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Synthesis of Nickel Nanoparticles (Ni, Co) in ethylene glycol-hydrazine -ammonia system

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1. Introduction

Monodisperse fine Ni particles are required for high technology applications in alkaline rechargeable batteries, magnetic recording media and chemical catalysts, etc., such as conducting inks, magnetic inks, and ferrofluids. Various methods have been reported for the synthesis of ultrafine nickel powders and include physical methods such as ball milling, pulsed electrodeposition (PED), thermal plasma, gas deposition methods (GDM), -radiation, chemical methods including sonochemical decomposition, chemical reduction, a microwave hydrothermal method, mechanical alloying and mechanochemical processing and polyol process. In our work, ethylene glycol was used to be the solvent, and no surfactants were used, a little amount of nucleating agent was used, and ammonia was used as the pH controller. No studies related to the same work have been reported.

2 Experimental

2.1 Materials

A commercially available nickel chloride was used as starting material, hydrazine monohydrate as the reductant, ammonia water as the pH modifier, ethylene glycol as the solvent and 0.1M silver nitrate solution as the nucleating agent.

2.2 Preparation and characterization

A suitable amount of nickel chloride was dissolved directly in ethylene glycol (EG). Then an appropriate amount of hydrazine and of ammonia water were added in sequence. After the temperature arrived at 85C, a very small amount of silver nitrate solution was added. The resulting suspension was stirred for 1 hour and then aged for 30 additional minutes, during which time the formation of Ni particles occurred. The mixture was filtrated and the residue washed by using ethanol. After centrifugal filtration, the sample was heated to 50C for a period of 5 hours to give Ni particles.

3. Results and discussion

3.1 Formatin of nickel nanoparticles

It is very interesting to observe the color change during the experiment. We supposed the process of the preparation could be understood from equations (1), (2), and (3)

$$Ni^{2+} + 3HOCH_2CH_2OH \quad Ni(HOCH_2CH_2OH)_3^{2+} \tag{1}$$

$$Ni(HOCH_2CH_2OH)_3^{2+} + 6N2H4 \quad Ni(N_2H_4)_6^{2+} + 3HOCH_2CH_2OH \tag{2}$$

$$Ni(N_2H_4)_6^{2+} + 2OH = Ni + N_2 + 5N_2H_4 + 2H_2O \tag{3}$$

3.2 Particle size and structure

From Fig. 1 that the particles essentially were very fine and well dispersed with a rough agglomeration size of 100~250 nm, and the crystalline size calculated from XRD is 25 nm. This XRD pattern also revealed that the final particles were pure face-centered cubic (fcc) nickel.

3.3 Effect of EG

It can be suggested that EG might form a protective layer around the particle surface via the interaction of OH group with nickel atoms, preventing the particle agglomeration or aggregation.

3.4 Effect of Ammonia

When $[Ni^{2+}]$ 10 mM, 25 millilitre of 0.1 M NH_3H_2O solution was enough. However, about 70 millilitre of 0.1 M NH3H2O solution was required when $[Ni^{2+}]$ = 50 mM. The role of trace ammonia in the synthesis of nickel nanoparticles is quite interesting. It was suggested that the trace ammonia might act as a catalyst.

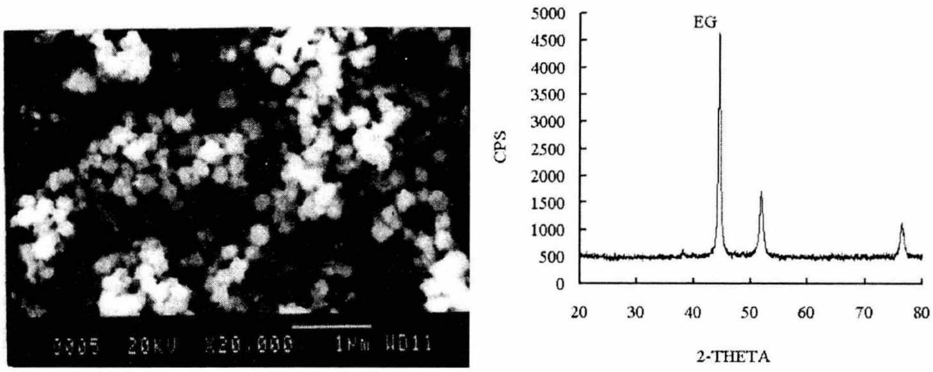

Fig. 1 SEM micrographs and XRD pattern for the nickel nanoparticles. $[Ni^{2+}]$ = 0.05 M; $[N_2H_5OH]$ = 0.5M.

3.5 Effect of nickel chloride and hydrazine

The effects $[Ni^{2+}]$ and $[N_2H_4H_2O]$ on the size of nickel nanoparticles, calculated from XRD pattern by Scherrel formula, were illustrated in Fig.2. It was found that, with increasing ratio of $[N_2H_4H_2O]$ / $[Ni^{2+}]$, the size decreased but almost remained unchanged when $[N_2H_4H_2O]$ / $[Ni^{2+}]$ 10. This can be explained by the influence of reduction rate on the nucleation.

3.6 Effect of Nucleating agent

The addition of nucleating agent was very important on acceleration of the reaction rate. The relationship between the concentrations of Ag+ and the size of nickel particles was studied.

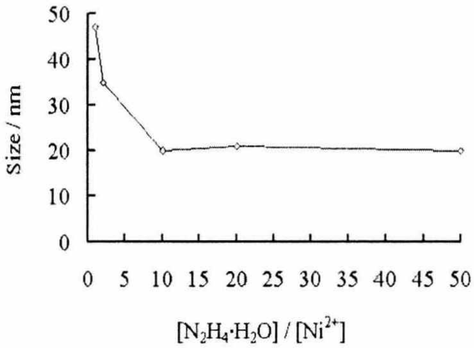

Fig. 2 Effect of $[Ni^{2+}]$ and $[N_2H_4H_2O]$ on the size of nickel nanoparticles.

4. Conclusion

(1) Using the nonaqueous media reduction methodin a EG-Hydrine-Ammonia system, nickel nanoparticles with an approximate size of 25 nm and a rough 100-200 agglomeration size were prepared.

(2) The concentration ratio was investigated and it was found that when [N2H4H2O] / [Ni2+] 10, the size of nickel particle was smaller.

(3) The formation mechanism and the nucleation mechanism were studied via analyzing the function of the system compositions.