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Microwave Assisted Formation of Magnetic Core-Shell Carbon Nanostructure

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This letter describes a facile high temperature microwave assisted process to form the magnetic core-shell carbon nanostructure from polyaniline (PANI)-magnetite (Fe_3O_4) nanocomposites. The amorphous combined with graphitized carbon shell is observed by the transmission electron microscopy (TEM). The crystalline metallic iron, cementite, Fe_3O_4 and iron oxide (Fe_2O_3) are observed in the magnetic core in the Mössbauer spectrum measurements. The increased magnetic properties are observed in the formed core-shell carbon nanostructure after microwave annealing. The formed solid carbon nanostructure can protect the material from the acid dissolution and magnetic core favors the recycling of material.
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Recently, core-shell structure materials, especially for the magnetic core and protective shell materials, have gained more interests because the introduction of inert shell can provide a stabilized magnetic properties and oxidative resistance and protect the materials from the dissolution under acidic conditions.[1–4] They have the broadened potential applications such as catalysis,[5,6] giant magnetoresistance (GMR) sensing,[7,8] microwave absorption[9,10] and biomedical area.[11,12] Carbon materials are often introduced as shell materials to protect the magnetic metallic nanoparticles from oxidation/dissolution[4,13] and the synthesized magnetic core-shell structure materials have potential applications in magnetic data storage, ferrofluids magnetic hyperthermia and magnetic resonance imaging.[14–16]

The carbon coated magnetic nanoparticles are often fabricated by the chemical vapor deposition (CVD) method and the shell is formed by the annealing.[4] The conventional annealing method often uses hotplates or thermal ovens to achieve the heating process and has many problems such as energy loss and low efficiency of energy usage.[17] Microwave annealing is an efficient and energy saving approach to heat materials,[18] and has been already used to synthesize the core-shell structure materials, such as Pd@Pt core-shell nanostructures,[19] core-shell Au-Pd bimetallic nanoparticles,[20] core-shell selenium-carbon colloids and hollow carbon capsules[21] and core-shell iron-carbon nanoparticles,[22,23] etc. Recently, it has been reported that the doped conducting polymer can rapidly lose heteroatoms, dopant ions, etc., and then convert to the graphitic nanocarbons after microwave heating method.[24,25] Based on these findings, we use the conducting polymer polyaniline (PANI) as the heating sources to form the carbon nanostructures.

In this work, we report on the facile high temperature (750–800°C) microwave-assisted approach to convert magnetite (Fe_3O_4)/PANI polymer nanocomposites (PNCs) into the magnetic core-shell carbon nanostructure. The synthesized magnetic core-shell carbon nanostructure is characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), room temperature Mössbauer spectra, thermogravimetric analysis (TGA), and magnetic property.

Experimental

Materials.— Aniline (C_6H_7N), ammonium persulfate (APS, $(NH_4)_2S_2O_8$), p-toluene sulfonic acid (PTSA, $C_7H_8O_3S$) were purchased from Sigma Aldrich. Fe_3O_4 NPs with an average size of 12 nm were obtained from Nanjing Emperor Nano Material Co., Ltd. All the chemicals were used as-received without any further treatment.

Synthesis process.— The Fe_3O_4/PANI nanocomposites were fabricated by surface initiated polymerization (SIP) method. Briefly, in the SIP method, the Fe_3O_4 NPs (1.44 g, Nanjing Emperor Nano Material Co., Ltd., China), PTSA and APS (30.0 mmol and 18.0 mmol, respectively, Sigma Aldrich) were added into 200.0 mL deionized water in an ice-water bath for one hour of mechanical stirring combined with sonication. Then the aniline aqueous solution (Sigma Aldrich, 36.0 mmol in 50.0 mL deionized water) was mixed with the above Fe_3O_4 nanoparticle suspension and mechanical and sonicated continuously for an additional hour in an ice-water bath for further polymerization. The product was vacuum filtered and washed with deionized water until the pH was about 7 and was further washed with methanol to remove any possible oligomers. The final PNC powders were dried at 50°C overnight.

The detailed information about microwave experimental setup and microwave annealing method is provided in the supporting information, SI.

Characterization.— The particle nanostructure was characterized by a transmission electron microscopy (TEM, FEI Tecnai G2 F20) with field emission gun, operated at an accelerating voltage of 200 kV. The TEM samples were prepared by drying a drop of samples/ethanol suspension on carbon-coated copper TEM grids. X-ray diffraction (XRD) analysis was carried out with a Bruker AXS D8 Discover diffractometer with GADDS (General Area Detector Diffraction System) operating with a Cu-Kα radiation source filtered with a graphite monochromator ($\lambda = 1.5406$ Å). Data were collected in a range of 10 to 70°. The Mössbauer spectrometer was set to produce a high precision Doppler velocity modulation of the source γ radiation. The effects of the Doppler velocity modulation on the absorption of g radiation were recorded synchronously in the 1024 channels of the multichannel analyzer. The result was 1024 numbers representing registered gamma quanta (representing a singular quantum) passing through the absorber under the condition of different Doppler velocity. A separate calibration procedure establishes the exact correspondence channel-velocity (Spectrometer calibration is performed by measuring a standard a-Fe absorber, which produces a well known six line spectrum. The whole velocity range is calibrated using these six velocity points). The shape of the absorption spectrum was fitted to a theoretical model line shape,

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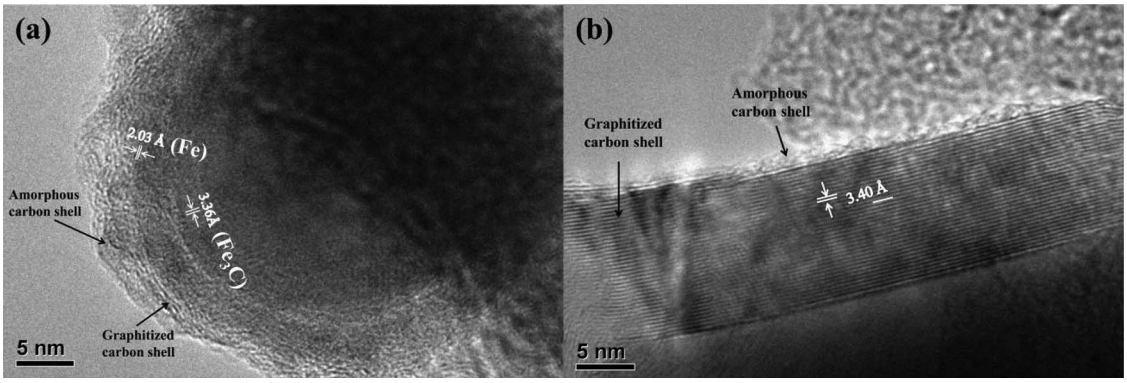

Figure 1. High resolution transmission electron microscopy (HRTEM) micrographs of microwave heat-assisted formed magnetic core-shell carbon nanostructure.

which was a superposition of singlets, doublets and sextets (^{57}Fe case) of a Lorentzian form. The result was investigated by chi 2 criterion and the theoretical line shape is tailored to fit experimental spectrum by the adjustment of spectral parameters like isomer shift, quadrupole splitting, hyperfine magnetic field and etc. Thermal stability of the synthesized nanocomposites was conducted in a thermogravimetric analysis (TGA, TA instruments, Q-500) with a heating rate of 10°C min^{-1} under an air flow rate of 60 mL min^{-1} from 25 to 800°C. The room temperature Mössbauer spectra characterization is written in the SI. The magnetic properties were investigated in a 9-Tesla Physical Properties Measurement System (PPMS) by Quantum Design.

Results and Discussion

Figure 1 shows the High resolution TEM microstructures of Fe_3O_4/PANI PNCs after high temperature microwave annealing. The core-shell structure is clearly shown in Figure 1a. The clear lattice fringe indicates the formation of highly crystalline nanoparticles. The calculated lattice distance of 0.203 nm corresponds to (1 1 0) plane of iron and the lattice distance of 0.336 nm is attributed to (0 2 0) plane of cementite (Fe_3C).[26] The surrounding of magnetic core (cementite and iron) is uniformly coated by graphitized carbon layer (which is confirmed in Figure 1b, the lattice fringe space of 0.34 nm corresponds to (0 0 2) plane of graphite carbon.) and a thin amorphous carbon layer. These results indicate that the high temperature microwave annealing favors the reduction of Fe_3O_4 to metallic iron and the formation of cementite and the PANI has converted to carbon structure (graphitized carbon and amorphous carbon.) The XRD test is studied to further confirm the crystalline structure of the microwave heated core-shell carbon nanostructure and the result is shown in Figure S2. The observed corresponding XRD patterns of cementite and iron indicate the coexistence of the cementite and iron in this core-shell carbon nanostructure after microwave annealing. However, the XRD tests can't provide the detail information about the component of the magnetic core if the amount of the component is very less.

To precisely identify the specific components of the core structure, the room temperature Mössbauer spectra are measured and shown in Figure 2a. The fitting results show that there are five components in the core structure. The component 1 at isomer shift (IS) = 0 mm/s corresponds to H1 = 329 kOe, which represents to body centered cubic alpha-iron metallic magnetically ordered state[27] with a contribution of 28%. The component 2 with a contribution of 37% at IS = 0.20 and H2 = 207 kOe is attributed to the cementite (Fe_3C). The component 3 at IS = −0.07 with a contribution of 23% corresponds to the alpha-iron, in which magnetic hyperfine structure has collapsed. The unusual change in electronic state IS = −0.07 instead of IS = 0 indicates some decrease in d-electron density on iron. The component 4 with a contribution of 6% at IS = 0.84 and H4 = 311 kOe indicates the presence of Fe_3O_4. The hyperfine field is much smaller than the expected 460 kOe due to the superparamagnetic relaxation in small particles. The component 5 with a contribution of 6% at IS = 0.35 and H5 = 288 kOe corresponds to the Fe^{3+} in oxide environment (Fe_2O_3) and the hyperfine field is much smaller than expected 480 kOe, which is also due to the superparamagnetic relaxation in small particles. These results demonstrate that after high temperature microwave annealing, the formed magnetic core is composed of 4 components: alpha-iron, cementite, Fe_3O_4 and Fe_2O_3. The observed iron, and cementite are consistent with the results of TEM, Figure 1a. Normally, cementite has reported mainly synthesized by laser pyrolysis and high temperature methods.[28] This conclusion is also confirmed in our work.

Figure 2b shows the TGA decomposition profiles of the Fe_3O_4/PANI PNCs and microwave assisted core-shell carbon nanostructures in the air condition. In the TGA curve, the Fe_3O_4/PANI PNCs have two-stage weight losses from 250 to 600°C, which are due to the elimination of the dopant anions and thermal degradation of PANI chains, respectively.[29] From the weight residue of the TGA curve, it's obtained that the Fe_3O_4 nanoparticle loading in the Fe_3O_4/PANI PNCs is about 34.05 wt% for. However, after high temperature microwave annealing, the core-shell carbon nanostructures have two different decomposition profiles. The weight percentage of the core-shell carbon nanostructures increases to 105.3% as the temperature increases to 407°C which is due to the oxidation of iron in the air condition. After that, the weight loss of the core-shell carbon nanostructures starts and stops until temperature increases to 680°C. The weight residue of the final nanoparticles loading obtained from TGA is 62.05%. The high temperature microwave annealing carbonizes the PANI matrix and reduces the oxide shells. The mass loss and shrinkage of the PANI matrix effectively increases the particle loading for the final core-shell carbon nanostructures. The thermal stability of the formed core-shell carbon nanostructures (15% weight loss is 525°C) is obviously improved compared with the Fe_3O_4/PANI PNCs (15% weight loss is 339°C).

Figure 2c depicts the room temperature magnetization curves of the as-received Fe_3O_4 nanoparticles, Fe_3O_4/PANI PNCs and microwave assisted core-shell carbon nanostructures. For the as-received Fe_3O_4 nanoparticles and Fe_3O_4/PANI PNCs, there is no hysteresis loops observed in the curve, in which coercivity (H_c) approaches zero Oe, exhibiting a superparamagnetic behavior.[30] Normally, the presence of an oxide shell around the metallic core is reported to increase the blocking temperature of nanoparticles through the exchange coupling interaction between the ferromagnetic metal core and the antiferromagnetic oxide shell.[31] Thus the reduction of Fe_3O_4 to iron and the disappearance of exchange coupling in the microwave assisted core-shell carbon nanostructure should decrease the H_c. However, the H_c increases to 78 Oe after high temperature microwave annealing. The increased H_c is attributed to the increased magnetic exchange coupling due to the presence of cementite.[28] The saturation magnetization (M_s) of the as-received Fe_3O_4 nanoparticles, Fe_3O_4/PANI PNCs and

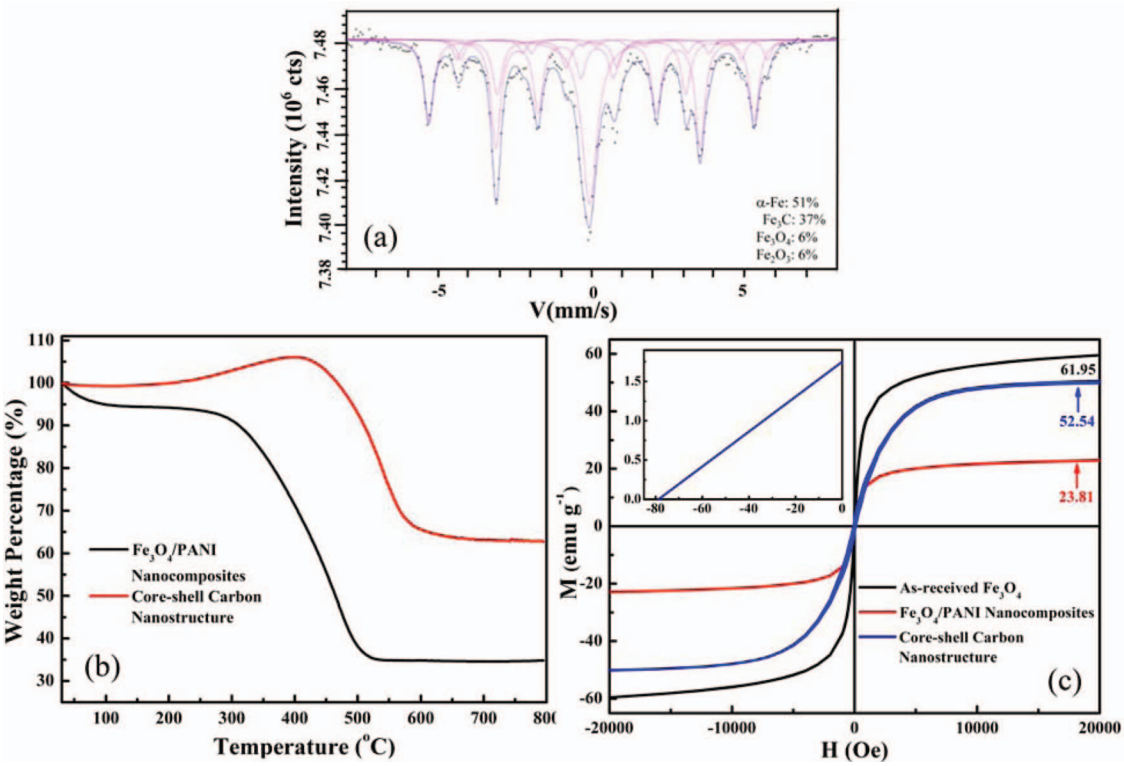

Figure 2. (a) Room temperature Mössbauer spectra of microwave heat assisted formed magnetic core-shell carbon nanostructure; (b) TGA curves of PANI/Fe_3O_4 nanocomposites and microwave heat-assisted formed magnetic core-shell carbon nanostructure; (c) Magnetic properties of as-received Fe_3O_4 nanoparticles, PANI/Fe_3O_4 nanocomposites and microwave heat assisted formed magnetic core-shell carbon nanostructure.

microwave assisted core-shell carbon nanostructures is not reached even at high magnetic field and determined by the extrapolated saturation magnetization obtained from the intercept of $M \sim H^{-1}$ at high field.[32,33] The calculated M_s of the as-received Fe_3O_4 NPs is 61.95 emu g^{-1}, which is lower than the bulk Fe_3O_4 (92∼100 emu g^{-1}).[34] The M_s value of the Fe_3O_4/PANI is observed to be saturated at a lower field and is about 23.81 emu g^{-1}. However, the M_s value of the microwave assisted core-shell structure is 52.54 emu g^{-1}. The increased M_s value is attributed to the formed metallic iron and cementite, in which the pure bulk value is 222 emu g^{-1} and 130 emu g^{-1}, respectively.[35,36]

The acid stability of this microwave assisted core-shell carbon nanostructure was tested using 1 M HCl solution compared with samples synthesized by conventional annealing with the same condition. The results are shown in Figure S3. The microwave fabricated core-shell carbon nanostructure shows the solid structure and can protect the magnetic core from the acid dissolution. Meanwhile, it can be easily recycled by the permanent magnet, Figure S3-a. However, the conventional annealing fabricated sample has dissolved in the acid solution and produced many bubbles, which confirms the samples synthesized by conventional annealing is porous structure, Figure S3(b).

Conclusions

In conclusion, we have fabricated core-shell carbon nanostructure from Fe_3O_4/PANI PNCs using the facile high temperature microwave assisted method. The microwave heat has carbonized the PANI matrix to graphitized carbon and amorphous carbon structure and formed the metallic iron, cementite, Fe_2O_3 and Fe_3O_4 magnetic core. The formed solid carbon nanostructure protects magnetic core from acid dissolution and magnetic core favors the easy recycle of this core-shell carbon nanostructure material. This core-shell carbon nanostructure has the potential applications in the environmental remediation application, especially in water treatment, e.g. the removal of heavy metals from polluted water.[2,4]

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