A Solution Route to Synthesize Nickel Thiospinels

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Ni_3S_4, $CoNi_2S_4$, and $NiCo_2S_4$ thiospinels were synthesized by a pH-controlled homogeneous precipitation method at 70 °C with metal-chlorides and thioacetamide in the ammonium chloride–ammonia buffer solutions adjusted to pH = 9.9.

Metal sulfides are materials of particular interest for their catalytic, electrochemical, and opto-chemical properties. Especially, thiospinels of transition metals were found to be highly active electrocatalysts for oxygen cathode in acid electrolyte.[1] So far, thiospinels have been mainly prepared by allowing metals to react with sulfur in an evacuated tube or by allowing oxides to react with H_2S at higher temperature than 500 °C.[2] Although these methods are efficient, these techniques using H_2S gas flow, vacuum vessels or autoclaves are rather complicated and they do not allow of appropriate process control. On the other hand, solution routes using a thioacetamide or a sodium sulfide as a sulfur source offer simple technique to produce metal sulfides at relatively low temperatures. There is a rather extensive study on the attempts to synthesize the various kinds of metal sulfides by wet-chemical methods. Metal mono sulfides (MS: M = Ni, Zn, Cu, Pb, Cd)[3] or metal disulfides (MS_2 : M = W, Ti)[4] were successfully synthesized. There are, nevertheless, a few studies succeeded in the preparation of thiospinels via solution route. Lundqvist had first reported the possibility to synthesize a Ni_3S_4 thiospinel with a reaction of $NiSO_4$ and $Na_2S_2O_3$ in neutral solution at boiling point.[5] However, the preparation conditions as well as the characterizations of the product were still uncertain.

We have found that a large amount of nickel thiospinel (Ni_3S_4) was precipitated in a homogeneous precipitation process of the reaction between nickel chloride and thioacetamide (TAA) from basic solutions, when NH_4OH has been employed as a basic reagent for the decomposition of TAA at 70 °C. In further study, it was revealed that the yield of the thiospinel (Ni_3S_4) was largely dependent on the initial pH, i.e., Ni_3S_4 was well synthesized from the pH = 9.9 solution containing $NiCl_2$, TAA, and NH_4OH–NH_4Cl. In this paper, the simple precipitation method was reported for the synthesis of some thiospinels.

Thiospinel of Ni_3S_4 was prepared by a pH-controlled homogeneous precipitation method. $NiCl_2{\cdot}6H_2O$ (15 mmol) of commercial origin was dissolved in 200 mL distilled water with various basic reagents (0.5 mol) (Route A) or NH_4OH–NH_4Cl (20 mmol) buffer solutions adjusting to the various pH (Route B). The solutions were then added to the solution containing thioacetamide (20 mmol) in distilled water (200 mL), at 25–100 °C. The mixing speed was controlled with a dropping funnel. The obtained mixed solutions were boiled at 100 °C for 1 h in an open vessel (Route A) or refluxed at 60–80 °C for 12 h with a reflux condenser (Route B). The precipitates thus obtained were filtered, washed with distilled water, and finally dried at 120 °C in Ar flow (or vacuum dried at RT). The thermal or vacuum drying processes gave similar X-ray diffraction patterns. The products were characterized by X-ray diffractmetry (XRD) (JDX-3500K, JEOL) using Cu $K\alpha_1$ radiation, and scanning electron microscopy (SEM) (JSM-6320F, JEOL).

Table 1 shows the effects of base materials, the mixing temperatures, the mixing speed for the formation of various nickel compounds via Route A. When NH_4OH was used as basic reagent under slow mixing at 70 °C, the largest (64%) amount of Ni_3S_4 was obtained, although the product was still consisted of Ni_3S_4, NiS_2, and $Ni(OH)_2$. On the other hand, NiS_2 could be also synthesized with nickel chloride, NaOH, and thioacetamide under quick mixing at 40 °C, while the preparation method for the metal-disulfides will be reported later.

Table 1 Synthetic conditions for the thiospinel by the homogeneous precipitation method

Base material	Mixing temp. / °C	Mixing speed	Yield / %[a]			
			Ni_3S_4	NiS	NiS_2	$Ni(OH)_2$
NaOH	25	Quick	41	29	31	0
NaOH	40	Quick	0	0	100	0
NH_4OH	25	Quick	16	42	42	0
NH_4OH	70	Quick	27	55	0	18
$(NH_2)_2CO$	70	Slow	33	67	0	0
NH_4OH	70	Slow	64	0	22	14
NH_4OH	100	Slow	43	57	0	0

[a] From the relative XRD intensity of the strongest peak.

The NH_4OH-based process was further investigated being focused on the initial pH. Table 2 shows the effect of the initial pH on the formation of Ni_3S_4 via Route B. The initial pH was adjusted with NH_4OH–NH_4Cl buffer solutions and the reactions were carried out in refluxing to avoid the pH change by the evolution of NH_3. It was found that Ni_3S_4 could be well synthesized from the solution of pH = 9.9 at 60–70 °C. The decreasing of the refluxing temperature to 40–50 °C at pH = 9.9 increased the formation of impurity phases of $Ni(OH)_2$ and NiS_2 or NiS. Although the reaction mechanism on the formation of Ni_3S_4 thiospinel is not clear, formation of nickel–ammonia complexes and their reaction with hydrogen sulfide, which was produced from hydrolysis of thioacetamide, seems to play an important role in the formation of nickel thiospinels. Lowering of the initial pH should decrease the formation of col-

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Table 2 Synthetic conditions for the thiospinel by the homogeneous precipitation method using NH_4OH–NH_4Cl buffer solution

Refluxing temp. / °C	pH	Yield / %[a]			
		Ni_3S_4	NiS	NiS_2	$Ni(OH)_2$
70	10.0	89	7	4	0
70	9.9	100	0	0	0
70	9.7	74	0	26	0
70	9.5	76	0	24	0
70	9.3	66	20	14	0
60	9.9	100	0	0	0
50	9.9	78	10	0	12
40	9.9	0	0	72	28

[a] From the relative XRD intensity to the strongest peak.

loidal nickel hydroxide as well as the reaction activity to decompose TAA, so that the optimum pH seems to be 9.9. Further investigation of the reaction mechanism is underway. Figure 1 shows the XRD pattern of Ni_3S_4 powder produced by the pH-controlled homogeneous precipitation method. All of the reflections could be indexed to the cubic Ni_3S_4 with a cell constant a = 9.489 Å, which are consistent with the reported value (JCPDS, 8-106). No peaks of other phase and impurities were detected. The SEM image of Ni_3S_4 powder revealed that the particle size of Ni_3S_4 was ca. 50–100 nm.

$CoNi_2S_4$ and $NiCo_2S_4$ thiospinels could be also synthesized by the same method using their chloride salts of the total metal amount of 15 mmol with a desired proportion.

In summary, Ni_3S_4, $CoNi_2S_4$, and $NiCo_2S_4$ thiospinels were synthesized by a pH-controlled homogeneous precipitation method at 70 °C with metal chlorides and thioacetamide in the ammonium chloride–ammonia buffer solutions oft pH = 9.9.

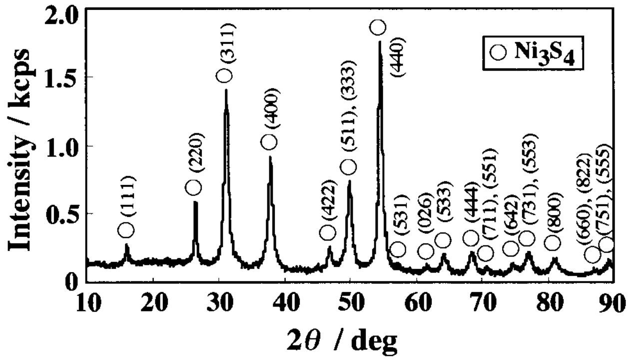

Figure 1. X-ray diffraction pattern of Ni_3S_4 powder synthesized by the pH-controlled homogeneous precipitation method.

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