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Selective synthesis of metallic nickel particles with control of shape via wet chemical process

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ABSTRACT

Metallic nickel particles with shapes varying from sea urchin-like to spherical have been selectively synthesized via aqueous chemical reduction. The phase structure and morphology of particles have been investigated by means of X-ray diffraction and scanning electron microscopy. It was found that sodium carbonate greatly accelerated the reduction process to form needle-like dendrites under atmospheric pressure. The probable formation mechanism of the sea urchin-like particles is also discussed. In the mild reduction process, the particle size of nickel nanospheres could be easily controlled by adjusting the experimental parameters.

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1. Introduction

Ultrafine nickel particles are of great research interest due to their potential applications in optical, electronic, catalytic, magnetic materials, and so forth [1–5]. Since the morphology, structure and dimension of nanoparticles (NPs) have great influence on their properties, different applications have different needs. To date, it is still challenging to develop synthesis strategies that enable systematically tailor the morphology and the structure of the Ni NPs to fine-tune their properties, especially, using inexpensive precursors.

The search for understanding of nonequilibrium pattern-forming mechanisms has attracted enormous attention albeit mainly in theoretical studies [6,7]. Among the existing mechanisms, the boundary-layer model (BLM) has been widely utilized to investigate the solidification of crystal, especially a dendritic growth, from an undercooled or supersaturated liquid [8–10]. According to the BLM mechanism, spherical solidification takes place in a relatively steady-state case, in which the critical radius of nuclei (R^*) is determined by capillary length, d_0 , and undercooling, Δ , as $R^* = d_0/\Delta$. As the particle grows larger, typically in the submicron range, dendrite forming instabilities originate and the solidification follows a dendritic growth mode. Especially, a dendrite with sharp tip can be obtained under rapid solidification. Usually, a higher reduction temperature (T_{Red}) will accelerate the reaction rate for

growing larger particles. In aqueous solution, however, it is difficult to realize high growth velocity under atmospheric pressure owing to the restricted temperature. Although there have been some reports on the preparation of sea urchin-like nanostructures such as α -MnO₂, Ni_{0.85}Se, Co_{0.85}Se and NiO, almost all reductions proceeded at high temperature (higher than 150 °C) under high pressure (using an autoclave) [11–13].

Until now, there have been few reports on the systematic study of nickel particles with various shapes and sizes in aqueous solution. In this study, the reduction of nickel ions was accelerated upon the addition of sodium carbonate and achieved the conditions for growing needle-like structures. Based on the BLM mechanism, nickel particles with shapes varying from sea urchin-like to spherical have been selectively synthesized.

2. Experimental details

The chemical reagent tetraethylene glycol (95%), *n*-butanol (99%), *n*-dodecane (99%), and hydrazine monohydrate (98%) were all reagent grade and used without further purification.

2.1. Synthesis of sea urchin-like particles

Typically, a given amount of sodium hydroxide (NaOH) was added into 8 ml of 1.4 M nickel sulfate (NiSO₄) solution to control the pH value. Unless otherwise mentioned, the pH value of the solution was fixed at 13.5. Sodium carbonate (Na₂CO₃) was added to speed up the reaction; the molar ratio of Na₂CO₃ to Ni²⁺ was 4.0. An appropriate amount of surfactants were added, as needed. Then, 10 ml hydrazine monohydrate



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Fig. 1. SEM images of sea urchin-like nickel particles obtained at 90 °C at pH (a) 12.8 and (b) 13.5. c) A high-magnification view for a single particle taken from (b).



Fig. 2. Schematic illustration of the formation of sea urchin-like nickel particle. a) Generation of nuclei; b) Solidification of nickel droplets on particle surface with release of solidification heat (q). c) Appearance of dendrite-forming instabilities. The arrows indicate the dendrite-forming sites. d) Diffusion process of reduced nickel at the dendrite tip.

 $(N_2H_4$ · $H_2O)$ was poured into the solution at a temperature higher than 85 °C. The products obtained by filtration were washed repeatedly with distilled water and finally dried in an oven at 100 °C for 1 h.

2.2. Synthesis of spherical particles

 $[Ni(N_2H_4)_3]SO_4$ was produced by agitating the mixture which was made up of 10 ml N_2H_4 : H_2O and 8 ml of 1.4 M NiSO_4 solution. 10 ml of *n*-butanol was added, and then the slurry was heated to the reduction temperature. After adding 5 ml of 6.8 M NaOH, the reduction reaction proceeded until the solution turned black. The final metallic precipitates were filtered and washed with distilled water, and dried at 100 °C for 1 h.

2.3. Characterization

The phase structure was identified by X-ray diffraction (XRD, Rigaku Geigerflex) using Cu K α radiation with a graphite monochromator. The particle size and morphology analyses were performed

using field emission (FE-) scanning electron microscopy (SEM, Hitachi S-4500, with accelerating voltage of 30 kV).

3. Results and discussion

3.1. Morphology control of sea urchin-like particles

The reduction was first carried out at 90 °C. After pouring the hydrazine hydrate, the solution boiled intensely with copious evolution of gas bubbles. SEM images of the products obtained at different pH levels are shown in Fig. 1. Clearly, the nickel particles are sea urchin-like in shape and each of the dendrite grows into a needle-like crystal with a very sharp tip. These sharp and long dendrites greatly increase the particle surface area. For instance, the measurement of BET specific surface area reveals that the SSA of the particles shown in Fig. 1 c is 4.29 m²/g, which is nearly 8 times larger than that of a sphere of the same size ($0.52 \text{ m}^2/g$). The role of sodium carbonate in the preparation of sea urchin-like shaped particles is interesting. It was found that the solution remained quiescent and no needle structure was observed in the absence of Na₂CO₃.

Since the dendrites grow radially at almost the same rate in different directions, the particle size was determined by measuring the tip distance between two reverse dendrites. The average particle size is about 2.5 μ m (Fig. 1a) and 1.6 μ m (Fig. 1b), respectively. It is believed that the formation of nickel nanostructures originates from liquid nickel droplets produced in Reaction (1) [14].

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni(\text{liquid droplet}) + N_2 + 4H_2O \qquad (1)$$

The pH of the reaction medium can have a major impact upon the redox potential of the solutes. With increasing the pH value of the solution, the enhanced driving force of the reduction favors the generation of more nuclei in the nucleation step, resulting in the formation of smaller nickel particles. It suggests that the particle size could be adjusted through controlling the pH of the mixture.

It is considered that dendritic solidification follows an unconstrained growth mode, in which the solidification heat flows from the crystal into the solution [15]. Shown in Fig. 2 are schematic models for the growth of sea urchin-like nickel particles. Base on the BLM model, we consider the process consists of four important steps: i) Ni nuclei are generated. ii) Ni droplets solidify following spherical growth mode. As mentioned by Langer [16], the growth velocity (v_R) of a sphere has a relationship with particle size (R) as

$$v_R = \frac{D}{R} \left(\Delta - \frac{2d_0}{R} \right) \tag{2}$$

where *D* is diffusion coefficient. At this stage, the growth rate is rapid due to the small particle size. iii) Dendrite-forming instabilities originate. As the particle grows larger, according to Eq. (2), the growth rate is slower. In the rapid reduction process, therefore the spherical growth mode was interrupted. iv) To maintain rapid growth, the solidification process then follows dendritic growth mode using the instability sites. As well known, an increase of temperature is favorable for the reduction of Ni ions by hydrazine monohydrate. As shown in Fig. 2d, a larger amount of Ni droplets are produced in the



Fig. 3. SEM images of the particles synthesized at 85 °C with the addition of (a) 20 ml, b) 10 ml of tetraethylene glycol, and c) 4 ml of n-butanol and 20 ml of n-dodecane.



Fig. 4. (a) XRD measurement of nickel particles obtained at different T_{Red}. (b) Dependence of particle size on the T_{Red}. (c) Representative SEM image of the nickel spheres synthesized at 62 °C. (d) SEM image of the nickel spheres obtained at 60 °C in a w/o microemulsion.

local higher temperature region caused by solidification heat (*q*). Therefore the concentration gradient of produced Ni increases, and this region is the favored growth domain. In Ref. [15], it also reveals that the solidification process proceeds mainly at the dendrite tip. Derived from Mullins and Sekerka's results [17–19], the relationship between growth rate (ν) and the curvature of the dendrite tip (ρ) must have the form:

$$\sigma = \frac{2d_0 D}{\rho^2 v} \tag{3}$$

where σ is a constant independent of dynamic quantities like ρ and v. It means that rapid solidification process will lead to forming sharp dendrite. In Fig. 1, the formation of needles also demonstrates the reduction proceeds with high velocity.

To modify the shape of sea urchin-like particles, a certain amount of surfactants was added before reduction. Fig. 3 shows the SEM images of the particles synthesized at 85 °C in the presence of surfactants. In Fig. 3a and b, the particles are of fat dendrites while the number of dendrites decreases, which becomes more obvious upon increasing the volume of tetraethylene glycol. It suggests that tetraethylene glycol plays a role in the decrease of diffusion coefficient of reduced Ni droplets, thus slowing down the growth process. When the mixture of *n*-butanol and *n*-dodecane was added into the solution, the reduction rate was further decreased and the dendrite tips were no longer sharp. The prolate dendrites obtained have relatively rough surfaces.

3.2. Study of the spherical particles

Fig. 4a shows the XRD patterns of the particles synthesized at different reduction temperature. The peaks located at 44.5°, 51.8°, 76.4°, and 92.9° correspond to Ni(111), (200), (220), and (311) planes, respectively. Metallic nickel with face-centered cubic (fcc)



Fig. 5. SEM images of the particles synthesized at 60 °C. a) [NiSO₄]=0.35 M; b) [NiSO₄]=0.7 M.

phase was obtained when reduced at 55 °C. However, no matter how long the reaction proceeded, the resulting powder contained metallic nickel and nickel hydroxide when reduced at temperatures below 50 °C.

The dependence of particle size on the reduction temperature is shown in Fig. 4b. Due to the increase of chemical potential, a reduction performed at higher T_{Red} will generate a larger concentration of nuclei, conducive to the formation of small particle size. Note that an increase of T_{Red} can also accelerate the reaction velocity to form larger particles. Taken together, the optimum T_{Red} to grow small particles is around 60 °C. Fig. 4c shows the SEM micrograph of the particle obtained at 62 °C.

General speaking, the presence of the surfactant decreases the surface tension of the aqueous solution, thereby decreasing the capillary length to achieve small R^* [20]. It is a more effective way to reduce the surface tension using a water-in-oil (w/o) emulsion. Herein, 10 ml of *n*-butanol mentioned above was substituted by 10 ml of *n*-dodecane to prepare a w/o microemulsion. A SEM micrograph of the nickel spheres synthesized at 60 °C is shown in Fig. 4d. The average particle size is less than 80 nm, which is far smaller than those previously reported [14,21].

Using dilute solutions, the reduction was carried out and the SEM images of the particles synthesized are shown in Fig. 5. Owing to the low concentration of nuclei generated, the particles were nearly 1 μ m in size. Stable spherical growth was interrupted to originate dendrite-forming instability, and the resulting particle took on a rough surface. The dendrites could not grow into sharp needle-like shape in this case due to the much slower reduction rate.

4. Conclusion

We have reported here the systematic preparation of nickel particles with different shapes based on BLM mechanism. In a rapid reaction accelerated by sodium carbonate, sea urchin-like particles with needle-like dendrites have been synthesized under atmospheric pressure. Upon the addition of surfactants, the particles grow with fat dendrites, eventually with quite rough dendrite surfaces. In the synthesis of nickel spheres, the optimum temperature for growing small particles is about 60 °C. A diluted solution leads to the formation of large particles with rough surfaces. XRD characterization showed that the pure metallic particles could be produced only at temperatures higher than 50 °C.

References

- [1] Ni XM, Su XB, Yang ZP, Zheng HG. J Cryst Growth 2003;252:612.
- [2] Yu K, Kim DJ, Chung HS, Liang H. Mater Lett 2003;57:3992.

- [3] Degen A, Macek J. Nanostruct Mater 1999;12:225.
- [4] Li YD, Li CW, Wang HR, Li LQ, Qian YT. Mater Chem Phys 1999;59:88.
- [5] Song J, Wen L, Xia Z, Chen J. Fuel Process Technol 2007;88:443.
- [6] Halsey TC. Phys Rev Lett 1994;72:1228.
- [7] Witten Jr TA, Sander LM. Phys Rev Lett 1981;47:1400.

- Witten Jr IA, Sander LM. Phys Rev Lett 1981;47:1400.
 Ben-Jacob E, Goldenfeld N, Langer JS, Schon G. Phys Rev Lett 1984;51:1930.
 Ben-Jacob E, Goldenfeld N, Langer JS, Schon G. Phys Rev A 1983;29:330.
 Ben-Jacob E, Goldenfeld N, Kotliar BG, Langer JS. Phys Rev Lett 1984;53:2110.
 Zhang Z, Mu J. Solid State Commun 2007;141:427.
 Bai L, Yuan F, Hu P, Yan S, Wang X, Li S. Mater Lett 2007;61:1698.

- [13] Liu X, Zhang N, Yi R, Qiu G, Yan A, Wu H, et al. Mater Sci Eng B 2007;140:38.
- [14] Park J, Chae E, Kim S, Lee J, Kim J, Yoon S, et al. Mater Chem Phys 2006;97:371.[15] Kurz W, Fisher DJ. Fundamentals of Solidification. Aedermannsdorf, Switzerland: Tran Tech Publications; 1998. p. 65.[16] Langer JS. Rev Mod Phys 1980;52:1.

- [16] Langer JS. Rev Mod Phys 1980;52:1.
 [17] Mullins WW, Sekerka RF. J Appl Phys 1963;34:323.
 [18] Mullins WW, Sekerka RF. J Appl Phys 1964;35:444.
 [19] Wang SL, Sekerka RF. Phys Rev E 1996;53:3760.
 [20] Gao J, Guan F, Zhao Y, Yang W, Ma Y, Lu X, et al. Mater Chem Phys 2001;71:215.
 [21] Kim K, Park H, Lee S, Hwa W, Hong S, Lee G, et al. Mater Chem Phys 2005;92:234.