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Large-scale preparation of carbon-encapsulated cobalt nanoparticles by the catalytic method

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ABSTRACT

With strategical selection of the water-soluble sodium chloride (NaCl) as the supporting material, we realized large-scale production of carbon-encapsulated cobalt nanoparticles with a productivity of almost 100%. The products can be fully separated from the supporting materials by simple washing process. When NaCl, NaF and Al_2O_3 were used as supporting materials, the morphologies of the carbon products changed from carbon-encapsulated magnetic nano-particles (CEMNs) to an intermediate state (quasi-nanocages) between CEMNs and carbon nanotubes (CNTs), and then to CNTs, respectively. NaCl shows strong inhibiting effects on the growth of CNTs, favoring the formation of CEMNs.

1. INTRODUCTION

Magnetic metal nanoparticles (such as Fe and Co) have wide range of applications such as high-density magnetic data storage, magnetic toners in xerography, magnetic inks and ferrofluids [1,2]. However, the poor oxidation resistance of the bare metal nanoparticles sets a great barricade for further exploring their applications. In the past few years, carbon-encapsulated magnetic nanoparticles (CEMNs) have aroused great research interests around the world due to the fact that the protective carbon layers prevent the rapid environmental degradation of bare metal nanoparticles. Moreover, the carbon coatings can endow these magnetic particles with the biocompatibility and stability in many organic and inorganic media. These combined attributes make CEMNs the interesting candidates for many bio-engineering applications including drug delivery, biosensors, magnetic hyperthermia and magnetic contrast agents for magnetic resonance imaging [3,4].

Various techniques have been developed for synthesizing CEMNs, such as standard carbon arc techniques [5], tungsten arc technique [6], magnetron and ion-beam co-sputtering, [7] RF plasma torch technique [8], and modified arc deposition technique [9]. However, these techniques are apparently not suitable for producing CEMNs in large quantities. In contrast, the catalytic method is of great promise due to low costs, the ready availability of raw materials and the simple processing setup. However, so far the employment of catalytic methods in the synthesis of CEMNs has not been so successful

because of relatively low productivity and the problems regarding the separation of CEMNs from the oxides supporting materials, especially the by-products carbon nanotubes (CNTs) [10]. Therefore, for the catalytic process, a strategy must be found to build up the favorable reaction kinetics that can strongly inhibit the growth of CNTs but favor the formation of CEMNs.

Our work is based on the strong effects of the supporting materials on the morphologies of carbon products, namely to find out a proper supporting material which may present the favorable thermodynamics and kinetics for the growth of CEMNs and the supporting material can be easily separated from the carbon products. In this Letter, we reported some new progresses of our group regarding these aspects.

Mechanical milling has been used for the fabrication of nano-powders in an efficient way [1,11]. Recently, we reported the growth of carbon nanotubes on the mechanical alloying-derived Ni/Al_2O_3 catalysts, which indicated that mechanical alloying could produce suitable and active enough catalysts for the catalytic decomposition of carbon-containing gas [12]. In this Letter, we demonstrate the synthesis of CEMNs with a productivity of almost 100% using the mechanical milling-derived Co/NaCl catalyst. The water-soluble supporting material NaCl enables as-obtained CEMNs to be fully separated from the supporting material after a simple washing process.

2. EXPERIMENTS

In this study, NaCl (Aldrich, purity: 99%; mean particle size: 60 μm), NaF (Aldrich, purity: 99%; mean particle size: 100 μm) and α-Al_2O_3 (Fluka, purity: 99%; mean particle size: 10 μm) were chosen as the supporting materials. The mixtures of co-precipitated cobalt hydroxides and the supporting materials at the weight ratio of 1:8 were mechanically milled for 24 h with a SPEX 8000 Mixer/Mill. The as-milled samples were reduced in hydrogen at the temperatures between 300 and 700 ℃ for 1 h. The samples (Co/NaCl, Co/NaF and Co/Al_2O_3) reduced at 600 ℃ underwent the catalytic carbonization reaction at 600 ℃ for 1 h in the flow of CH_4 with a flow rate of 30 ml/min. For the samples after H_2 reduction and CH_4 treatment, their magnetic properties were studied using a superconducting vibration sample magnetometer (VSM, Oxford Instrument) at room temperature with the maximum magnetic field of 50 kOe. Their microstructures and morphologies were investigated under low and high-resolution transmission electron microscopes (JEM-100CX TEM and JEM-3010 HRTEM).

3. RESULTS AND DISCUSSION

3.1. The reduction of the as-milled samples

The formation of magnetic Co after H_2-reduction was monitored by magnetic measurements. The curve a in Fig. 1 shows the dependence of saturation magnetization (M_s) of the as-reduced Co/NaCl samples on the reduction temperature. M_s was as low as 0.6 emu/g for the as-milled sample, corresponding to the paramagnetic nature of cobalt hydroxides and diamagnetic nature of NaCl. After reduction at 300 ℃, M_s increased to

2.6 emu/g, indicating the formation of a small amount of metallic cobalt. With the increase of reduction temperatures, M_s increased continuously till 600 ℃. Further increase of temperature did not give rise to an apparent increase in M_s. The M_s of the samples reduced at 600 and 700 ℃ were 12.3 and 12.4 emu/g, respectively. Considering the fact that the initial mass ratio of cobalt hydroxides to NaCl was 1:8, the theoretical M_s of samples should be 12.3 emu/g, assuming that all the cobalt hydroxides were completely reduced into metallic cobalt. The results show that the reduction of cobalt hydroxides can be fulfilled at 600 ℃. It should be noted that Co nanopowders reduced at 600 ℃ possess relatively high coercivity (0.6 kOe, as shown by the insert in Fig. 1), indicating their potential in hard magnetic applications. For the as-reduced Co/NaF and Co/Al$_2$O$_3$ catalysts, their magnetic properties after H$_2$ reduction showed the same tendency as Co/NaCl and also suggested that 600 ℃ was high enough to fulfill the complete reduction of cobalt hydroxides.

Figs. 2a–d show TEM images of as-reduced cobalt particles after removing NaCl by washing. The mean particle size of the as-milled sample was around 10 nm. After reduction at 300 ℃, no significant change in particle size was observed, as shown in Fig. 1b and 2a. With the increase of the reduction temperature, the accelerated particle growth was observed as shown by the curve b in Fig. 1 and 2b–d. After reduction at 600 ℃ (which is the required temperature for completion of reduction), the mean particle size was 22 nm. For the as-reduced Co/NaF samples, although the enhanced particle coarsening behavior was also observed with the increase of reduction temperatures, the mean particle size of Co particles was apparently smaller than those in Co/NaCl samples reduced at the same temperature, as shown by Curve c in Fig. 1 and 2e. After reduced at 600 ℃, the mean particle size of Co particles was 18 nm with relatively narrow particle-size distribution. While for the alumina supported Co nanoparticles, their coarsening behavior was quite different from those supported by NaCl and NaF. As shown by the Curve din Fig. 1, no accelerated growth of cobalt particles was observed when the reduction temperature was increased from 300 to 700 ℃. TEM analysis showed that he mean particle size of Co nanoparticles was around 12 nm after reduction at 600 ℃. As shown in Fig. 2f, the as-reduced Co nanoparticles were anchored on the surface of alumina particles.

The accelerated growth of Co nanoparticles in NaCl matrix was probably associated with the relatively low melting temperature (Tm = 800 ℃) of NaCl. At the temperatures close to the melting temperature of NaCl, the diffusion of cobalt species is enhanced in NaCl and thus the particle growth was accelerated. While for NaF (T_m = 996 ℃) and Al$_2$O$_3$ (T_m = 2054 ℃), due to their relatively high melting temperatures, the diffusivity of cobalt species in these media was limited, which helped to inhibit the rapid coarsening of Co nanoparticles.

On the other hand, for alumina substrates, it is possible that there are alloying effects between cobalt oxides and alumina after long-time mechanical milling, namely the formation of CoAl$_x$O$_y$ solid solution phases. In one of our work, we have reported that NiAl$_2$O$_4$ solid solution phase were formed in NiO-Al$_2$O$_3$ powder after 36-h mechanical milling. In present study, although we have not got the evidence regarding the formation

of $CoAl_xO_y$ phases, it is possible that weak bonding is formed between the between Al_2O_3 and CoO after mechanical milling for 24 h. Definitely, the bonding formation benefits not only the uniform dispersion of cobalt oxides but also inhibition of the surface diffusion of cobalt species. This accounts for the slow coarsening behavior of Co nanoparticles supported by alumina substrate. For NaCl and NaF supported catalysts, although we also have not got the evidences regarding the bonding formation between cobalt oxide and NaCl or NaF after mechanical milling, it is still possible that bonding effects might play important roles in affecting the diffusion behaviors of Co species in these matrices. This needs further investigations.

It is worthy to be noted that, by using NaF as the dispersion medium, we presented a convenient process for fabricating cobalt nanoparticles with relatively narrow particle-size distribution.

3.2. The catalytic encapsulation of Co nanoparticles

In this study, we chose the samples reduced at 600 ℃ as the catalyst for producing CEMNs. It is interesting to find out that no CNTs but only CEMNs were observed under both SEM and TEM. After the removal of water-soluble NaCl, TEM analysis showed that almost all the cobalt particles were encapsulated with carbon coatings, as shown in Fig. 3a. HRTEM analysis revealed that most of the Co nanoparticles were encapsulated with 5–6 graphite layers, as shown in Fig. 3b. TEM and HRTEM examinations showed that the productivity of CEMNs was almost 100%. These carbon encapsulated Co particles exhibited good corrosion resistance. Without the carbon encapsulation, the saturation magnetization (Ms) of cobalt particles reduced at 600 ℃ decreased 33% after the exposure in air for 20 days. The decrease in Ms was due to the formation of paramagnetic cobalt oxide. For the carbon-encapsulated Co particles, the decrease in M_s was only 3% after exposure in air for the same period. After the removal of NaCl, the saturation magnetization of carbon-encapsulated Co nanoparticles was 138 emu/g.

The experimental results indicated that the formation of carbon nanotubes (CNTs) was totally inhibited, when NaCl was used as the supporting material. Such kinds of inhibiting effects might stem from two main factors, namely the size effects and the substrate effects. For the size effects, it has been well recognized that, for catalytic nanoparticles, generally only those smaller than 20 nm in diameter can be active enough for the growth of CNTs [13]. For Co/NaCl catalysts reduced at 600 ℃, although the mean particle size of Co particles was as large as 22 nm, there still existed some small particles with the size around 10–15 nm, which should be active enough for the formation of tubular products. However, the contrary experimental results suggested that size effects might not be responsible for the inhibited growth of CNTs as observed, and substrate effects might play active roles. To further check substrate effects, we chose NaF and Al_2O_3 as supporting materials for the further investigations.

When the Co/Al_2O_3 nanocomposites were used as the catalysts, CNTs were obtained with a high production yield as shown in Fig. 4a. The result was within the anticipation since we have reported the production of CNTs using the mechanical milling-derived

Ni/Al$_2$O$_3$ catalyst [12]. However, when the supporting material was replaced with a mixture of 50 wt% Al$_2$O$_3$ and 50 wt% NaCl, the growth of CNTs was completely inhibited and no CNTs could be observed under both SEM and TEM. The asused catalytic precursors were produced through adding NaCl into as-milled Al$_2$O$_3$/cobalt hydroxides (24 h) and milling for another 24 h (the mass ratio of NaCl: Al$_2$O$_3$: cobalt hydroxides was 8:8:1). TEM analysis showed that the particle size of Co nanoparticles were in the range of 10 nm–20 nm after reduction and carbonization at 600 ℃. The fact provided the further evidence to exclude the size effects of catalysts as the main factor to suppress CNTs growth in NaCl-containing samples.

When the Co/NaF powder reduced at 600 ℃ was used as the catalysts, it was interesting to find out that most carbon products took the form as an intermediate state between CNTs and CEMNs. As seen from Fig. 4b, cobalt nanoparticles were encapsulated into either carbon nanocages or tubelike carbon shells. These poor-developed tubes were short, thick and quite irregular, as an intermediate form between CNTs and carbon nanocages. We can call them quasi-nanocages. However, when using a mixture of 50 wt% NaF and 50 wt% NaCl as the supporting materials, the tube-like carbon products were once again eliminated.

Above experimental results clearly verified the inhibiting effects of NaCl on the growth of CNTs. Such kinds of substrate effects might arise from two mechanisms. On one hand, the presence of chlorine impurities might be responsible for the promoted carbon encapsulation of Co nanoparticles. It has been reported that the Cl atoms could initiate the radical reactions of both surface and gas-phase species that were precursors to the carbonaceous layers and could create radical reaction sites on the evolving graphite layers for the further growth by molecular mass addition, namely favoring the formation of carbon-encapsulated nanoparticles [14]. In terms of this view, the inhibiting effects of NaCl on the growth of CNTs could be ascribed to the effects of Cl atoms.

On the other hand, we suggest that the thermal properties of the supporting materials might possess great influences on the morphologies of the final carbon products. It has been well recognized that the major driving force for the growth of carbon filaments lies in the thermal gradient built inside the catalytic metal particles [15]. The building-up of the thermal gradient should be intimately correlated with the physical properties of supporting materials, such as thermal capacity and thermal conductivity. It is possible that the relatively high diffusion coefficient and thermal conductivity of NaCl phase might strongly interfere the building-up of the temperature gradient inside cobalt particles, because the carbonization temperature (600 ℃) is close to the melting temperature of NaCl (800 ℃). In this case, the isotropic precipitation of carbon species on the surface of cobalt particles takes place, favoring the formation of CEMNs. Such kind of interference effects will be different for the supporting materials with different thermal properties. Generally, the substances with lower melting points have higher thermal conductivity and diffusion coefficients, and thus can present stronger interfering effects on the building-up of the thermal gradient inside the catalytic nanoparticles. Based on this view, among NaCl, NaF and Al$_2$O$_3$, the interference effects of NaCl should be strongest, while those of Al$_2$O$_3$ should be weakest. Therefore, When NaCl, NaF and

Al$_2$O$_3$ were used as supporting materials, the morphologies of the carbon products changed from carbon-encapsulated magnetic nanoparticles (CEMNs) to an intermediate state (quasi-nanocages or quasi-nanotubes), and then to CNTs, respectively.

Our future work will be concentrated on the more detailed investigation of the mechanisms. A better understanding of the mechanisms may lead to the better control of the formation of high-quality carbon nanocapsules and nanotubes.

4.CONCLUSION

The large-scale production of nanosized CEMNs was realized by using mechanical alloying-derived Co/NaCl catalysts. The employment of NaCl as the supporting material enabled full separation of CEMNs after simple washing process. When NaCl, NaF and Al$_2$O$_3$ were used as supporting materials, the morphologies of the carbon products changed from CEMNs to an intermediate state (quasi-nanocages), and then to CNTs, respectively. The strong inhibiting effects of NaCl on the growth of CNTs might be related to the effects of chlorine atoms and the strong interference effects of NaCl on the building-up of the thermal gradient inside the Co nanoparticles.

The work may provide a cost-effective and convenient approach to the large-scale production of CEMNs and cobalt nanoparticles in commercial applications.

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List of Figures

Figure 1   Saturation magnetization (M_s) as a function of reduction temperature for Co/NaCl samples (a) and the dependence of mean particles size (D_{mean}) of the as-reduced powders on reduction temperature for Co/NaCl (b) and Co/NaF (c) and Co/Al$_2$O$_3$ (d), respectively. (Insert: the magnetic hysteresis loop of Co/NaCl reduced at 600 ℃.

Figure 2   TEM images of cobalt particles after reduction at different temperature (after washing) (a) 300 ℃, Co/NaCl; (b) 500 ℃, Co/ NaCl; (c) 600 ℃, Co/NaCl; (d) 700 ℃, Co/NaCl (e) 600 ℃, Co/NaF; (f) 600 ℃, Co/Al2O$_3$.

Figure 3   TEM (a) and HRTEM (b) images of the CEMNs obtained after CH$_4$ carbonization at 600 ℃ for Co/NaCl after washing.

Figure 4   TEM images of the carbon nanotubes grown on Co/Al$_2$O$_3$ catalysts (a); and the carbon products synthesized with the Co/NaF catalysts (b) at 600 ℃.
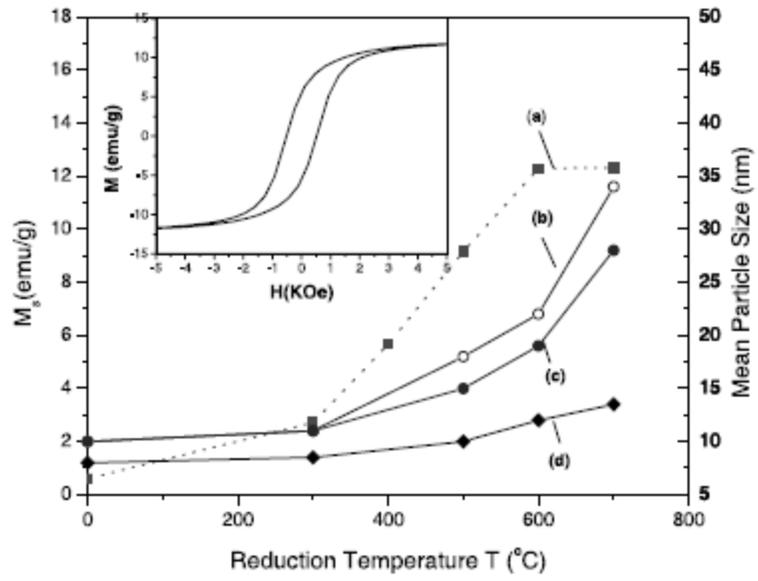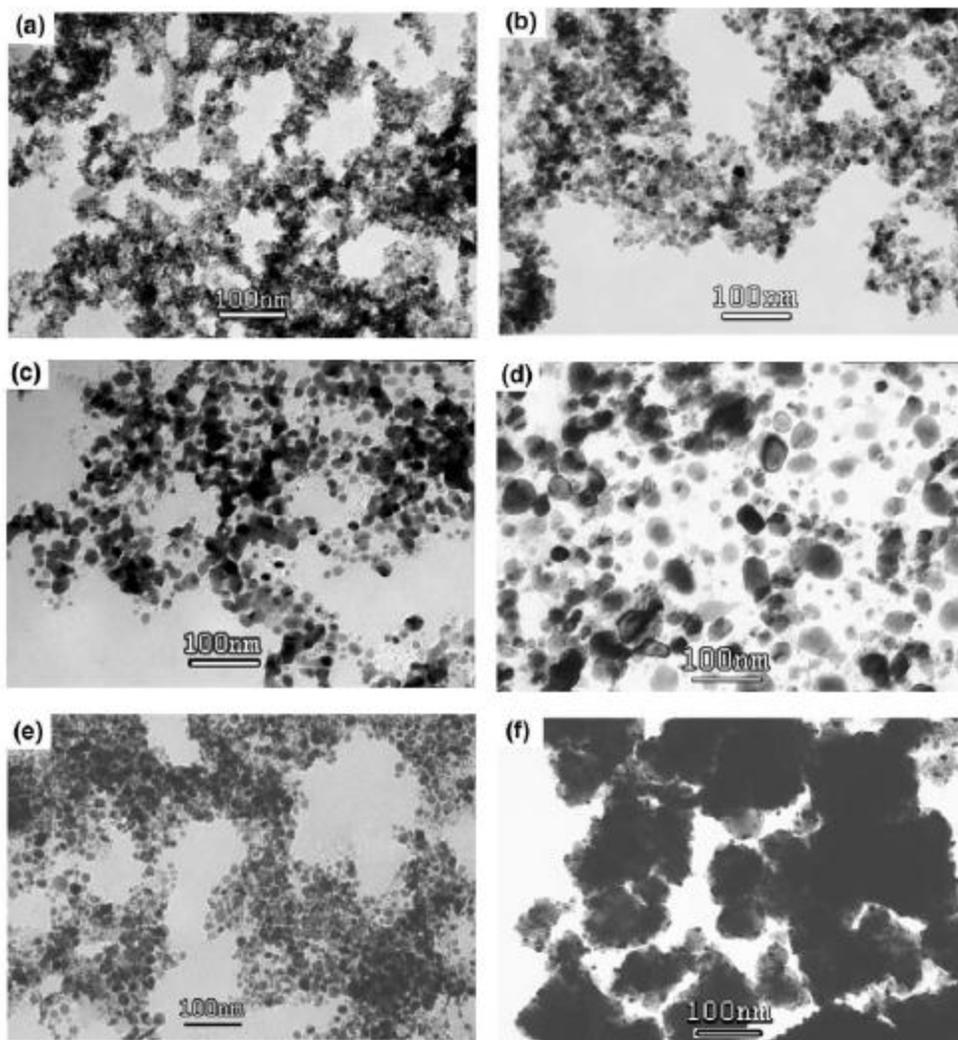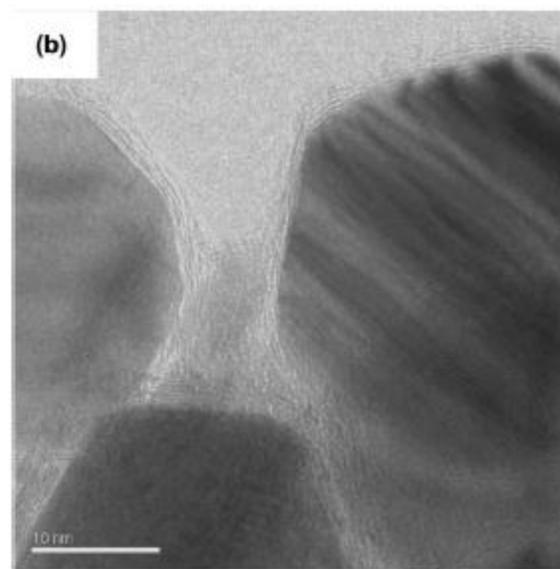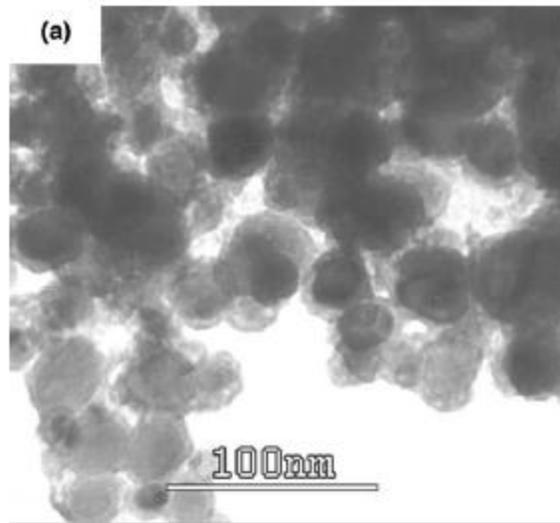
Figure 1

Figure 2

(a)

100nm

(b)

Figure 3

Figure 4