

Structural features and magnetic property of nano-sized transition metal dispersed carbons from naphthalene by pressure

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Abstract The transition metal nanoparticle dispersed carbon materials were synthesized by co-carbonization of naphthalene with transition metal compounds, i.e., ferrocene, cobalt acetate and nickel acetate at 540 °C for 6 h under autogenous pressure. The morphologies, structural features and magnetic properties of these metal/carbon nanomaterials were compared by means of SEM, TEM, XRD and VSM measurements. It was found that, coalescent spherulites with uniform diameters from 2 μm to 10 μm were obtained via the co-carbonization of naphthalene and transition metal compounds. The metals mainly exist in the form of elementary metal particles with the size from several nanometers to 300 nm. The Fe particles were encapsulated by carbon layers with well-ordered arrangement to form encapsulation. Otherwise some of Ni species showed the nanorod morphology coating by carbon layers. The formation mechanisms of these metal/carbon nanomaterials were briefly discussed. The magnetization curves of these materials at room temperature exhibited the characteristics of superparamagnetism response.

Introduction

Composites of metal nanoparticles dispersed in a carbon matrix generally exhibit interesting properties and can be widely used as electronic, electrical, and magnetic materials, oxidation/reduction catalysts, adsorbents and anti-

bacterial agents [1], depending on the nature and structure of the metal and carbon. The synthesis of carbon clusters in spherical or tubular form encapsulating transition metals has been accomplished by using an arc plasma discharge between composite electrodes of carbon-metal or carbon-metal oxide [2, 3]. Ion implantation into graphite by physical means has also been carried out [4, 5]. Most significantly, the synthesis of metal dispersed carbon by pressure pyrolysis from soluble organometallic polymers [6] and macromolecular-metal complexes [1] at temperatures from 650 °C to 1,400 °C for 1–2 days in an inert gas atmosphere was developed by Yogo and co-workers. In this approach, various organometallic compounds such as metallocenes and organometallic polymers were specially synthesized and used alone or together with other polymers for the source of carbon matrix. However, it involves a very complicated sequence of steps including polymer synthesis, dissolution, evaporation and carbonization, and usually needs very high pressures and temperatures (>100 MPa, above 600 °C) [1, 6–8], resulting in the difficulty and high cost of production on a large scale. Another approach is to use the pitches with high carbon yield for carbon sources. The combinations of an ordinary coal tar pitch and mesophase pitch with organometallic complexes have been reported by Yasuda and Kodama [9, 10]. However, as well known, pitch is a very complicated compounds containing many molecular weight substances, and it is difficult to control the component and molecular structure of final carbon materials. Moreover, pitches usually contain some amount of ash and O, N, S elements, which are disadvantageous to the preparation of carbon/metal composites with high quality.

It is well known that the formation of liquid-crystals (mesophase) from pyrolyzing pitch system is by a process of homogeneous self-assembly. However, if presenting

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some amount of infusible substances such as primary quinoline insoluble fraction (primary QI), carbon black or metal compounds, etc., the mesophase formation shows the heterogeneous behavior, in which sometimes the foreign substances as catalyst can accelerates the formation of mesogens in the immediate vicinity of the catalyst. Thus a “cloud” of mesogens of limited size is created. These immediately self-assemble to form the mesophase which then encompasses the catalyst entity. By controlling the reaction conditions, nano-sized metal particles would be obtained. Huttinger et al. [11] reported the studies of the catalysis of mesogen formation by ferric chloride, ferrocen and iron benzoate and naphthoate, and found these catalysts certainly promote the formation of mesophase. At the comparable temperature of 440 °C, non-catalyzed system produces no mesophase. Braun and Huttinger in 1996 [12] developed a spherulitic mesophase pitch with about 50 vol% of quiet uniform 10–25 µm diameter by iron-catalyzed pyrolysis of a coal tar pitch.

The aim of this work is to prepare the nano-sized metal dispersed carbon composites by a simple polymerization and condensation from polyaromatic hydrocarbons with some metal compounds such as ferrocene, and then to investigate their special properties such as magnetic, electrochemical and catalytic properties for their applications. In this paper, nano-sized transition metal (i.e., Fe, Co and Ni) dispersed carbon materials from naphthalene were synthesized by pressure carbonization. The purpose of choosing naphthalene as the carbon source is owing to its high purity and simple molecular structure, which is suitable to the control of the pyrolysis degree and the investigation of the relationship between structural features of precursors and the morphologies and structures of final carbon/metal composites. The morphologies, structural features and magnetic properties of metal dispersed carbon materials were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and Vibrating Sample Magnetometer (VSM). The formation mechanism of metal nanoparticles was discussed briefly.

Experimental

Materials

Naphthalene, which was purchased from the Beijing Chemical Plant, was chosen as the carbon source. The transition metal compounds, namely ferrocene, cobalt acetate and nickel acetate, purchased from the Beijing Chemical Reagent Company, were chosen as the metal sources. They are all analytical grade pure and are not further purified.

Preparation

The mixtures of naphthalene and metal compounds in the weight ratio of 3:1 were introduced into a 200 ml autoclave. After replacing the air in the vessel with pure N₂, the reaction vessel was sealed and then heated at a rate of 3 °C/min to 540 °C under autogenous pressure to carry out the reaction. After 4 h at 540 °C, the reaction system was cooled to room temperature and the gotten reaction product was washed with analytical pure acetone three times to remove the un-reacted naphthalene and small molecular species completely [13]. The acetone insoluble fraction was used as the desired product. Some of the products were further heat treated at 900 °C in argon gas atmosphere to get the carbonized samples.

Characterization

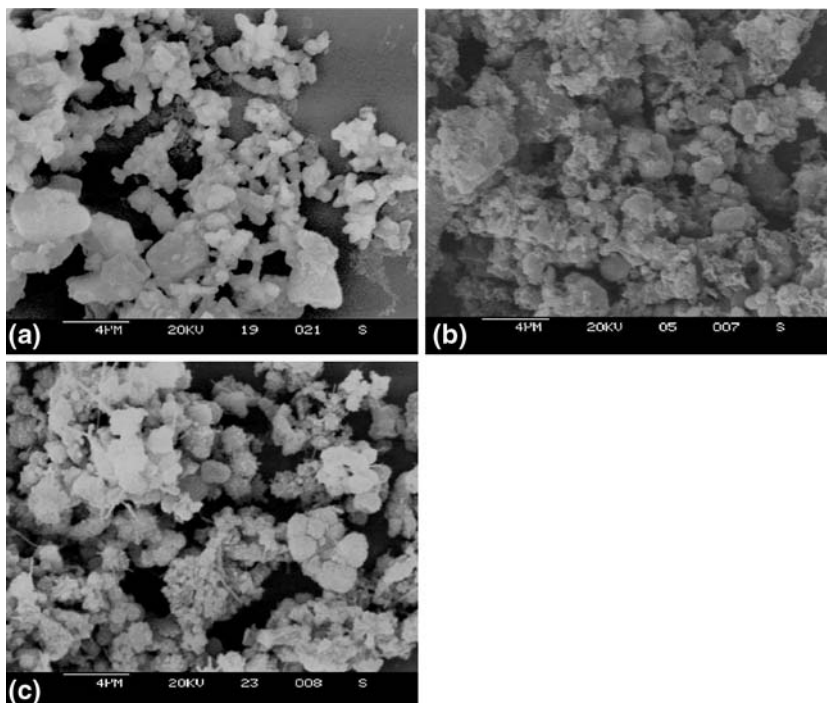
The SEM photographs were obtained at the Cambridge S-250MK3 scanning electron microscope. XRD determination was carried out using a Rigaku D/max-2400 system with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) over the range of 5–100 degrees (2θ). TEM and HREM measurements were conducted using Hitachi H-800 and H-9000 microscopes, respectively. The samples for TEM and HREM were prepared by dispersing the products in acetone and immersing in an ultrasonic bath for 30 min. A few drops of the resulting suspension were placed on a copper grid for observation. The magnetic properties of nanometal/carbon composites were measured by a Vibrating Sample Magnetometer (VSM, LDJ 9600) at 25 °C.

Results and discussion

Morphologies of carbonized products of naphthalene with metal compounds

Figure 1a–c shows the morphologies of carbonized products of naphthalene with ferrocene, cobalt acetate and nickel acetate, respectively. From this Figure, it can be observed that coalescent carbon spherulites with uniform diameters from 2 µm to 10 µm were obtained via co-carbonization of metal compounds with naphthalene. Besides the spherulites of carbon, there are coalescent polyhedral carbon morphologies presenting in the products, in which the size of each polyhedron was less than 2 µm. In nickel acetate/naphthalene pyrolytic product, there are a small amount of filamentous product accompanying the matrix of coalescing spherulites, which can be attributed to the nanorod of nickel crystal. It will be discussed in detail in the next part.

Fig. 1 Morphologies of co-carbonization products of naphthalene with (a) Ferrocene, (b) Cobalt acetate and (c) Nickel acetate, respectively at 540 °C for 6 h by SEM



Dispersed state of metal particles in carbon matrix

Figure 2 shows the distribution of metals in carbon matrix observed by TEM. In Fig. 2a, iron particles with uniform size distribution of below 10 nm were formed. The cobalt particles with size of about 20–50 nm were also observed in Fig. 2b. Figure 3 shows a representative HREM image of iron/carbon microstructure. It exhibited a carbon-encapsulated core-shell structure, where the carbon layers with well-ordered arrangement were closely compacted to form the quasi onion nanostructure and surround the dark iron nanoparticles. Outside the carbon onions, the carbon layers were in the disordered structure. In Fig. 2c, the product of naphthalene/nickel acetate system, a very interesting phenomenon is the presence of filamentous structure. Compared with the Fe and Co nanoparticles, most of nickel filaments have rather wide diameter distribution in the range 30–300 nm. From the HREM and SAD measurements in Fig. 4, it is verified to be the nickel nanorods which was encapsulated by carbon. So we can say that it provides a new and simple method for the preparation of metal nanorods or nanowires by co-carbonization of naphthalene with metal salts.

Crystal structure of nano-metal/carbon system

XRD profiles of the products from transition metals and naphthalene are shown in Fig. 5a, b and c, respectively. Owing to the crystal structure of nanometals with high intensity of diffraction peaks, the carbon diffraction peaks

locating at about 25° exhibited the weak and dispersed diffraction, implying the formed carbon is of a turbostratic structure. Most of the metals are presented in the form of elementary metals [14], otherwise in the products of naphthalene/ferrocene and naphthalene/cobalt acetate systems, a small amount of oxides, i.e., Fe₃O₄ and CoO were also formed seen in Fig. 5a and b. The Fe₃O₄ may come from the oxidation of iron nanoparticles with oxygen in air when the product was removed from the autoclave, and the latter CoO may be from the uncompletely decomposition of cobalt acetate. When it was further heat treated at 900 °C for 1 h, the CoO were transformed into elemental Co shown in Fig. 5b.

Formation mechanism of nano-metal/carbon materials

As well known, aromatic hydrocarbons such as naphthalene can form polyaromatic hydrocarbons, even mesophase pitches through middle temperature heat treatment (350–550 °C) at inert gas atmosphere via polymerization and condensation reactions. The addition of foreign materials such as carbon black and some organometallic compounds such as ferrocene can accelerate the polymerization and the development of carbon [15, 16]. The catalytically generated carbon layers with well-ordered arrangement would accumulate on the surface of metal species, resulting in encapsulation. Once it was completely encapsulated, the catalysis of the metal species was impeded. Naphthalene is a very stable aromatic compound with the critical temperature of 470 °C and the critical pressure of 4 MPa when

Fig. 2 TEM images of co-carbonization products of naphthalene with (a) Ferrocene, (b) Cobalt acetate and (c) Nickel acetate at 540 °C for 6 h

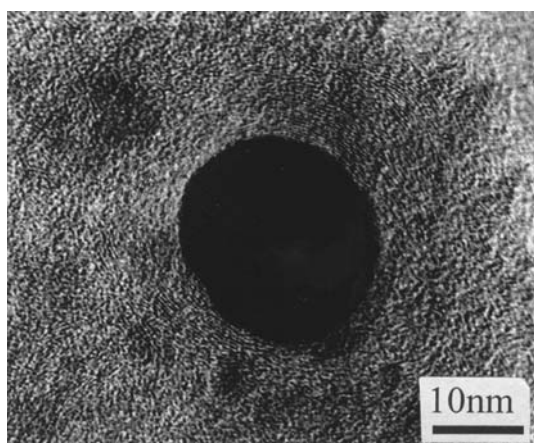
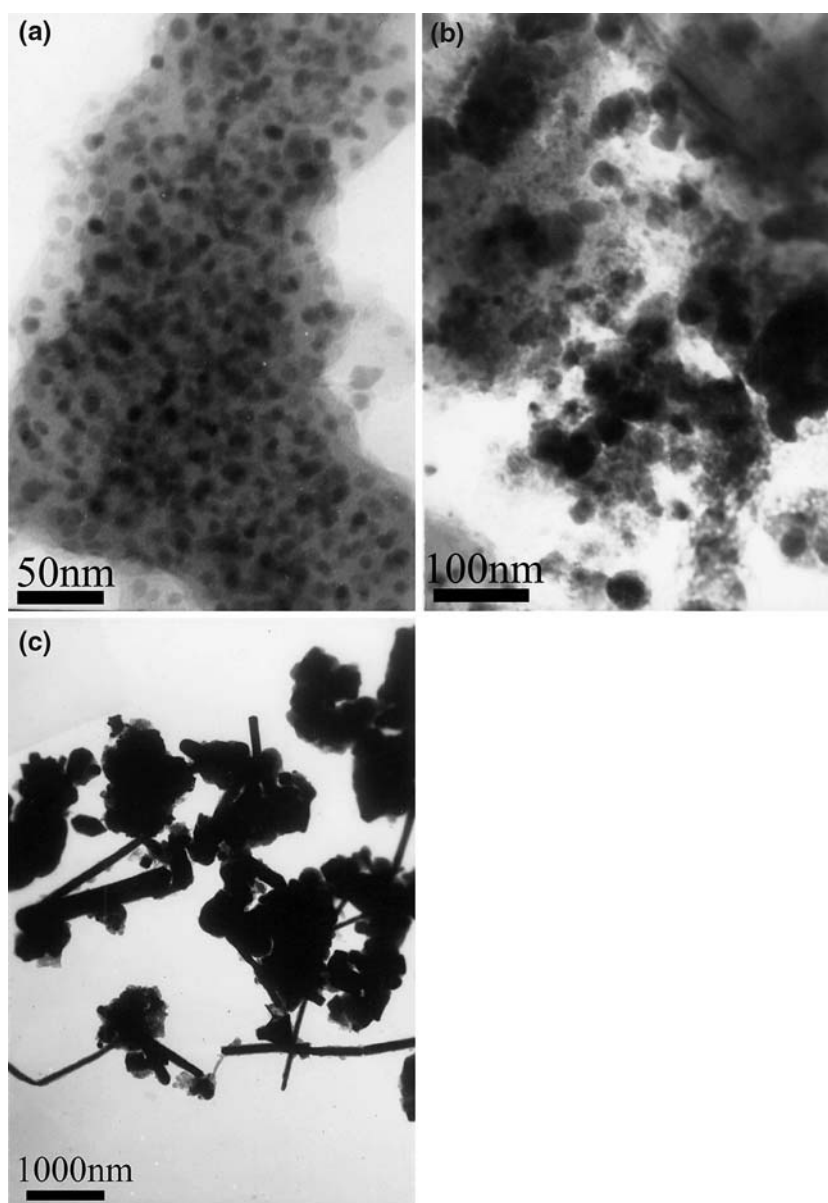


Fig. 3 HREM image of iron nanoparticles/carbon composites

was heated in an inert gas atmosphere. Ferrocene is also a very stable organometallic compound, which was decomposed above 450 °C. When the mixture of naphthalene and ferrocene was treated at 540 °C, ferrocene decomposed to yield iron atoms and then aggregated to iron nanoparticles or clusters, which showed a very high catalytic activity for the carbonization of naphthalene. As a result, the iron nanoparticles were gradually coated by carbon layers from the catalytic pyrolysis of naphthalene, resulting in a carbon-encapsulated iron nanoparticle structure. On the other hand, naphthalene far from the iron species pyrolysed to form active free radicals, which would polymerized and condensed to form the standard disordered carbon structure. This type of carbonization is a general feature of carbon doped with iron by this method and is dependent

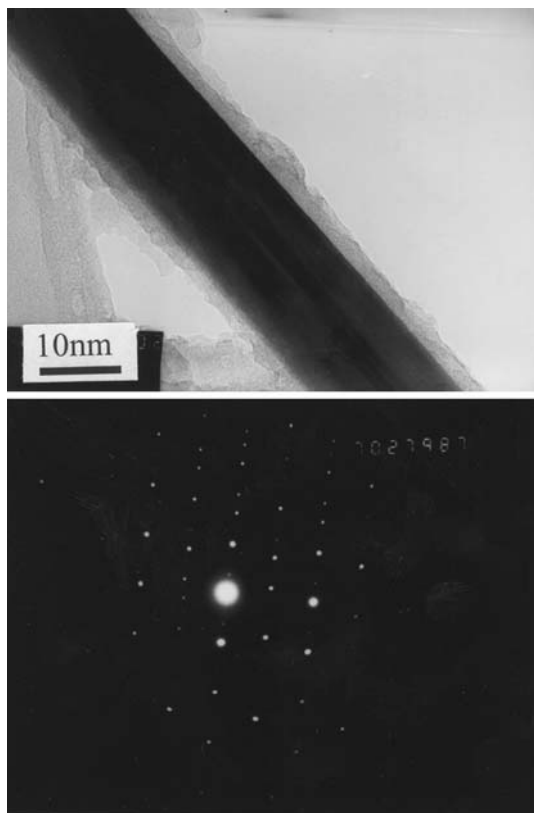
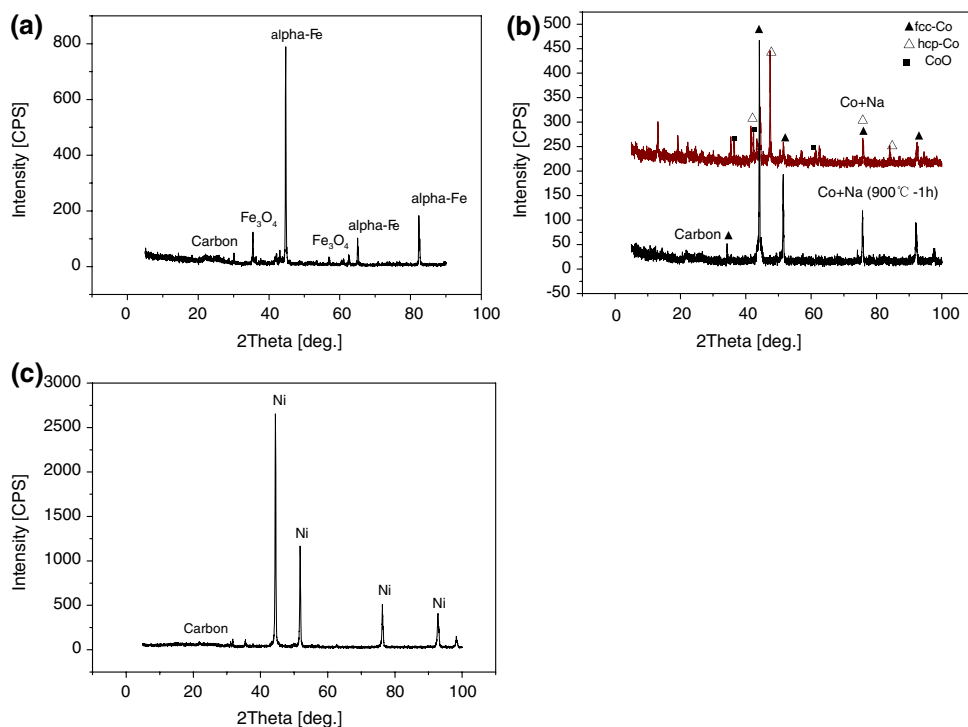


Fig. 4 HREM and SAD images of nickel nanorod/carbon composite

upon the abilities of the iron atoms derived from the ferrocene and carbon source [17].

In comparison with ferrocene, acetate cobalt and acetate nickel show the different decomposition behavior when were heated at 540 °C with naphthalene. The decomposition process is not the direct formation of elemental metal particle like ferrocene pyrolysis, they were usually through a middle product, e.g., oxides, and then were reduced into elemental metal particles in an reduction atmosphere [18]. The release of hydrogen and small molecules from naphthalene pyrolysis creates a reduction environment. The primary pyrolytic products of acetate cobalt and acetate nickel can be reduced gradually into elemental metal particles which exhibited catalytic activity. The metal particles in the form of metal-carbon solid solution [19] (resulting from reaction between naphthalene and metal) are free to move at high reaction temperatures, so that they can sinter together to form metal nanorods or nanowires capped inside carbon. This may be the reason why the carbon-encapsulated nickel nanorods were obtained. The plausible reaction mechanism would involve the absorption and decomposition of naphthalene molecules on the surface of Ni nanoparticles. Subsequently, the carbon atoms dissolve and diffuse into the nanoparticle interior to form a metal-carbon solid solution. Nanotube growth occurs when supersaturation leads to carbon precipitation into a crystalline tubular form [19]. The formation of metal nanorods or nanowires inside the carbon can be probably either because the metal particles inside the carbon coalesce

Fig. 5 XRD patterns of metal nanoparticles/carbon composites (a) Ferrocene, (b) cobalt acetate and (c) Cobalt Nickel



together at high reaction temperature to form metal nanowires, or the metal nanoparticles sinter and coalesce together and the nanotube precipitates around this so formed metal nanowire after supersaturation with carbon. In these studied transition metals, Nickel has the lowest melting point of 1,455 °C compared with the other two metals, e.g., Fe and Co. It is well known that the melting point of nanocrystalline particles depends strongly upon the grain size. Theoretical calculation indicated that the melting temperature of single crystals encapsulated in carbon nanotubes is strongly suppressed [20]. The above factors should be the reasons that nanorods were generated from nickel acetate pyrolysis in the presence of naphthalene, correspondingly nanoparticles were formed from ferrocene and cobalt acetate.

Magnetic properties of nano-metal/carbon system

The VSM magnetic measurements for three metal/carbon nanoparticles are shown in Fig. 6a, b, and c. It is well known that, the magnetic behavior is therefore size-dependent and should be understood in conjunction with thermal energy and surface anisotropy aspects [21]. The carbon-encapsulated Fe nanoparticles, with an average size of about 10 nm, may be considered to have just a single magnetic domain, the origin of magnetic hysteresis

being spin rotation [22]. It is evident that, at room temperature the remnant magnetization (Mr) and magnetic coercivity (Hc) are greatly reduced compared to their coarse polycrystal counterparts. The reduced Mr and Hc values at room temperature are close to one of the characteristics of superparamagnetism response (Table 1). On the other hand, carbon encapsulated Co and Ni nanomaterials with average sizes of 20 and 30–300 nm, respectively, showed the increased Ms, Mr and Hc values than that of Fe–C materials (Fig. 6 and Table 1). These superparamagnetic behaviors implied many potential applications including ferrofluid technology, magnetocaloric refrigeration and etc. [22].

Conclusion

Transition metal particles uniformly dispersed in carbon matrix were synthesized by co-carbonization of naphthalene with ferrocene, cobalt acetate and nickel acetate, respectively. The metals mainly exist in the form of elementary metal particles with the size from several nanometers to 300 nm. The morphologies of Fe and Co were spherulites and polyhedral. Otherwise Ni shows the nanorod morphology with diameters from 30 nm to 300 nm, which was coated by carbon. These nano-metal/carbon

Fig. 6 Magnetization curves of nanometal/carbon composites (a) Fe, (b) Co and (c) Ni

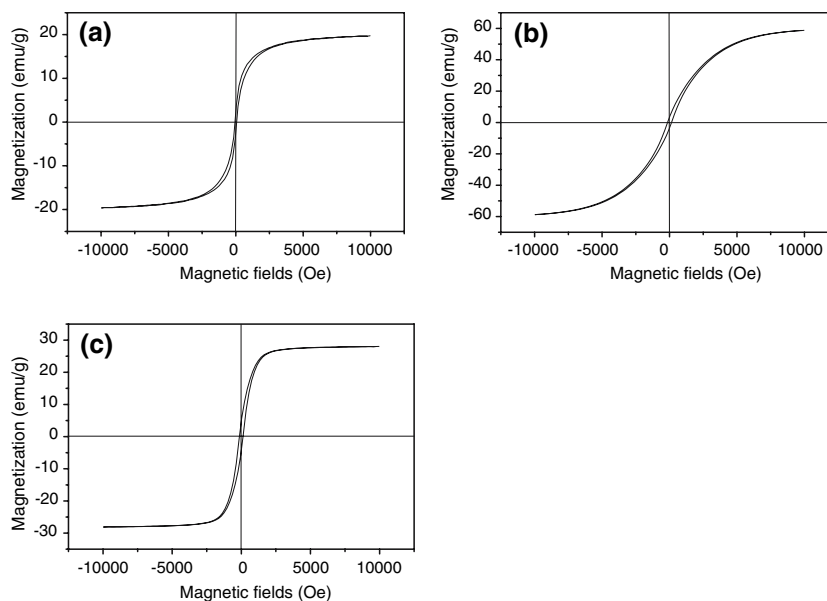


Table 1 Comparison of saturation magnetization (Ms), remanent magnetization (Mr), coercivity (Hc) for carbon/metal nanoparticles

Samples	T (K)	Ms (emu/g)	Mr (emu/g)	Hc (Oe)	d (nm)
Fe (C)	300	19.73	2.318	62.378	10
Co (C)	300	58.80	3.541	149.696	20–50
Ni (C)	300	28.03	4.795	134.579	30–300

materials showed the superparamagnetism behavior when were magnetized at room temperature.

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