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The synthesis of nickel nanoparticles with controlled morphology and SiO_2/Ni core-shell structures

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Abstract

The magnetic nanopowders can be potentially applied in wide range of fields such as magnetic storage, magnetic fluid, medical diagnosis, conducting paints, rechargeable batteries, optoelectronics, magnetic recording media, drug delivery system and catalysis. They have attracted interest in the past decade and have also been studied extensively because of their size- and shape-dependent physical-chemical and magnetic properties for applications in various useful technologies. In this work, we present our experimental results on the preparation of nanosized Ni nanoparticles with different shapes by using a wet chemical solution route. Ni nanoparticles were prepared by reducing a Ni-complex formed between nickel-acetate and hydrazine solution under basic condition. Then through the control of reaction temperature and ageing time, nanosized Ni particles with different morphologies could be formed. The morphology and sizes of synthesised nanostructures were studied by scanning electron microscopy (SEM). Structural properties of nanoparticles were examined by X-ray diffraction. We also report the core-shell structures of micro-composites of silica-nickel (SiO_2/Ni). The composite core-shell structures were formed by the control of the surface charges of particles in aqueous solutions. A specific composite (SiO_2/Ni) can be produced by controlling the surface charge, the pH and the molar ratio of the components. Core-shell structures are stable at room temperature.

Keywords: Spherical nickel nanoparticles, Star-shape nickel, Flower shape nickel, Magnetic materials, Zetapotential, Core-shell structure, SiO_2 */Ni composite*

1. Introduction

Nanomaterials have attracted interest in the past decade and have been studied extensively because of their size-and shape-dependent physical-chemical and magnetic properties for applications in various useful technologies. In recent years, with growing interest in building advanced materials using nanoscale particles, there is a need for general approaches to controlling the size and shape of nanocrystals [1, 2]. Nanoscale metal materials have attracted much attention owing to their promising potential in magnetic storage, magnetic fluid, medical diagnosis and catalysis. Small metal particle arrays have been used to build single-electron devices [2-4]. More attention has been attracted on nanoscale magnetic transition metal-based materials, including Ni, Co and Fe duo to their magnetic properties and application potential. For such crystallites, the physical and chemical properties depend sensitively on particle size and shape [2-11]. In the last few years, nickel nanomaterials with the following shapes have been synthesized: nanotubes, nanorods, hollow spheres, nanobelts, nanoprisms, and hexagonal flakes [2-6]. Magnetic nanoparticles are being widely used in rechargeable batteries [7], optoelectronics [8], chemical catalysts [9], conducting paints [10], magnetic recording media, ferro-fluids, magnetic resonance imaging contrast enhancement, drug delivery [11] and magnetic hyperthermia [12, 13]. Several methods have been developed to synthesize particles with controlled size and shape. These methods include photolytic reduction [14], radiolytic reduction [15], sonochemical method [16], solvent extraction reduction [17], microemulsion technique [18], polyol process [19], and chemical route [20]. Chemical control over the size and shape of nanocrystals presents a challenge to this field. Li et al. [21] have reported the synthesis of pure black powder Ni through reduction of aqueous $NiSO_4$ with hydrazine. Ni et al. [22] have synthesized distinct flowery shapes of Ni nanocrystals using a hydrothermal chemical reduction containing a mixture of $Ni(N_2H_4)_3^{2+}$ and $Ni(dmg)_2$ (nickel dimethylglyoximate) as the nickel source. In this paper, we report our experimental results on the preparation of nanosized Ni nanoparticles with different shapes by using a modified version of the wet chemical solution route used by Li et al. [21]. Through the control of reaction temperature and ageing time, nanosized Ni particles with different morphologies were prepared. We also report a core-shell structure of SiO_2/Ni composite synthesized by an electrophoretic method.

2. Experimental Procedure

Chemicals used in this paper are: Tetra-ethyl ortho-silicate (TEOS), Isopropanol, Nitric acid (HNO_3), Kerosene, Sorbitan monooleate (Span 80), $Ni(CH_3COO)_2{\cdot}2H_2O$, $N_2H_4{\cdot}2H_2O$, HCl and NaOH. All the chemicals and solvents used in the synthesis of particles were purchased from Aldrich (UK) and used without further purification.

2.1 Preparation of spherical nickel nanoparticles, star-like nanoparticles and flower-like microparticles

The current synthetic procedure is a modified version of the method developed by Choi et al. [20]. Fig.1 shows a flow chart of the synthesis procedure of spherical nickel nanoparticles, nanostars and microflowers. In the synthesis, spherical nickel-metal nanoparticles were prepared by the thermal decomposition of Ni-hydrazine complexes and subsequent reduction of Ni ions. The following procedure describes the synthesis of nickel nanoparticles. First, nickel acetate (0.1 mol) aqueous solution was heated to 50 ºC and then hydrazine ($N_2H_4{\cdot}H_2O$, 0.25 mol) was added to the solution with vigorous stirring. The solution was then heated to 65 ºC, which results in light violet precipitate. When the solution was cooled to 50 ºC, an aqueous solution of sodium-hydroxide (0.3mol) was added to it. To obtain the spherical nanoparticles, the solution was again heated to 55 ºC and remained for 1hr. To obtain nanosize nickel stars, to the N-hydrazine complex added an aqueous solution of sodium-hydroxide (0.1 mol) and then the solution was heated to 70 ºC and remained for 3hrs. When the solution was aged for 24 hrs at 70 ºC, the product was microsized nickel flower. The precipitated particles were retrieved by centrifugation. The yield of the overall synthesis was 60% based on the amount of Ni acetate. The formed black Ni precipitate was finally washed five times with distilled water and dried at 40 ºC in oven overnight.

2.2 Preparation of hollow silica particles

The process is a combination of sol-gel process and water-in-oil (W/O) emulsion based on the work described in [23]. For the water phase: TEOS, H_2O, isopropanol and nitric acid (HNO_3) were mixed at the molar ratio of 1: 4: 3: 0.01. The solution was vigorously stirred at 50 ^{o}C for 60 min. For the oil phase, kerosene and sorbitan monooleate were mixed at 3:1 molar ratio. The water phase and oil phase were then mixed in a Teflon beaker and stirred at 80 ^{o}C for 60 min. The obtained precipitates (SiO_2) were washed with acetone, isopropanol and water to remove any impurity and dried in vacuum oven at 100 ^{o}C for 10 hrs, and finally the powders were calcined at 700 ^{o}C for 8 hrs in a furnace.

2.3 Preparation of Ni coated SiO_2 particles

The principle of synthesis for core-shell structure used in this study is based on the electrostatic attraction between particles having opposite surface charges. The surface charge of particles in solution can be determined by the measurement of Zeta potential. Because the zeta potential of the particles is a function of pH value of the solution, it is possible to control the sign of the zeta potential by adjusting the pH of the solution through adding either HCl or NaOH. Fig. 2a shows a flow chart of the synthesis procedure of core-shell structures. SiO_2 core and Ni shell particles were suspended in deionised water, respectively, in a volumetric flask and the particle concentration of SiO_2 core particles in solution was $0.1 gL^{-1}$ and the particle concentration of Ni varies depending on the requirement of coating thickness. Higher Ni concentration leads to thicker coated layer. The SiO_2 and Ni suspensions were then placed in an ultrasonic bath for 30 min. At this stage, HCl or NaOH was added to the SiO_2 and Ni suspensions to adjust the pH value. Based on the results of zeta potential measurements of particle colloids in water, core and shell particles would produce opposite surface charges at the certain pH regions. The core and shell particle colloids with such pH values were then mixed and placed to the orbital shaker for 30 min. The electrostatic force on the surfaces of the core and shell particles would make the attraction of different charged particles to each other and thus form a core-shell structure (Fig. 2b). The core-shell particles were then dried in the oven at 40 ºC overnight.

2.4 Characterization

Scanning electron microscopy (S-FEG SEM) was performed on a Philips XL30. X-ray diffraction studies used a standard XRD θ-2θ measurement in the range 2θ = 20°-60° on a Siemens D5005 diffractometer with CuK_α radiation and a Goebel mirror. The crystallite size is determined from the X-ray line broadening using Scherrer formula given by $D = 0.9\ \lambda / \beta \cos \theta$, where D is the average crystallite size, λ is the X-ray wavelength used (1.5406 Å), β is the angular line width of half maximum intensity and θ is the Bragg's angle in degree. The pH values of particles in water were measured using a Jenway 3540 pH meter. Electrophoresis measurements were performed using a Malvern Zetasizer 3000.

3. Results and Discussion

A schematic illustration of the formation mechanism of Ni nanostructures is shown in Fig. 1. Ni-complex such as $[Ni(NH_3)_6](CH_3COO)_2$ or $[Ni(N_2H_4)_3](CH_3COO)_2$ is decomposed by NaOH forming $Ni(OH)_2$. Subsequently the Ni^{2+} ion was reduced to nickel nanoparticles.

Previous publications [22, 24 and 25] on the synthesis of nickel nanocrystals by hydrothermal reduction from different complexes described the possible mechanisms of formation of the nickel nanoflowers. For example, Ni et al. [20] used two complexes, $Ni(N_2H_4)_3^{2+}$ and $Ni(dmg)_2$ as the nickel source in hydrothermal synthesis and they think that the reaction process involves two steps: firstly, $Ni(N_2H_4)_3^{2+}$ is reduced, and the resulting spherical nanocrystals serve as the flower centers. Then $Ni(dmg)_2$ yields swordlike nanocrystals which grow radially on the existing spherical centers as petals [22]. In our case, a chemical solution synthesis method is used. The formation mechanism of the nickel nanocrystals is possibly similar to the ones described in [6, 21]: Hydrazine reacts with nickel ions in aqueous media to form hydrazine complex [26-27].

$$Ni^{2+} + 3N_2H_4 \leftrightarrow [Ni(N_2H_4)_3]^{2+} \qquad (1)$$

Then $[Ni(N_2H_4)_3]^{2+}$ reacts with OH^- in alkali system as following:

$$2[Ni(N_2H_4)_3]^{2+} + 4OH^- \rightarrow 2Ni\downarrow + N_2 + 4H_2O + 5N_2H_4 \qquad (2)$$

Hydrazine is a powerful reducing agent. Temperature and time of the reaction influence the products. Between 50 and 70 °C and under the basic condition, the reaction (2) proceeds fast and leads to spherical Ni particles. If the temperature of the reaction (2) is higher (70-85°C), crystals grow fast on the spherical Ni particles. Therefore, star-like Ni particles would yield. The pH value of the solution also influences the products. At 50 – 70 °C, NaOH is necessary for the formation of pure spherical powder of metal nickel. If temperature rises to 85 – 95 °C, Na_2CO_3 can be used to obtain pure powder of metal nickel. pH value in both NaOH and Na_2CO_3 situations should be adjusted to 10 – 12 in order to keep the reaction speed and products under control.

The low concentration of NaOH solution ($\leq$ 0.1 mol) and the high reaction temperature ($\geq$ 70°C) can generate nanosize star-like Ni particles and longer reaction time (aging time 24hrs) can lead to the formation of flower-like nickel crystal with micro size. $Ni(N_2H_4)_3^{2+}$ was first reduced and yielded spherical nickel particles, which were dispersed in the system. The newly formed Ni nanoparticles serve as seed sites for the further reduction of $Ni(N_2H_4)_3^{2+}$ and crystal growth as the reaction proceeds at high temperature.

It is reasonable to think that the concentration of Ni^{2+}-ion in solution changes and the Ni nuclei sites gradually increase with the reaction proceeding, which result in the formation of Ni irregular nanoparticles when ageing. Ni^{2+}-ion concentration in the solution with high pH ($\geq$ 13) supports the crystals growth along a certain direction until all the Ni^{2+}-ions are consumed. Therefore to control the shape of Ni particles, it is important to monitor the pH. The other factors that need to be considered are the temperature of the solution and the ageing time.

At higher temperature (> 85 °C) and shorter time it will produce nanoparticles. Because, at higher temperature, Ni^{2+}-ions move faster, which makes the crystal growth slower and therefore it needs longer time to age the solution in order to obtain star or flower shape crystals.

The morphology of the samples was investigated by field emission scanning electron microscopy (FE-SEM). Fig. 3 shows the SEM images of spherical shape Ni nanoparticles (Fig. 3a - 3f) with the average size between 80-400 nm. Ni particles are spherical (Fig 3a - 3f) while particles are more or less flower shape in Fig 4a - 4c and stars shape in Fig. 4d - 4e. All the particles showed a narrow particle size distribution. Due to the large surface to volume ratio and strong magnetic attraction forces, the Ni nanoparticles tend to agglomerate in order to minimize the total surface energy of the system. The produced nanoparticles are spherical with the size between 80 nm to 400 nm depending on the molar ratio of $Ni(CH_3COO)_2$ /N_2H_4 between 0.4 to 0.07.

Fig. 4f shows the SEM images of SiO_2 particles coated with nickel nanoparticles (the average size of SiO_2 particles is about 15 μm and the average size of nickel nanoparticles 100 nm). The SiO_2 particles remain spherical after they were coated with Ni. The thickness of the shell can be controlled through the mediation of the ratio of core and shell particles and the reaction time.

Fig. 5 shows the zeta potential values of the SiO_2 and Ni particles in water as a function of pH. Zeta potential measurement gives the information about the overall surface charge of the particles and how this is affected by the changes in the environment (e.g. pH). The measured colloid suspensions were prepared without adding any surfactant. The results of the electrophoresis measurements revealed that the zeta potentials of core (SiO_2) and shell (Ni) particles in their solution have opposite signs at $4.3 < pH < 10.7$. The zeta potential for SiO_2 particles was between 0 and -50 mV while the zeta potential of Ni particles was between + 40 and 0 mV. This allowed for the easy attachment of the nickel nanoparticles on the surface of SiO_2 particles in this pH region.

Fig.6a shows the XRD patterns of spherical Ni nanoparticles with size between 80-400nm and Fig. 6(b) shows the XRD patterns of the core/shell SiO_2 /Ni. Three characteristic peaks for nickel ($2\theta = 44.5^\circ$, 51.8°, and 76.4°), corresponding to Miller indices (111), (200), and (222), were observed. The intensity of these peaks increases with the increase of Ni nanoparticles size. The appearance of those peaks reveal that the resultant particles are pure face-centred cubic (fcc) nickel at these samples (JCPDS, No. 04-0850). The XRD patterns revealed only nickel. The calculated size values for all Ni samples by Scherrer formula [28] at 2θ of 44.5º are general approximates to those of SEM observation (Fig. 3, 6).

4. Conclusions

Spherical Ni nano-particles, star-shaped Ni nanocrystals and flower-shaped Ni micro-particles were successfully prepared by using a wet chemical solution method. All these products were synthesed by reduction of the complex of $[Ni(N_2H_4)_3]^{2+}$ in alkaline solution with hydrazine hydrate. The present work realized the control of the crystal shape through controlling various Ni-ions reduction reaction parameters to adjust the crystal nucleation and growth processes. Also, through adjusting the solution pH values of core and shell particles, Ni nanoparticles were successfully coated onto the SiO_2 particles in an aqueous solution forming core-shell nanostructure. The resultant nickel nanoparticles, nano-star and micro-flower and the core-shell particles have been confirmed by XRD, SEM analysis.

5. References

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Figure captions:

Figure 1: Schematic illustration of the possible formation process of the spherical nickel nanoparticles and Ni nanostars- and microflower-structures.

Figure 2: (a) Synthesis route of core-shell particles; (b) Schematic diagram of the formation of core-shell particles.

Figure 3: SEM images of spherical nickel nanoparticles. a:80nm, b:100nm, c:120nm, d:150nm, e:300nm, f:400nm

Figure 4: SEM images of microflower of nickel (a-c) and nanostars of nickel (d-e) and SEM of a single SiO_2 particle coated with nickel particles (f).

Figure 5: Zetapotentials of SiO_2 and Ni particles in water as function of pH. Adjustment of the pH was carried out by adding standard HCl and NH_4OH solutions.

Figure 6: X-ray powder diffraction patterns of spherical Ni nanoparticles (a) and SiO_2/Ni core-shell composite at room temperature (b).

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