Synthesis of hollow microspheres of nickel using spheres of metallic zinc as templates under mild conditions

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In recent years, hollow spheres of nanometer to micrometer dimensions have attracted special interests because of their potential applications in many areas [1, 2]. For example, they can serve as extremely small container for encapsulation which may benefit the control of delivery and release process of drugs and protection of environment-sensitive materials such as enzymes [3]. When it comes to fillers in making composite materials, hollow spheres can also show some advantages over their counterparts for their relatively low densities [4].

Various approaches have been proposed for preparing hollow spheres. For example, hollow polymer, oxide and glass composite spheres in micrometer-size range can be synthesized by physical methods such as spray drying techniques [5, 6]. Chemical methods can also be used to fabricate hollow spheres and soft template synthesis is a general one [7, 8]. For example, Micrometer-sized hollow spheres of CdS have been also been synthesized through an in situ source-template interface reaction route [9]. However, so far there are few reports on the fabrication of metal hollow spheres by chemical methods [10, 11]. Fortunately, a template-engaged method has been introduced recently and presents good prospect for the synthesis of metal hollow spheres by simple chemical methods [12]. But in this approach, only noble metals were used as templates and no further experimental data were given to prove the possibility of applying this method to other metals. Here our experiment will give a strong support to the generality of this method and provide a cheap approach to fabricate hollow nickle spheres for future industrial application. In our experiment, we utilize the replacement reaction between nickel and zinc to form nickel shells on the surfaces of zinc spheres by reacting nickel salt solution with solid template of zinc under carefully controlled conditions. Hollow nickel micrometer spheres were obtained by removing the residual cores of zinc and zinc oxide via washing with NaOH aqueous solution.

In a typical experiment, 0.50 g zinc powders were first dispersed into 5 ml acetone, which was then added into 100 ml distilled water. After strongly stirring for 10 min, the mixture of zinc and water were kept for 40 s to separate the few large zinc spheres from the main part of zinc spheres by gravity, and then the suspended part was transferred into a 250 ml beaker. In the same time 3.0 g $NiCl_2 \cdot 2H_2O$ was dissolved in 50 ml distilled water in another beaker and the blue coordination compound solution was obtained while 20 ml 25 v/v% ammonia solution was added into the solution after strongly stirring for 10 min. Then the solution was added dropwise into the first-prepared suspended mixture of zinc. The reaction was carried out for 10 hr under stirring. The solid products were precipitated and separated by placing a magnet under the beaker. All the procedures were carried out at room temperature.

For purifying the products, the obtained black products were treated with 20 ml 0.8 mol/l NaOH for two times and continually treated with 20 ml 11.0 mol/l NaOH. The black products prepared were washed with distilled water and alcohol for several times, respectively.

The samples obtained were characterized by X-ray powder diffraction (XRD) using a 18 kW advanced X-ray diffractometer with CuKα radiation ($\lambda = 1.54056$ Å). The scanning electron microscopy (SEM) was also taken on an AMRAY-1000B type microscope. Magnetic hysteresis loop was measured using a Vibrating Sample Magnetometer (VSM, BHV-55). For magnetization measurements, the powder was pressed strongly and fixed in a small cylindrical plastic box.

Fig. 1 shows a typical image of zinc micrometer spheres with diameters mainly ranging from 3 to 8 μm and few zinc spheres larger than 8 μm was removed by suspension treatment. A magnified image of one zinc sphere is also shown in the inset of Fig. 1. These zinc spheres will serve as good hard templates to fabricate various hollow spheres since it is easy for metal to be reduced on their surfaces and form metal shells and the cores of zinc and zinc oxide can be removed completely by washing with NaOH aqueous solution for their amphoteric chemical properties. In our experiment, the smooth surfaces of these zinc spheres will be converted to thick nickel shells in nickel salt solution by the replacement reaction of Ni^{2+} with zinc under carefully controlled conditions. In the same time some parts of the inner zinc core have been oxidized into ZnO in aqueous solution, which was revealed by XRD analysis of the sample without NaOH treatment (Fig. 2). These impurity cores of zinc and zinc oxide were removed completely by washing with 11.0 mol/l

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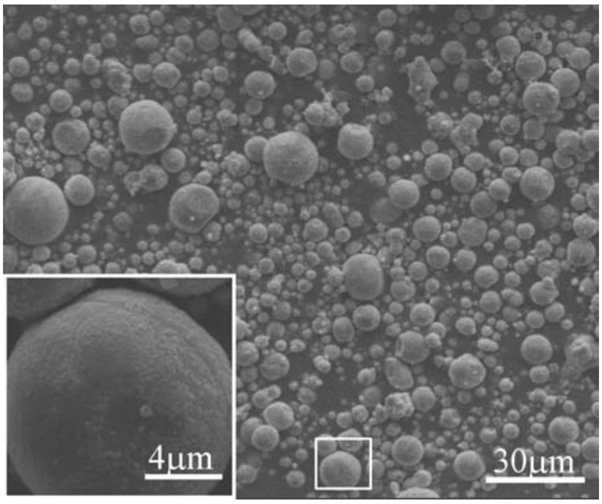

Figure 1 SEM image of zinc micrometer spheres used as hard templates and the sphere in the boxed area was enlarged shown in the inset.

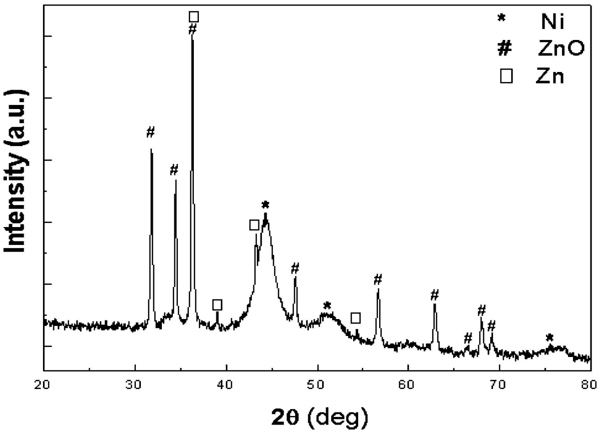

Figure 2 XRD pattern of the as-prepared sample without NaOH treatment.

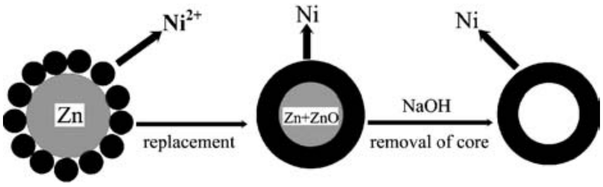

Figure 3 Schematic illustration for the formation mechanism of the hollow nickel spheres.

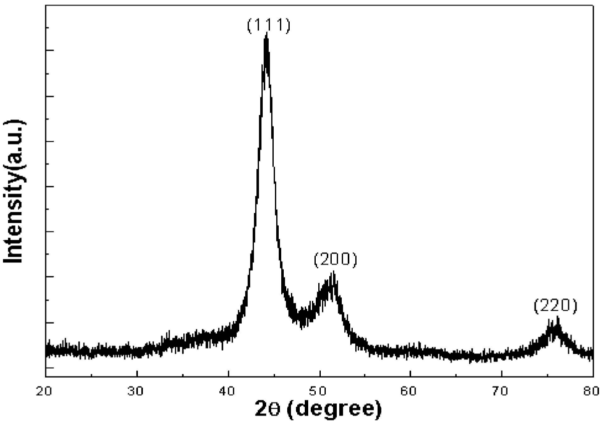

Figure 4 XRD pattern of the as-prepared pure hollow spheres of nickel.

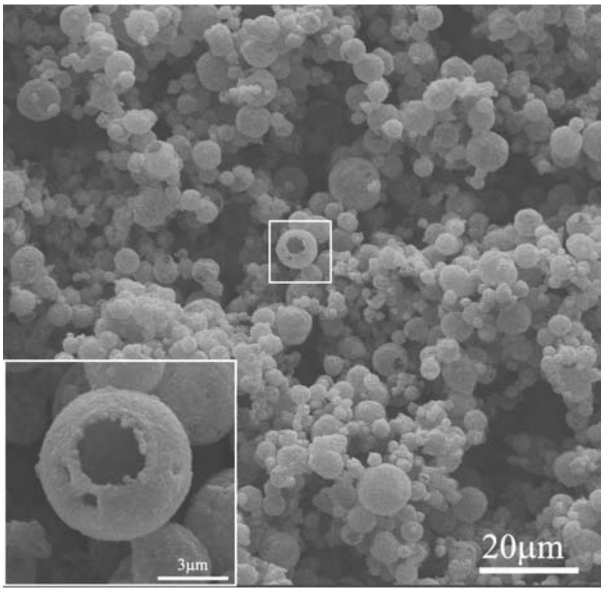

Figure 5 This figure shows a typical view of the nickel hollow spheres with diameters mainly ranging from 3 to 8 μm. A magnified image of a broken nickel hollow sphere was shown in the inset.

NaOH solution, pure hollow spheres of nickel are then obtained. The whole formation process of nickel hollow spheres was illustrated in Fig. 3.

The XRD pattern of the pure product prepared is shown in Fig. 4. They can be well indexed with the reflections of face-centered cubic Ni (PDF standard cards, JCPDS 04-0850, space group Fm3m). The broadening of the peaks is obvious, and the size of the crystallite forming the nickel spheres is about 5 nm, calculated by the Scherrer's equation from the full width at half maximum (FWHM) of (111) and (200) reflections. The size is below the stable single domain range of the magnetic particles [13].

Fig. 5 is a representative SEM image of the synthesized nickel hollow spheres and the diameters of them mainly range from 3 to 8 μm, which are in accordance with the sizes of the solid template of zinc spheres. The broken shells observed on some of the spheres in Fig. 5 indicate the hollow structure of them, and a magnified image of one hollow sphere with the broken part just toward us is shown in the inset of Fig. 5, confirming the hollow structure of these nickel spheres. To further prove the hollow structure of these nickel spheres, ultrasonic treatment is introduced and the whole image of the sample after a strong ultrasonic treatment for half an hour shows many fragments of sphere shell due to complete damage of the spheres (not shown).

To understand the formation of the hollow nickel spheres, the experiment was carried out under various synthetic conditions. As the experiment was carried out in the absence of ammonia, the microstructure of the obtained product was irregular and very few hollow nickel spheres were formed. This phenomenon indicates that ammonia favors the formation of regular nickel hollow spheres, the reason may lie in the fact that ammonia attack the surface of zinc spheres and get rid of ZnO and other impurities that may hinder the formation of shells of nickel spheres on zinc surface. The other contribution of ammonia may lie in its coordination with nickel salt to form a complex of $[Ni(NH_3)_6]^{2+}$ and slow down the replacement reaction speed of nickel on zinc surface which is also favorable for the formation of regular shape [14]. However, it should be careful that ammonia can also dissolve zinc, excessive ammonia or high concentration of ammonia will lead to nothing. Temperature factor is also taken into consideration. With the increase of temperature no expected regular microstructure or smooth surface comes into being. It seems that temperature is not a key factor for the synthesis of hollow spheres of nickel in our experiment. Furthermore, with the increase of the concentration of nickel salt, the microstructure turns irregularly and some irregular shapes come into being. High concentrations of nickel salt could promote the reduction of nickel salt on zinc surface, which is not favorable for the homogeneous growth of sphere shell of nickel, and some irregular shapes may come into being due to the increasing rate of replacement reaction.

It is well known that the shape and structure are inextricably linked with the properties or utility of the catalyst, nickel hollow spheres with the large surface to volume ratio may have potential applications in catalysis, which was also demonstrated by the previous work in our lab [15]. In that work the hollow spheres of nickel-silica composite exhibit high catalytic activity and good selectivity in acetone hydrogenation reaction at 373, 423 and 473 K. Therefore, our as-prepared pure nickel hollow spheres with more nickel percentage are also expected to have good catalytic activity, further work is underway to evaluate the catalysis of these hollow spheres.

The magnetic properties of the nickel hollow spheres with diameters in the range of 3–8 μm were measured at room temperature, and the hysteresis loop of the nickel hollow structure was shown in Fig. 6. The coercivity is 101.8 Oe, which is around the value of bulk nickel material (Hc = 100 Oe) [16]. The saturation magnetization, M_s, and remnant magnetization, M_r, of these hollow nickel spheres are 11.2 emu/g and 4.4 emu/g, respectively. The M_s value is smaller than that of the nanoscale Ni particles reported in the literature ($M_s = 32$ emu/g) [17], which may result from the large surface to volume ratio of hollow sphere structure. As we know, the large surface is not favorable to improve M_s for the spin disorder on the surface and surface oxidation [18]. In addition, the poor crystallinity of the nanosized particles forming nickel hollow spheres and superparamagnetic relaxation of these nanosized particles may also contribute to the reduction of saturation magnetization M_s of our sample [19].

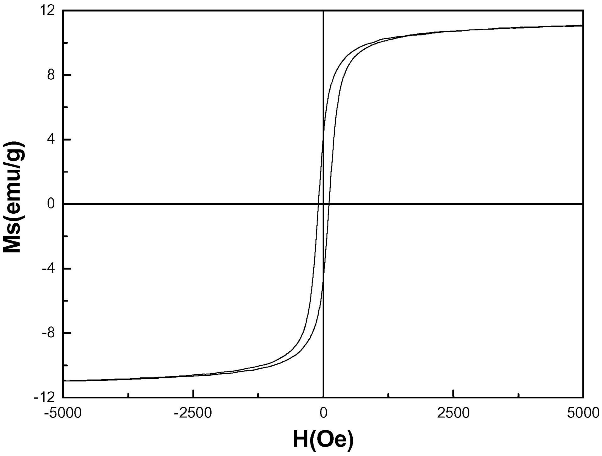

Figure 6 The hysteresis loop measured at room temperature for the hollow nickel micrometer spheres.

In conclusion, micrometer-sized hollow spheres of nickel with diameter ranging from 3 to 8 μm have been prepared at room temperature by the reaction of $NiCl_2 \cdot 2H_2O$ with zinc spheres in aqueous solution. It was found that ammonia and the concentration of nickel salt solution are two key factors for the formation of regular nickel hollow spheres. Such hollow spheres may have potential applications as catalysts, magnetic and gas storage materials, and low-density materials.

Acknowledgments

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