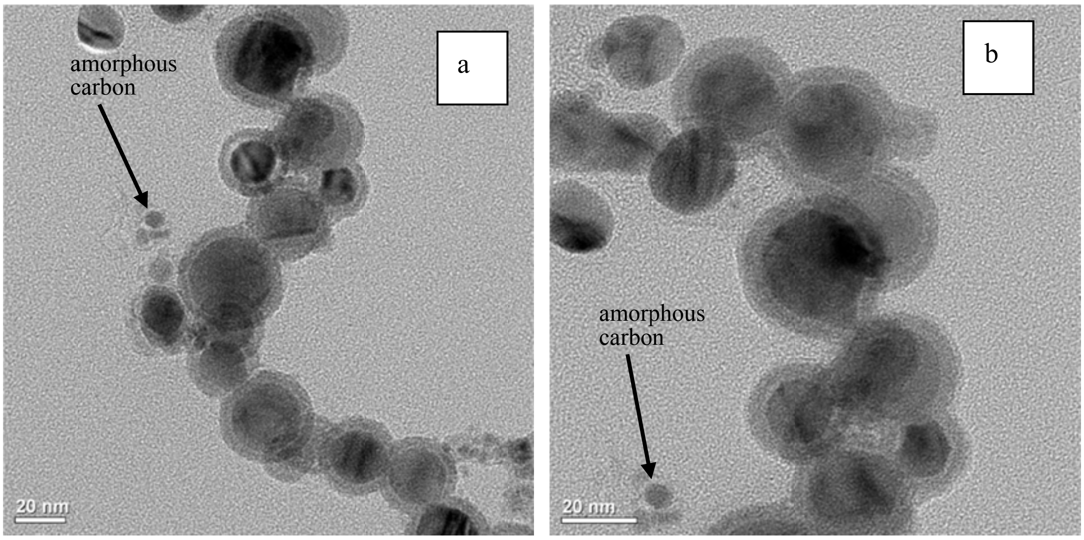

Fig.2. TEM images of carbon coated iron nanoparticles

Fig.2 shows TEM image of carbon-coated iron nanoparticles, which reveal the general morphology, a typical core-shell structure of the nanocapsule materials, nanoparticles are spherical particles with a diameter of 20-40 nm, particle size is fairly uniform. The core (dark part) is metal iron, outside (light part) is carbon layers, except carbon-coated iron nanoparticles in the specimen, there is a small amount of amorphous carbon particles(the arrows in Figure 2a, 2b). These amorphous carbon particles, also explained why there is not a strong diffraction peak of carbon in the XRD pattern of the sample which the iron content is 20% (carbon content 80%).

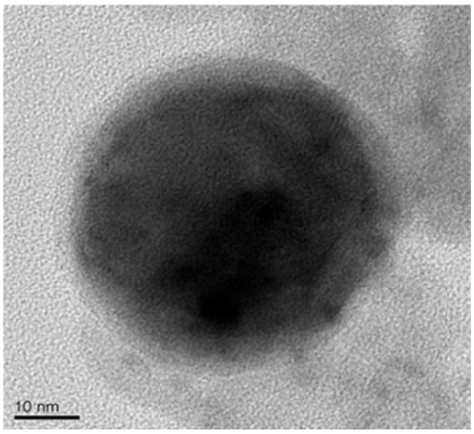

Fig.3. HRTEM image of carbon coated iron nanoparticles

HRTEM image of carbon-coated iron nanoparticles, as shown in fig.3, reveals fine structure of these nanocapsules, the thickness of outside carbon layer is 5-10 nm, the iron core is about 25 nm in diameter. Carbon layers that close to iron core are regular stripes structure, carbon layers that away from the iron core are relatively disordered stripes, this is because in the carbonation process iron nanoparticles could promote carbon around them be graphite structure, due to the lack of the presence of iron catalyst, carbon layers away from iron core formed amorphous structure.

3.2 Magnetic property of carbon-coated iron nanoparticles

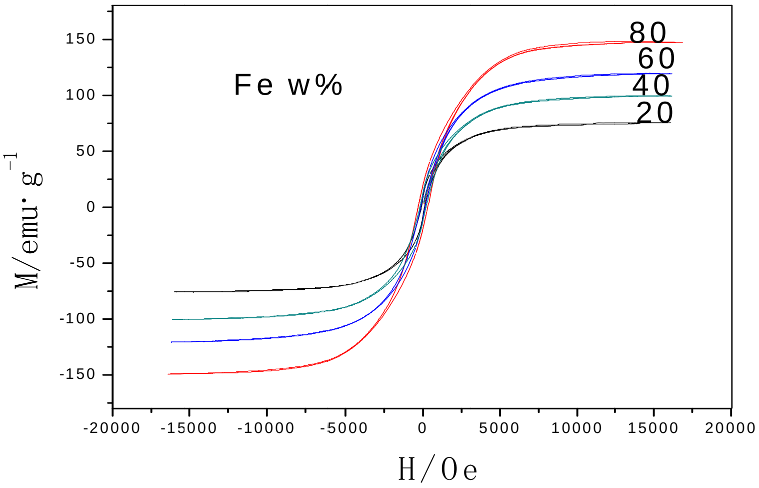

Fig.4. Magnetic field dependence of magnetization of different content iron carbon coated

Carbon-coated iron nanoparticles as a means of potential applications of magnetic record materials. It is useful to study the magnetic properties of the products. The hysteresis loops at room temperature of carbon coated iron nanoparticles (Fig.4) show the saturation magnetization of samples increase with the increasing of iron content, at the same time remanent magnetization and intrinsic coercivity also increase with the iron content increase. Sample of 20% Fe, the saturation magnetization is 75.46 emu/g, remanent magnetization is 8.48emu/g, intrinsic coercive force is 95 Oe, while the saturation magnetization, remanent magnetization and intrinsic coercive force of iron content 80% sample is 146.8emu/g, 19.35 emu/g, 307.3 Oe respectively.

The magnetic properties of materials could be valued by ratio of remanent and saturation(Mr/Ms). Mr/Ms of the iron content of 20% and 80% samples is 0.11and 0.13. Mr/Ms less than 0.25[14] is the soft magnetic materials, so the carbon-coated iron nanoparticles is soft magnetic materials.

3.3 Thermal stability of carbon-coated iron nanoparticles

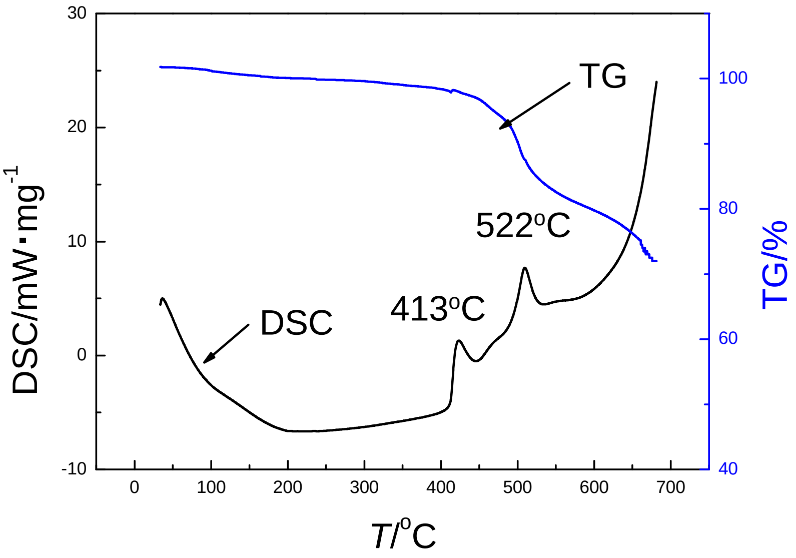

Fig.5. DSC /TG curve of carbon coated iron nanoparticles.

A DSC /TG was employed in order to examine the antioxidant ability, the DSC / TG curves shown in Fig.5. From the DSC curve we can see that there are two exothermic peaks with the increasing of temperature. The two exothermic peaks appeared in 413 °C and 522 °C respectively, obviously the TG curve can be divided into 3 stages with the temperature increase. From room temperature to 413 °C, sample have a small amount of weight loss, this is the reason for the surface adsorbate evaporation; from 413 °C to 522 °C, because of the decomposition of amorphous carbon, samples have a greater weight loss; after 522 °C there are not obvious weight changes , while the exothermic peak in DCS curve of 522 °C is due to a enthalpy occurred in the carbon-coated iron nanoparticles. throughout the period, there is not weight gain phenomenon. This fully shows that the external carbon layers can effectively protect the internal iron core from been oxidized.

4. Conclusions

Carbon-coated iron nanoparticles can be synthesized by the starch coating method, they are spherical particles with the size of particles 20-40nm in diameter. It is believed that the nanoparticles have a typical core-shell structure with carbon layer outside and iron core inside. The oxidation experiment shows that the carbon layers can protect the iron core from been oxidized. Hysteresis loops show as-made materials have good superparamagnetic properties, with the increase of iron content their magnetic properties is enhanced.

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