

## Research Article

# Synthesis and Characterization of Hollow Magnetic Alloy (GdNi<sub>2</sub>, Co<sub>5</sub>Gd) Nanospheres Coated with Gd<sub>2</sub>O<sub>3</sub>

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Uniform magnetic hollow nanospheres (GdNi<sub>2</sub>, Co<sub>5</sub>Gd) coated with Gd<sub>2</sub>O<sub>3</sub> have been successfully prepared on a large scale via a urea-based homogeneous precipitation method using silica (SiO<sub>2</sub>) spheres as sacrificed templates, followed by subsequent heat treatment. Nitrogen sorption measurements and scanning electron microscope reveal that these hollow-structured magnetic nanospheres have the mesoporous shells that are composed of a large amount of uniform nanoparticles. After reduction treatment, these nanoparticles exhibit superparamagnetism that might have potential applications in medicine. Furthermore, the developed synthesis route may provide an important guidance for the preparation of other multifunctional hollow spherical materials.

#### 1. Introduction

Hollow nanospheres with tailored structures have attracted tremendous interest due to their higher specific surface area, better permeation, lower density than their bulk counterparts, and their extensive potential applications in magnetic, catalysis, chemical reactors, drug delivery, and optical materials [1-10]. Generally, templating methods are to coat nanocrystals on the hard or soft templates [11-15] followed by removing the templates through etching or calcinations [16]. Moreover, the diameter of the hollow spheres and the thickness of shells can also be tuned by varying the size of cores and the times of the precipitation procedure. Importantly, the shell-shell structure of hollow spheres is involved in immobilizing desired materials on template surfaces due to potential incompatibilities between materials [17], which are well exhibited without affecting the others. It is known that Re<sub>2</sub>O<sub>3</sub> (where Re is the rareearth element) compounds have been widely used as heatresistant materials, high-performance luminescent devices, and catalysts based on the electrical and optical properties of their 4f electrons of lanthanide [18]. Among different RE<sub>2</sub>O<sub>3</sub> materials, gadolinium oxide (Gd<sub>2</sub>O<sub>3</sub>) is promising as host

matrix for down- and upconversion luminescence due to its good chemical durability and low phonon energy [19]. Meanwhile, magnetic microspheres were introduced into the area of biosciences in the 1970s [20]; the synthesis of micro-(or nano) magnetic carriers has received increasing interest due to their wide promising applications.

As a form of nanocomposites, the particles combine magnetic materials and gadolinium oxide to integrate the functions of magnetic and optical responses of the individual components. In particular, shell/shell nanocomposites of magnetic materials and Gd<sub>2</sub>O<sub>3</sub> combine the advantages of individual shells to enhance space utilization of the capsules and greatly extend the application. However, few studies have been involved in preparation of such shell/shell nanocomposites. Recently, template-directed synthesis, with soft templates and hard templates, has been demonstrated to be an effective approach to prepare inorganic hollow spheres. Up to now, using carboxylate silica particles [17], melamine formaldehyde (MF) [21], and silica colloidal particles as sacrificial templates has become the mainstream. Among them, silica is usually employed because it can very efficiently adsorb proteins and is highly stable even in organic solvents [22]. Notably, gadolinium oxide doped

SiO <sub>2</sub>	$M(NO_3)_y$ : $ZH_2O$ (M = Fe, Co, Ni)	Gd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O
1.2 g	$0.21 \mathrm{g} \mathrm{Fe}(\mathrm{NO}_3)_3 \cdot 9 \mathrm{H}_2\mathrm{O}$	0.23 g
1.2 g	$0.15 \text{ g Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.23 g
1.2 g	$0.15 \mathrm{g}\mathrm{Ni}(\mathrm{NO}_3)_2 \cdot 6\mathrm{H}_2\mathrm{O}$	0.23 g



FIGURE 1: Schematic illustration of the preparation of  $M@Gd_2O_3$  (M = GdNi<sub>2</sub>, Co<sub>5</sub>Gd, Fe<sub>3</sub>O<sub>4</sub>) hollow nanospheres.

with europium ions  $(Gd_2O_3 : Eu^{3+})$  has been proven to be an important red-emitting phosphor [23], which emits light in the near-infrared (NIR) window, between 700 and 900 nm and is of particular interest [24]. Along these lines, luminescent and magnetic nanoparticles may be an appropriate answer to major advances in biological and biomedical imaging.

In this work, we have successfully prepared monodisperse shell/shell nanocomposites comprising magnetic hollow spheres and  $Gd_2O_3$  shells. The main steps of the preparation involve synthesis of monodisperse SiO<sub>2</sub> templates, installation of inorganic seeds, and growth and formation of inner or outer inorganic shells via a layer-by-layer deposition process [25]. However, the inorganic phase of  $Gd_2O_3$  was partly soluble in the magnetic shell when the products were reduced in H<sub>2</sub> gas at 450°C. Fortunately, the alloys (GdNi<sub>2</sub> and Co<sub>5</sub>Gd) still possess superparamagnetism. The synthesis strategy is based on a self-assembly diffusion process as illustrated in Figure 1. Our work may open new possibilities to synthesize hollow spheres of other nanocomposites and extend their applications.

#### 2. Experimental

2.1. Materials. Nickel nitrate hexahydrate, cobalt nitrate hexahydrate, and gadolinium (III) nitrate hexahydrate were from Aladdin Chemistry Co. Ltd. Iron (III) nitrate nonahydrate was from Sinopharm Chemical Reagent Co. Ltd. Other reagents were used without further purification.

2.2. Preparation of Nickel-Silica Composite Spheres. The synthesis procedure of silica/Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> [26] involves (1) preparation of uniform silica balls (500 nm) [27] and (2) preparation of nickel-silica composite spheres via a ureabased homogeneous precipitation approach. The whole synthesis process is illustrated briefly in Figure 1. The synthesis details are as follows: 1.20 g of SiO<sub>2</sub> spheres were separately dispersed in 100 mL of solution containing 0.15 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.30 g of CO(NH<sub>2</sub>)<sub>2</sub>. The mixture (100 mL) was stirred mildly at a constant temperature of 95°C for 4 h for a complete precipitation.

2.3. Preparation of GdNi<sub>2</sub>@Gd<sub>2</sub>O<sub>3</sub> Hollow Spheres. The concentrations of gadolinium nitrate, urea, and nickel-silica monodisperse spheres were 0.005 M, 0.05 M, and 12 g/L, respectively, which were prepared by following the same procedure. By immersing the products in 200 mL of 0.5 M NaOH, the silica cores were dissolved by alkaline and the remainder shells were collected by centrifugation. Then, these powders were obtained through heat treatment at 800°C for 2 h in air at a heating rate of 10°C min<sup>-1</sup>. Finally, the particles were reduced in  $\rm H_2$  gas (40 cm³/min) at 450°C (at a rate of 10°C/min) for 2 h in the fixed-bed reactor. After the completion of the reduction process, the sample was protected at room temperature in the flowing-inert gas for 12 h. The core-shell structured  $M@Gd_2O_3$  (M = Fe<sub>3</sub>O<sub>4</sub>, and Co<sub>5</sub>Gd) are prepared by the same method (Table 1).



(d)

(e) (f)  $\label{eq:sigma} \begin{array}{l} \mbox{Figure 2: SEM images of (a) SiO}_2 \mbox{ spheres, ((b) and (d)) silica/Ni}_3Si}_2O_5(OH)_4 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4 \mbox{ hollow spheres with an average size of 580 nm. ((c) and (e)) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. ((c) and (e)) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. ((c) and (e)) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. ((c) and (e)) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. ((c) and (e)) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. ((c) and (c)) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ core-shell structures, Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Gd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Cd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4@Cd}_2O_3 \mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with an average size of 580 nm. (c) SiO}_2@Ni}_3Si}_2O_5(OH)_4\mbox{ hollow spheres with$ 



FIGURE 3: SEM image of (a) iron-silica composite nanospheres. (b) Composite hollow spheres ( $400 \pm 5$  nm). (c) Iron-gadolinium hollow nanospheres (485 ± 5 nm). (d) After reduction. (e) Cobalt-silica composite nanospheres and (f) removing silica cores (510 ± 5 nm). (g) Precursor nanospheres and (h) removing silica cores after reduction (530  $\pm$  5 nm).

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FIGURE 4: EDS surface analysis of nickel-gadolinium, iron-gadolinium, and cobalt-gadolinium composite two-layer hollow spheres: ((a), (e), and (i)) dark field image, ((b), (f), and (j)) silicon map, (c) nickel map, (g) iron map, (k) cobalt map, and ((d), (h), and (l)) gadolinium map.

2.4. Measurements and Characterization. The structures of the samples were characterized by X-ray diffractometer (XRD) (Bruker D8 ADVANCE) using Cu-K $\alpha$  radiation (the wave length is 0.15418 nm). The morphology and elementsof the sample were measured by scanning electron microscope (FE-SEM SU-70) with energy-dispersive X-ray (EDAX). BET surface area was obtained by analyzing N<sub>2</sub> adsorption/desorption isotherm data and from micromeritics (ASAP 2020M) measurement. The magnetic properties of hollow nanospheres were measured by Quantum Design Vibrating Sample Magnetometer as a function of applied fields (-30 and +30 kOe) at 300 K.

#### 3. Results and Discussion

The layer-by-layer (LBL) route was adapted to fabricate the core-shells sphere using  $SiO_2$  as the sacrificed template, followed by deposition of desired coating chemicals or nanoparticles with opposite surface charges [28–30]. The  $SiO_2$  spheresare chosen as the sacrificed template due to their facile removal and their core-shell-shell structure composed of a hydrophobic core and a stabilizing shell that contains vast reactive oxygen functional groups [31]. These  $SiO_2$  spheres were prepared via a hydrolysis method as described above.

The SEM image shows that the SiO<sub>2</sub> spheres have a mean diameter of ~500 nm (Figure 2(a)). After being coated with a porous nickel layer, core-shell silica/Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> composite microspheres with  $Ni_3Si_2O_5(OH)_4$  thin layers of ~40 nm were obtained (Figure 2(b)). The subsequent LBL deposition process resulted in a continuous and uniform Gd<sub>2</sub>O<sub>3</sub> coating on the surface of the spheres (Figure 2(c)). Panels (d) and (e) in Figure 2 display typical SEM images of Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> and Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>@Gd<sub>2</sub>O<sub>3</sub> hollow microspheres, respectively, illustrating that the particles are well dispersed. From the high-magnification SEM image (inset of Figure 2(e)), one can clearly see the thickness of Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>@Gd<sub>2</sub>O<sub>3</sub> layer (approximately  $50 \pm 5$  nm). More interestingly, the size of products prepared can be controlled by varying the size of the cores used in the reactions. For example, the resulting Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>@Gd<sub>2</sub>O<sub>3</sub> hollow microspheres (~200 nm in diameter) are prepared by using  $SiO_2$  (180 nm) as the sacrificed template. Moreover, cobalt-silica and ironsilica hollow spheres were also synthesized via the LBL method by changing the metal precursor (Co, Fe), giving materials a similar spherical morphology and narrow particle size distribution (Co, ~560 nm; Fe, ~580 nm). Subsequently, depositing Gd<sub>2</sub>O<sub>3</sub> on the surface of the precursors, the sizes of the particles are about 595 nm and 610 nm after reduction. As shown, Fe<sub>3</sub>O<sub>4</sub>@Gd<sub>2</sub>O<sub>3</sub> and Co<sub>5</sub>Gd@Gd<sub>2</sub>O<sub>3</sub> hollow spheres



FIGURE 5: The X-ray powder diffraction patterns of  $GdNi_2@Gd_2O_3$ ,  $Fe_3O_4@Gd_2O_3$ ,  $Co_5Gd@Gd_2O_3$  hollow spheres after reduction in  $H_2$  current at 450°C for 2 h.

have been successfully prepared and the detailed information of sample was displayed in Figure 3.

To confirm the composition of products, EDS mapping was devoted for elaborate analysis of the hollow spheres, as shown in Figure 4. The color intensity serves as a tool to judge the relative amount of element present in this analysis and it allows the visualization of the relative location of the different elements in the sample. The EDS-mapping images ((b), (c), and (d)) labeled Si, Ni, and Gd are those obtained for respective elements in hollow spheres. As we have seen from the maps, elemental Ni, Gd, and Si are distributed throughout the whole hollow microsphere. Meanwhile, elemental Fe, Co, and Gd are homogeneously distributed on the shell-shell structures from the images ((e)–(l)). These powders were reduced in H<sub>2</sub> current (40 cm<sup>3</sup>/min) at 450°C (at a rate of 10°C/min) for 2 h in the fixed-bed reactor. After the completion of the reduction process, the sample was protected at room temperature in the flowing-inert gas for 12 h. These multilayer hollow spheres were also characterized by XRD as shown Figure 5, where the corresponding Bragg peaks are indicated. The diffraction peaks at  $2\theta = 28.6$ , 33.1, 47.5, and 56.4° are for (222), (400), (440), and (622) of cubic Gd<sub>2</sub>O<sub>3</sub> [32], in good accordance with reported data (JCPDS Card number 43-1014). It can also be seen that the diffraction peaks of the Gd<sub>2</sub>O<sub>3</sub> particles are very strong and sharp, indicating that outer shell layer with high crystallinity can be synthesized by this method. This is important for phosphors because high crystallinity



FIGURE 6: Room-temperature (300 K) magnetic hysteresis loops of  $GdNi_2@Gd_2O_3$ ,  $Fe_3O_4@Gd_2O_3$ , and  $Co_5Gd@Gd_2O_3$  hollow spheres, respectively. The upper left inset of (a) shows  $GdNi_2@Gd_2O_3$  hollow spheres suspended in water and separated from solution under an external magnetic field and the lower right shows close-up of the central region of the magnetization curves. The inset of (b) shows the highlight of low field region.

generally means fewer traps and stronger luminescence [33]. However, a problem has puzzled us that inorganic phase (Gd<sub>2</sub>O<sub>3</sub>) is partially soluble in the magnetic shell during the reduction process. Fortunately, the alloy (GdNi<sub>2</sub>, Co<sub>5</sub>Gd) has desired magnetic properties. In comparison, a set of very weak diffraction peaks assigned to face-centered cubic GdNi<sub>2</sub> (JCPDS Card number. 65-9978), hexagonal Co<sub>5</sub>Gd (JCPDS Card number 65-9914), and orthorhombic Fe<sub>3</sub>O<sub>4</sub> (JCPDS Card number 89-6466) was detected at the positions marked by arrows, accompanying the predominant diffraction peaks. No other crystalline impurities were detected by XRD.

The magnetic properties of the heterodimers of  $Gd_2O_3$ and  $GdNi_2$  nanoshells are measured using a vibrating sample magnetometer at room temperature. As shown in Figure 6(a), the sample presented a saturation magnetization (Ms) of 3.7 emu/g and a low coercivity of about 10 Oe at room

temperature. The magnified hysteresis loops further confirm the superparamagnetism of these hollow spheres. Compared with the saturation magnetization of the MUC-F-NR (1.28 emu/g) [34], it can more easily be directed by an external magnetic field to a specific target. Furthermore, the magnetization values of Co<sub>5</sub>Gd@Gd<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>@Gd<sub>2</sub>O<sub>3</sub> were 3.38 and 3.15 emu/g (see Figures 6(b) and 6(c)), respectively. For our sample, the main reason may be that the hollow sphere is a compound of GdNi<sub>2</sub>@Gd<sub>2</sub>O<sub>3</sub>, not pure nickel. The Gd<sub>2</sub>O<sub>3</sub> layer also serves as a magnetic layer and exhibits superparamagnetism [35]. Despite this, the powder dried Gd<sub>2</sub>O<sub>3</sub>-coated GdNi<sub>2</sub> magnetic shells could be well redispersed in aqueous solutions, and the suspended particles were well collected using a magnet within 0.5 min (Figure 5(a), left inset), which suggests that they can be manipulated by an external small magnetic field. Remarkably,



FIGURE 7: The pore diameter distribution and the inset of  $N_2$  adsorption/desorption isotherm of the hollow spheres. (a)  $GdNi_2@Gd_2O_3$ ; (b)  $Fe_3O_4@Gd_2O_3$ ; (c)  $Co_5Gd@Gd_2O_3$ .

the separation between the  $Gd^{3+}$  ions in the matrix is too far to render sufficient overlap of the orbitals associated with the partially filled 4f electrons shells of the  $Gd^{3+}$  ions, which is necessary for ferromagnetism [36]. And increasing thickness of magnetic nanoshell by the times of coating, the saturation magnetization of products will be much enhanced.

The specific surface area and porosity of the asprepared  $M@Gd_2O_3$  (M = GdNi\_2, Co\_5Gd, Fe\_3O\_4) hollow spheres were determined by nitrogen sorption measurements. Figure 7 shows the nitrogen sorption isotherms and the corresponding pore-size distribution of as-prepared GdNi\_2@Gd\_2O\_3, Fe\_3O\_4@Gd\_2O\_3, and Co\_5Gd@Gd\_2O\_3 hollow spheres. These samples exhibit a typical IV isotherm with the leap start-points at relative pressures of  $P/P_0 = 0.2-0.3$ , which demonstrates the ordered mesoporous structure. Meanwhile, a large H1-type hysteresis loop appears in its isotherm, which represents narrow pore distributions. The pore size of the product obtained from the analysis of the adsorption branch using the Barrett-Joyner-Halenda (BJH) method was centered at 4.97 nm, as shown in the inset of Figure 7(a). The shell-shell  $GdNi_2@Gd_2O_3$  hollow spheres have a specific surface area of  $33.84 \text{ m}^2 \cdot \text{g}^{-1}$  and a pore volume of  $0.0031 \text{ cm}^3 \text{ g}^{-1}$ , which is close to those of Fe<sub>3</sub>O<sub>4</sub>@Gd<sub>2</sub>O<sub>3</sub> (22.97 m<sup>2</sup> \cdot \text{g}^{-1}/0.0024 \text{ cm}^3 \cdot \text{g}^{-1}), and Co<sub>5</sub>Gd@Gd\_2O\_3 (35.00 m<sup>2</sup> \cdot \text{g}^{-1}/0.0033 \text{ cm}^3 \cdot \text{g}^{-1}) (shown in Figures 7(b) and 7(c)). It is clear that the luminescent layer (Gd\_2O\_3) should be responsible for such a low pore volume because the GdNi<sub>2</sub> shell with mesoporous structure

is covered by  $Gd_2O_3$  particles. It is worthwhile to point out that the obtained multifunctional microspheres with mesoporosity still have large BET surface area and small pore volume due to their mesoporous shell-shell structure.

#### 4. Conclusions

In summary, we have demonstrated a feasible route to prepare uniform hollow shell-shell microspheres of composite materials (M@Gd<sub>2</sub>O<sub>3</sub>, M = GdNi<sub>2</sub>, Co<sub>5</sub>Gd, Fe<sub>3</sub>O<sub>4</sub>) by a template-directed method with silica microspheres as templates. Moreover, the nanoshells thickness can be easily tuned by the times of coating and the diameter of microsphere can also be altered by changing the size of the core. The as-prepared composite materials exhibit excellent adsorption performance for N<sub>2</sub> and superparamagnetism at room temperature and are expected to be useful in water treatment, drug delivery, and many other applications. Thus, the facile synthesis method can readily be extended to the preparation of other magnetic layers @RE<sub>2</sub>O<sub>3</sub> functional materials with shell-shell structure.

#### **Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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