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EFFECTS OF SYNTHESIS CONDITIONS ON STRUCTURE OF NICKEL NANOWIRES PREPARED BY REDUCTION METHOD

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Abstract. Nickel nanostructures prepared by various methods have received considerable attentions due to their numerous applications. In this study, one-dimensional nickel nanowires (NiNWs) were synthesized by the reduction of nickel (II) chloride in polyol medium. Polyvinylpyrrolidone (PVP) served as the surfactant and hydrazine hydrate was used as the reductant. The effects of different experimental parameters, i.e. concentration of Ni^{2+}, volume of N_2H_4, concentration of PVP and reaction temperature on the formation and morphology of NiNWs were studied. The structure, composition and surface morphology of the materials were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results showed that the morphology as well as the diameter of NiNWs could be effectively controlled by adjusting parameters of the synthesis process.

Keywords: nickel, one-dimensional, nanowire, morphology control, polyol method.

Classification numbers: 2.4.2, 2.10.2.

1. INTRODUCTION

Nanomaterials have, by definition, one or more dimension in the nanometer scale (≤100 nm) range and subsequently show novel properties from their bulk materials [1]. The synthesis, characterization, and applications of nanoparticles are among the most important sections of the wide range of nanotechnology areas falling under the general "nanotechnology" umbrella. In recent years, nanoparticles have been the center of attention of researchers in the field as the transition from microparticles to nanoparticles was seen to lead to immense changes in the physical and chemical properties of a material [2]. Nickel nanorods with a diameter of 8–10 nm and length of 100–200 nm had been successfully prepared by the reduction of nickel chloride ($NiCl_2$) with hydrazine hydrate in water/ butanol/potassium oleate/kerosene microemulsion [3]. Synthesis of nanowires in the aqueous phase is the preferred approach as it is non-flammable, cheap, environmental friendly, safe and feasible for large scale production [4]. Nickel nanowires

were also prepared by the template-free method which entailed chemical reduction in the presence of a magnetic field for directing the structure of nanowires [5]. In this research, nickel nanowires were prepared by a facile wet chemical reduction method using hydrazine hydrate as the reducing agent. The effects of reaction initial concentration of nickel ions, PVP and hydrazine monohydrate and temperature of reaction on the morphology of nickel nanowires formed were investigated.

2. MATERIALS AND METHODS

2.1. Materials and reagents

Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$, 99.0 %), Ethylene glycol (EG, 99.5 %), Hydrazine monohydrate ($N_2H_4.H_2O$, 80.0 %) were purchased from Sigma Aldrich. Polyvinylpyrrolidone (PVP, Mw = 40,000) was purchased from BDH Prolabo Chemicals.

2.2. Experimental set-up

Firstly, 20 mL of EG and a certain amount of PVP were added into a three necked flask equipped with a reflux condenser. After that, a various volume of 1.0 M $NiCl_2.6H_2O$ aqueous solution was added into to obtain desired Ni^{2+} concentration. The whole mixture was heated to 100 ^oC, and then $N_2H_4.H_2O$ was added in dropwise. The resulting solution turned black within a few seconds. The reaction was operated for 30 min, until the dark gray product appeared and floated at the solution surface. The obtained product was recovered by centrifugation several times (3000 rpm, 20 min) and stored in ethanol for further tests. The samples were dispersed in ethanol by ultrasonication and then dropped onto the copper grid, dried at room temperature. After that they were characterized by transmission electron microscopy (TEM, JEOL 2010, at an acceleration voltage of 100 kV). The product was dried at 60 ^oC for 24 hours in a vacuum oven. X-ray powder diffraction was carried out on D8 Bruker AXS X-ray diffractometer (CuKα radiation, 40 kV, 20 mA).

3. RESULTS AND DISCUSSION

3.1. Effect of Ni^{2+} concentration

Figure 1. Colour change of solution during 30 min of reaction. Ni^{2+}concentrations: (a) 5 mM (b) 20 mM.

In order to investigate the effect of initial nickel ions, a series of experiments was proceeded with various Ni^{2+} concentrations (5 to 30 mM). The other parameters of the synthesis solution were fixed at 0.5 mL of hydrazine and 1.5 w/v% of PVP concentration. The reaction

was carried out at 100 ^{o}C for 30 minutes. The detailed conditions and results of this series of experiments are summarized in Table 1. The mean diameters were calculated by using ImageJ software based on 25-30 items. The colour changes of all samples during 30 minutes of reaction is shown in Fig. 1. The colour of initial solution is depended on the amount of Ni^{2+} and varied from yellowish to bright green, considered the colour of compound $[Ni(EG)_a]^{2+}$ with various amount in solution. With the series of 5 mM to 15 mM, this reaction solution turned into black in about 6 seconds after hydrazine solution was added dropwise and then a black–grey product floating on a transparent solution surface appeared as in Fig. 1(a). However, as shown in Fig. 1(b), at the concentration higher than 15 mM, the resulting mixture changed turbid with bright blue colour as soon as hydrazine was added in. After that, the black-grey foam was formed and the solution in purple instead of transparent as lower concentrations. These phenomena can be explained that the higher concentration of nickel (II) ion were adjusted, the larger amount of hydrazine compounds $[Ni(N_2H_4)_m]Cl_2$ were generated, making the obtained solution in various colour if these complexes were not able to be reduced completely after 30 min of reaction. The blue one is identified as $[Ni(N_2H_4)_2]Cl_2$ while $[Ni(N_2H_4)_3]Cl_2$ is pink. Consequently, these two excessive complexes coloured the solution with purple [6]. The reactions occurred suggested in equations R1-R3.

$$Ni^{2+} + a\ EG \leftrightarrows [Ni(EG)_a]^{2+} \quad (R1)$$

$$[Ni(EG)_a]^{2+} + m N_2H_4 \leftrightarrows [Ni(N_2H_4)_m]^{2+} + a\ EG \quad (R2)$$

$$4[Ni(N_2H_4)_m]^{2+} + 4n N_2H_4 \rightarrow 4Ni + 4(m+n)\ NH_3 + 2(m+n)\ N_2 + (m+n)\ H_2 + 2(m+n)\ H^+ \quad (R3)$$

Table 1. Samples synthesized with different Ni^{2+} concentrations.

$[Ni^{2+}]$	Colour change	Results	
		Morphology	Diameter (nm)
5 mM	Very light yellow – Turbid, black – (Transparent + black gray solid)	Wires, smooth	123.22 ± 15.91
10 mM		Wires, smooth	133.63 ± 21.33
15 mM		Wires + particles, fairly uniform	149.03 ± 12.91
20 mM	Very light green – (Turbid, light blue + Black gray solid) – (Turbid, light purple + Black gray solid)	Wires + particles, rough	172.76 ± 37.07
25 mM		Wires + particles, rough	~ 300
30 mM		Wires + multiple particles, rough	~ 300

TEM images of samples prepared with different Ni^{2+} concentration are shown in Fig. 2. It is confirmed that concentration of Ni^{2+} has a strong influence on the products' surface morphology. The results showed that when increasing the amount of Ni^{2+}, the surfaces were more roughened as well as their average diameters summarized in Table 1 were larger. Besides, as shown in Fig. 3(a), the sample with 5 mM is the only one having no nickel particles in

obtained material while the others are the mixtures of wires and particles. Increasing concentration of Ni^{2+} caused local saturation, resulting in generating more Ni particles at the same time, making the particles tend to combine and growing in larger size [3, 7].

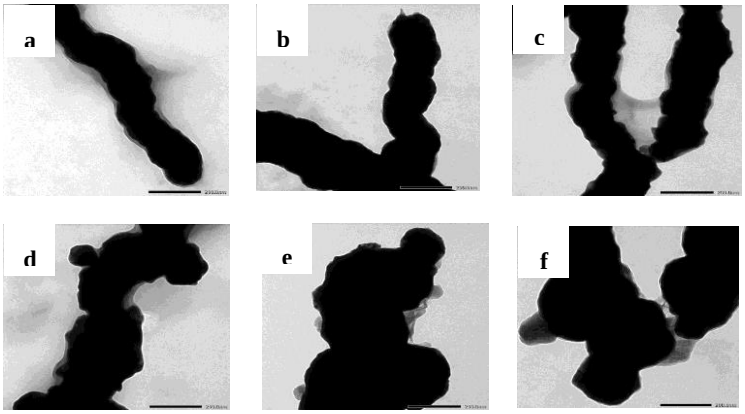

Figure 2. TEM images of samples prepared with different Ni^{2+} concentrations at 200 nm scale: (a) 5 mM; (b) 10 mM; (c) 15 mM; (d) 20 mM; (e) 25 mM; (f) 30 mM.

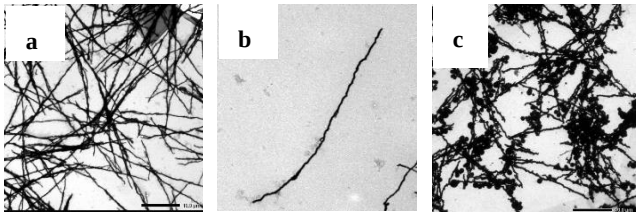

Figure 3. TEM images of samples prepared with different Ni^{2+} concentration at 10 µm scale: (a) and (b) 5 Mm, (c) 30 mM.

3.2. Effect of hydrazine volume

In the polyol process of synthesizing nickel nanowires, hydrazine is considered the most suitable reducing agent based on the standard E^0 values of Ni^{2+}/ Ni and N_2/N_2H_4 respectively of -0.257 V and -1.16 V. Furthermore, hydrazine also plays a vital role as bridging bidentate ligand which made the nanoparticles "bonded" together into nanowires [3].

The effect of this factor was investigated by conducting a set of experiments with volume of hydrazine from 0.50 mL to 0.90 mL at Ni^{2+} concentration of 5 mM. The TEM images of different synthetic samples are shown in Fig. 4 indicating that the higher the volume of hydrazine, the rougher the surface of the materials. This result is also similar to Krishnadas *et al.*'s report [8]. Besides, when the volume of hydrazine increases from 0.5 mL to 0.8 mL, the mean diameter of NiNWs increases from 123 ± 16 nm to 189 ± 59 nm. Meanwhile, the sample with the highest amount of hydrazine at 0.9 mL produced a large number of particles with size more than 200 nm. When more hydrazine is added, the balance of reaction R2 is shifted to the right, resulting in more $[Ni(N_2H_4)_2]Cl_2$, $[Ni(N_2H_4)_3]Cl_2$ and $[Ni(N_2H_4)_4]Cl_2$ are formed. As a consequence, more Ni (0) is formed (reaction R3). This makes the rate of Ni nanoparticle formation greater and these Ni nanoparticles will form nanowires with significantly larger diameters.

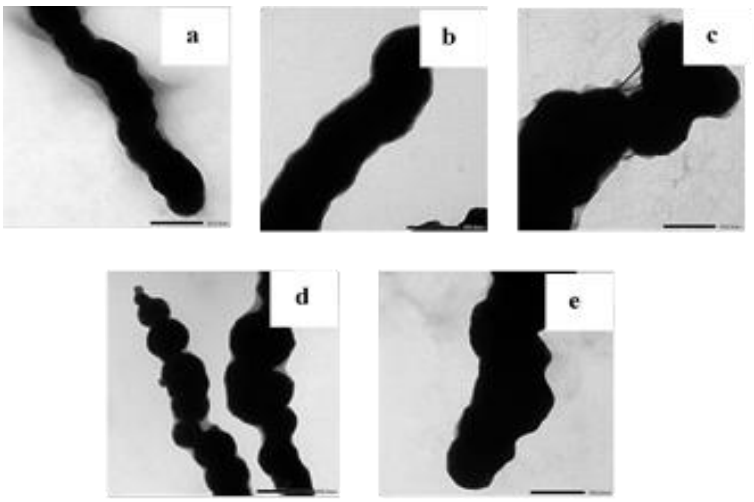

Figure 4. TEM images of samples prepared at different volumes of hydrazine, scale 200 nm: (a) 0.5 mL; (b) 0.6 mL; (c) 0.7 mL; (d) 0.8 mL; (e) 0.9 mL.

3.3. Effect of PVP concentration

PVP acts as a surfactant and reduces surface energy and thus prevents the aggregation of Ni atoms [9]. In this study, samples were synthesized with varying PVP concentrations from 0.5 to 2.5 w/v% and without PVP samples for comparison. Figure 5(b) and (c) show TEM images of obtained products in the operating reaction with 1.0 w/v% PVP and 1.5 w/v% PVP yielding a smooth surface, while with lower PVP concentration at 0.5 w/v% resulted in numerous nanopricks (Fig. 5a). In addition, with 2.0 and 2.5 w/v%, TEM images in Fig. 5(d) and (e) show that the "bonding" between the Ni particles through the N_2H_4 as the bridge to form the Ni wire was disadvantage, the wire clearly showing relatively discrete particles. Without PVP will lead NiNWs in inhomogeneous surface with different diameters. Moreover, the changing of average diameter of Ni nanowires when increase of PVP% in EG, Fig. 6 shows a gradual decrease in trend.

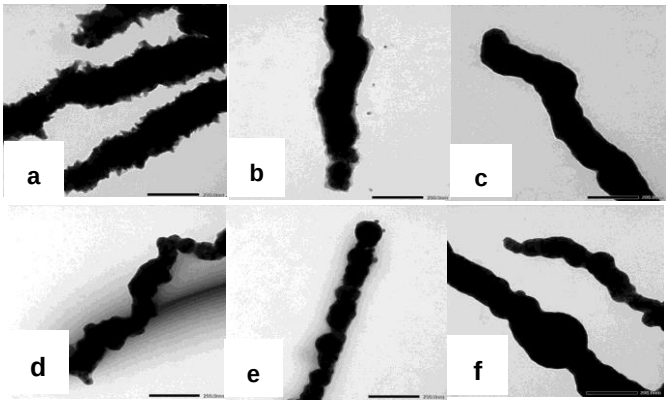

Figure 5. TEM images of %PVP set of experiments: at scale 200 nm: (a) 0.5 %; (b) 1.0 %; (c) 1.5 %; (d) 2.0 %; (e) 2.5 %; (f) without PVP.

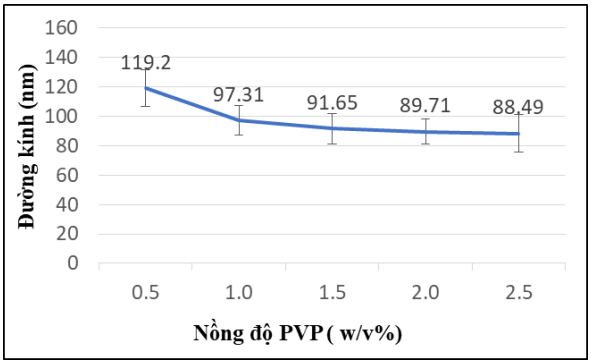

Figure 6. The influence of %PVP on mean diameter.

3.4. Effect of reaction temperature

The reaction temperature is always one of the most important parameters being studied in detail as it plays an important role in the formation and morphology of the obtained products. To investigate the effect of this parameter, the samples were synthesized at 50 ^{o}C, 60 ^{o}C, 80 ^{o}C, 100 ^{o}C, 120 ^{o}C and 140 ^{o}C for 30 minutes while the others were fixed at 0.5 mM of Ni^{2+} concentration, 0.6 mL of hydrazine and 1.5 w / v% of PVP.

The moment the solution turned dark which indicated the presence of nickel metal changed due to temperature and shown in Table 2. As shown in Table 2, increasing temperature of the reaction resulted in rapidly generating the dark product, proving that the reaction temperature has a strong influence on the rate of reduction of Ni^{2+} to Ni.

Table 2. Summary of samples prepared at different temperatures.

Reaction temperature	Time for solution to turn black	Yield of product for 30 minutes of reaction
50 ^{o}C	45 min	No product
60 ^{o}C	20 min	Very low
80 ^{o}C	15 min	Low
100 ^{o}C	10 s	High
120 ^{o}C	8 s	High
140 ^{o}C	5 s	High

Surface analysis of the materials through the TEM images at 200 nm scale in Fig. 7(c) and (d) show that the samples prepared at 100 ^{o}C and 120 ^{o}C are more uniformly homogeneous than the others. Conducting the reaction at 80 ^{o}C for 30 min resulted in many small pricks on the surface. When lasting the reaction until 60 min, TEM image in Fig. 7b indicates that the pricks tended to grow longer, and could be developed into branching of NiNWs. Meanwhile, at a high temperature of 140 ^{o}C, the obtained material tended to form particles due to the increase in the rate of reaction $[Ni(N_2H_4)_m]^{2+}$ to Ni.

The effect of reaction temperature on the mean diameter of nanowires was also investigated in detail by calculating the average size and shown in Fig. 8. It is observed that with the increase of the reaction temperature from 80 ^{o}C to 140 ^{o}C, the diameter of the NiNWs decreases from 115 nm to 83 nm.

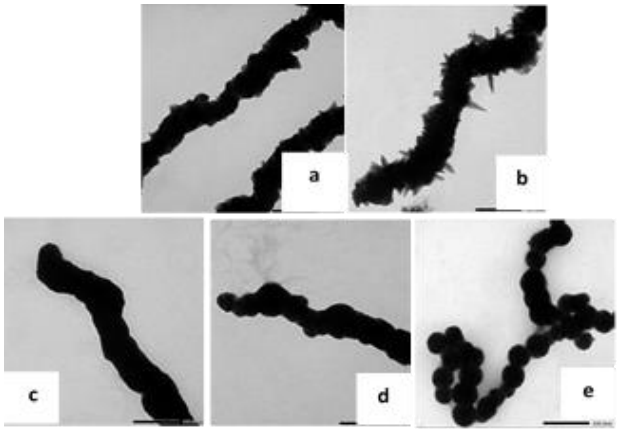

Figure 7. TEM images of samples prepared at different temperatures: (a) 80 ^{o}C; (b) 80 ^{o}C, 60 min; (c) 100 ^{o}C; (e) 120 ^{o}C; (f) 140 ^{o}C.

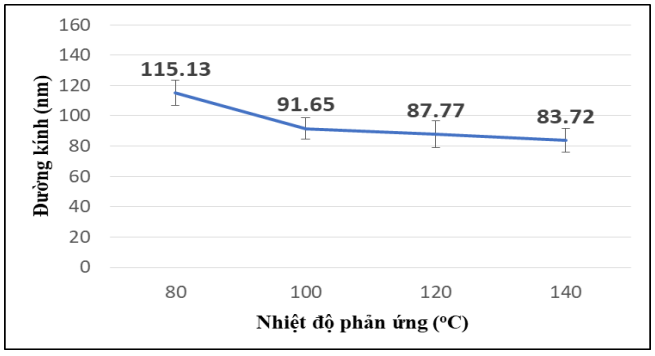

Figure 8. The influence of temperature on mean diameter.

3.5. XRD pattern of the nickel nanowires

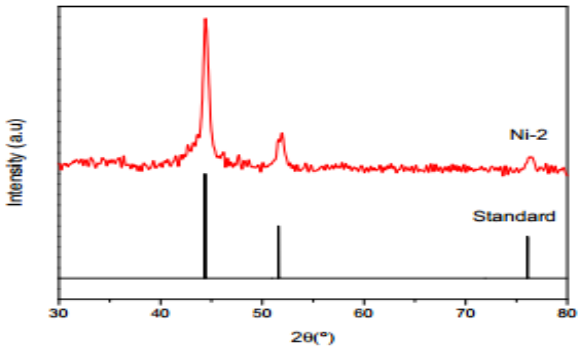

Figure 9. XRD pattern of NiNWs.

The XRD pattern of the NiNWs prepared at 5 mM is in Fig. 9 shows that the sample has the FCC structure of nickel [7]. The diffraction peak positions are well in coherence with a standard spectrum of nickel metal (JCPDS file No. 04-0850) at 2θ of 44.5^o; 51.8^o and 76.4^o respectively for (111); (200) and (220) crystal planes. There is also no any impurities such as oxide or hydroxide of Ni^{2+} observed in the product [5].

4. CONCLUSIONS

The high pure nickel nanowires were successfully synthesized via a simple and environment-friendly process. In this polyol approach of preparation NiNWs, it is observed that synthesis parameters such as nickel ion concentration, PVP concentration, volume of hydrazine and reaction temperature have strong effects on the diameter as well as morphology of nickel materials. The optimal NiNWs prepared at 5 mM of Ni^{2+}, 0.6 mL of hydrazine with 1.5 % w/v PVP at 100 ^{o}C for 30 min have smooth surface with mean diameter of about 92 nm.

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