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2004 J. Phys.: Condens. Matter 16 S1305

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Microwave–polyol process for metal nanophases

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Received 22 January 2004

Published 26 March 2004

Online at stacks.iop.org/JPhysCM/16/S1305

DOI: 10.1088/0953-8984/16/14/043

Abstract

The microwave-assisted polyol process was investigated for the synthesis of several nanophase metals under different conditions in the temperature range of 100 to 200 °C. Nanophase Ag metal particle synthesis using ethylene glycol (EG) was carried out at 100 and 150 °C in the presence of polyvinyl pyrrolidone (PVP), dodecyl amine (DDA), oleic acid (OA) or trioctylphosphine (TOP) to determine whether particle size and shape can be controlled. The Ag particle size was changed with different capping agents. The use of PVP led to well defined Ag nanoparticles in the range of about 30–50 nm. Morphologically well defined nanophase metals of Fe, Co and Ni were produced in the presence of both PVP and DDA, while the use of just PVP or PVP and TOP did not yield such particles. The results presented here show that a variety of well defined nanophase metals can be produced by using the microwave–polyol process and optimizing the metal capping agents.

1. Introduction

Nanophase metals have many applications in such diverse fields as catalysis, diagnosis and drug delivery, electronic materials, etc. There are numerous methods of metal preparation in the solid, liquid or vapour state. Among these, the liquid-based metal synthesis methods generally use low temperatures. Liquid-based methods involve the reduction of metal salts in some type of solvent which by itself can act as a reducing agent or a separate reducing agent can be used. Ethylene glycol, methanol, ethanol, etc, have been previously shown to be good reducing agents for several metals [1–6]. There have been several recent reports including our own, which showed that the use of microwaves with these reducing agents will increase the kinetics of metal formation [7–12]. The use of microwaves with a polyol reduction process was called the microwave–polyol (MP) process [10]. Controlling the size and shape of metal

Table 1. Syntheses of nanophase Ag metal at 150 °C under different conditions.

AgNO ₃ (g)	Ethylene glycol (ml)	PVP (g)	150 °C/15 min sample no.	TEM analysis
0.015	150	0.495	81 204	10–50 nm
0.015	50	0.495	81 205	10–80 nm; some faceted
0.015	67	0.495	81 208	20–80 nm; some faceted
0.03	50	1.0	81 218	10–60 nm

Table 2. Syntheses of Ag metal particles at 100 and 150 °C under different conditions.

AgNO ₃ (g)	EG (ml)	Oleic acid (g)	TOP (g)	DDA (g)	PVP (g)	150 °C/15 min sample no.	TEM analysis size (nm)	100 °C/15 min sample no.	TEM analysis size (nm)
0.0052	35			0.185		120 207	40–400 irregular	120 307	4–75 spheres
0.0052	35			0.093	0.05	120 212	10–80	120 312	10–80
0.0052	35	0.141		0.093		120 218	10–60	120 318	200; few
0.0052	35		0.193	0.093		120 219	10–100		

nanophases is an important aspect in applications and therefore the objective of this study was to see whether we can control the size and shape of different metals by using different capping agents with the microwave–polyol process.

2. Experimental details

The microwave-assisted polyol syntheses were conducted using AgNO₃ metal precursor for Ag metal, iron acetylacetonate, Fe(CH₃COCHCOCH₃)₂, for Fe metal, cobalt acetylacetonate, Co(CH₃COCHCOCH₃)₂, and cobalt acetate, Co(CH₃COO)₂, for Co metal and Ni acetate, Ni(CH₃COO)₂, for Ni metal. The various amounts of chemicals, volume of ethylene glycol and the time and temperature for treatments are given in tables 1–5. The metal precursors were mixed with ethylene glycol and the capping agents, PVP, DDA, TOP and oleic acid, in Teflon vessels and treated at 100–200 °C for 15 min in a microwave digestion system, MARS-5 (CEM Corporation). This system is normally used for the rapid dissolution of samples for chemical analysis but we have turned this into a microwave-hydrothermal synthesis apparatus [13–18]. This system operates at 2.45 GHz frequency. An on-board computer can control the power from 0 to 100% of full power (1200 ± 50 W), the temperature (a maximum of 240 °C) and the pressure (a maximum of 800 psi). The synthesis reactions were carried out in Teflon vessels which are surrounded by a high strength shell of polyetherimide. After the reactions were completed, all the samples were examined for particle size and shape by transmission electron microscopy (TEM) using a JEOL Model 2010 microscope (Tokyo, Japan). Prior to TEM observation, the reacted liquids were first diluted with water, ultrasonified for 20 min and a small drop of the liquid was placed and dried on a copper grid. Electron diffraction was done on some particles to identify their metallic nature.

3. Results and discussion

Table 1 gives the different experimental conditions for the synthesis of nanophase Ag metal. Silver nanoparticles of 10–80 nm are formed in all cases (figure 1). At both low and high concentrations of AgNO₃ (table 1), spherical but not very well defined metal nanoparticles resulted (figures 1(a) and (d)), but with 0.015 g of AgNO₃ in either 50 or 67 ml of ethylene glycol the particles appear to be more well defined (figures 1(b) and (c)). The particles exhibited very

Table 3. Syntheses of Fe, Co and Ni metal particles under different MP conditions.

Metal compound	Metal organic (g)	Ethylene glycol (ml)	PVP (g)	TOP (g)	200 °C/15 min sample no.	TEM analysis size (nm)
Fe acetylacetonate	0.010 16	20	0.06	0.212	120 604	Strings
Co acetylacetonate	0.020 5	20	0.12	0.421	120 605	10–120
Ni acetate	0.02	20	0.12	0.421	120 607	10–50
Co acetate	0.02	20	0.12	0.421	120 608	10–80
Fe acetylacetonate	0.010 16	20	0.06		120 612	Laths and particles

Table 4. Syntheses of Fe, Co and Ni metal particles using different chemicals.

Metal compound	Metal organic (g)	Ethylene glycol (ml)	PVP (g)	DDA (g)	200 °C/15 min sample no.	TEM analysis size (nm)
Fe acetylacetonate	0.010 16	20	0.06	0.102	120 609	20–25
Co acetylacetonate	0.020 5	20	0.12	0.202	120 616	15–30
Ni acetate	0.02	20	0.12	0.202	120 618	20–50
Co acetate	0.02	20	0.12	0.202	120 619	Plates and fibres

Table 5. Syntheses of Fe, Co and Ni metal particles using EG and PVP at 200 °C/15 min.

Metal compound	Metal organic (g)	Ethylene glycol (ml)	PVP (g)	200 °C/15 min sample no.	TEM analysis size (nm)
Fe acetylacetonate	0.010 16	20	0.12	101 504	Poorly defined
Co acetylacetonate	0.020 5	20	0.12	101 515	Few 300–600
Ni acetate	0.02	20	0.12	101 509	None detected
Co acetate	0.02	20	0.12	101 507	Few 150–200

different shapes but some nanoparticles are faceted. The reduction mechanism using ethylene glycol is well understood [1] and the role of PVP in preventing the growth of metal particles is also well known [6]. However, the control of morphology is not well understood. The results presented above show that there is little or no dependence of morphology on the concentration of AgNO₃ in ethylene glycol, albeit only a narrow concentration range was used here.

Table 2 shows the results of Ag metal formation in DDA with and without PVP, TOP or oleic acid. In the presence of DDA, large irregular particles were formed at 150 °C (figure 2(a)) while more or less rounded particles with a large size distribution were formed at 100 °C (figure 2(b)). A higher magnification of the particles at 100 °C (figure not shown) clearly shows that many 4–5 nm particles exist along with larger particles of 20–75 nm. At this low temperature of 100 °C, the growth of the particles was not complete in 15 min and hence a wide particle size distribution resulted. When PVP was present along with DDA, similar types of Ag nanophases were obtained at both temperatures (figure 3). When either oleic acid or TOP is present along with DDA, the nanoparticles obtained are rounded but not faceted (figure not shown) similar to those that can be seen in figure 1. Thus, among the various capping agents investigated, PVP appears to be the best for obtaining well defined and/or faceted Ag nanocrystals.

Table 3 shows the syntheses of Fe, Co and Ni metals by using acetylacetonate and acetate as metal precursors. Iron metal strings (figure 4(a)) were formed from Fe acetylacetonate in the presence of both PVP and TOP while in the presence of only PVP, discrete iron nanoparticles were formed along with thin laths of metal (figure 4(b)). Cobalt metal nanophases of non-uniform size were formed from Co acetylacetonate while somewhat uniform Co nanophases

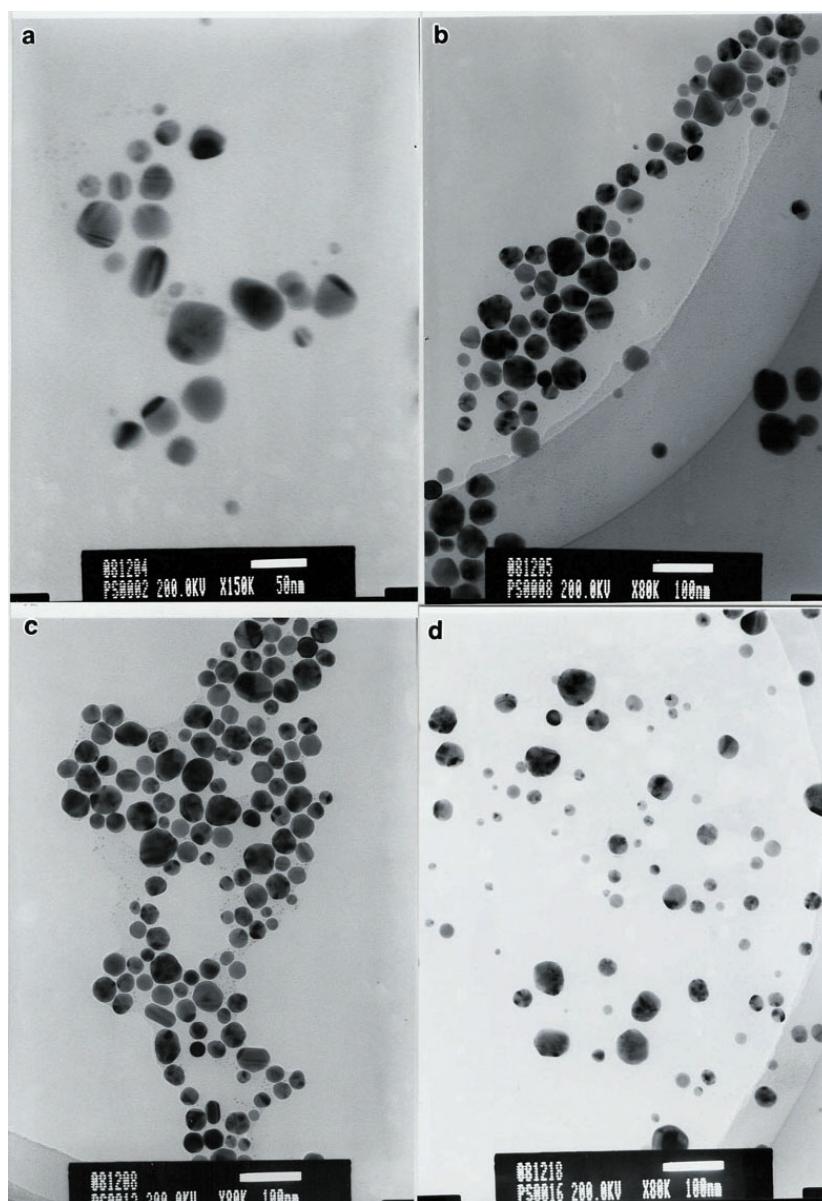


Figure 1. TEM pictures of Ag nanoparticles under different conditions at 150 °C/15 min: (a) 81 204, (b) 81 205, (c) 81 208 and (d) 81 218 (see table 1 for conditions).

(figures not shown) were formed from Co acetate in the presence of both PVP and TOP. Nickel metal nanophases (figure 5) were obtained from Ni acetate at 200 °C in the presence of both PVP and TOP.

Cobalt metal nanophases of uniform size (figure 6(a)) were formed from Co acetylacetonate while needle-like and very thin plates of Co nanophases (figure 6(b)) were formed with a Co acetate precursor in the presence of both PVP and DDA. Acicular Co nanophases were previously reported using a complicated procedure [19]. Thus it appears that the type of precursor is also controlling the particle morphology. More or less uniform

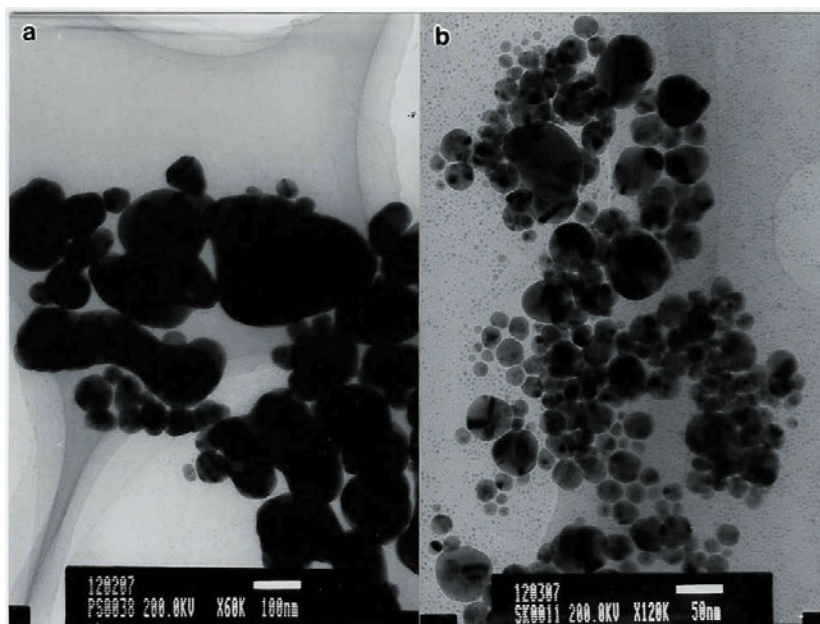


Figure 2. TEM pictures of Ag metal particles prepared by using EG and DDA: (a) 150 °C/15 min and (b) 100 °C/15 min.

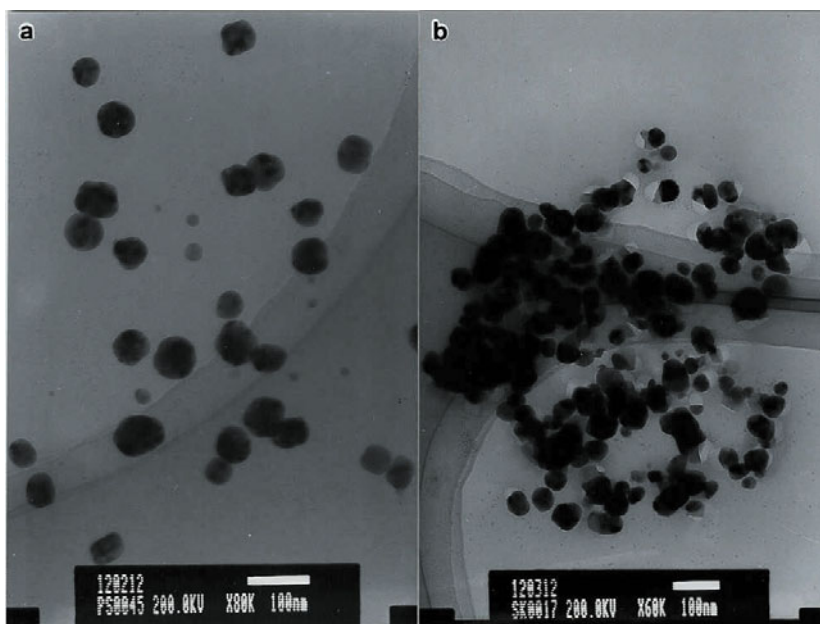


Figure 3. TEM pictures of Ag metal nanoparticles prepared by using EG, DDA and PVP: (a) 150 °C/15 min and (b) 100 °C/15 min.

nanophase metals of Fe and Ni (figure 7) were produced from acetylacetonate and acetate metal precursors, respectively, in the presence of both PVP and DDA. The nanophase Fe, Co

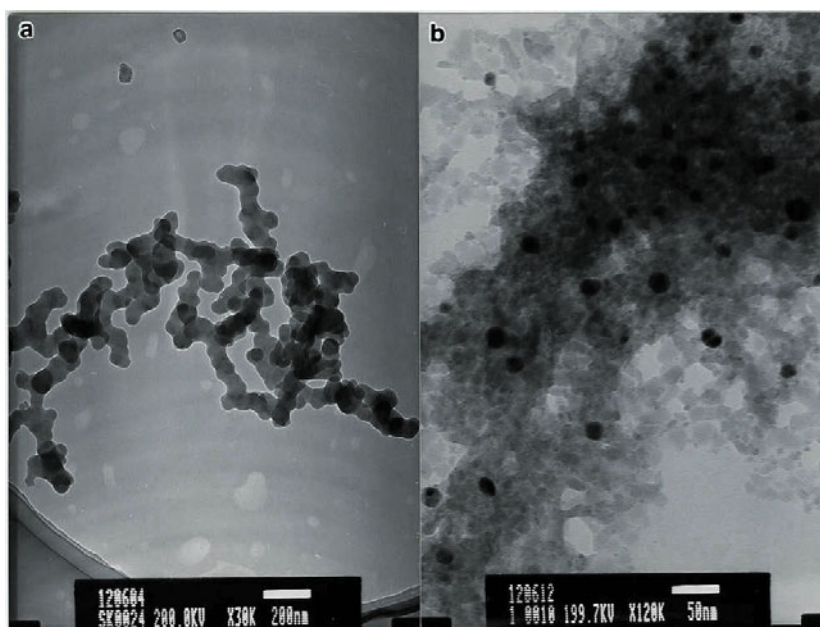


Figure 4. TEM pictures of Fe metal particles prepared by using Fe acetylacetonate, EG and PVP at 200 °C/15 min: (a) with TOP and (b) without TOP.

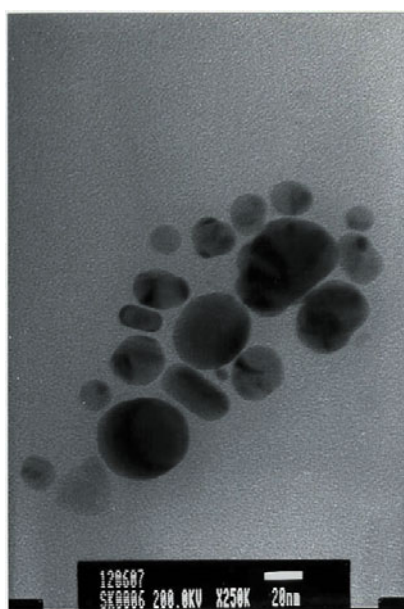


Figure 5. TEM pictures of Ni metal nanoparticles prepared by using Ni acetate in EG, PVP and TOP at 200 °C/15 min under MP conditions.

and Ni metals obtained with both PVP and DDA are well formed (figures 6 and 7) relative to the nanophases obtained using both PVP and TOP (figures 4–5) or PVP alone (figure not shown).

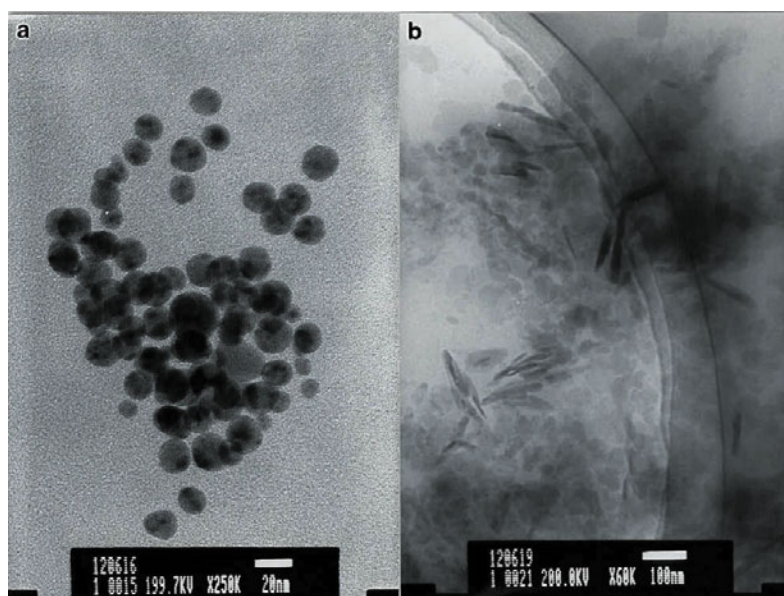


Figure 6. TEM pictures of Co metal nanoparticles prepared by using Co acetylacetonate (a) and Co acetate (b) in EG, PVP and DDA at 200 °C/15 min under MP conditions.

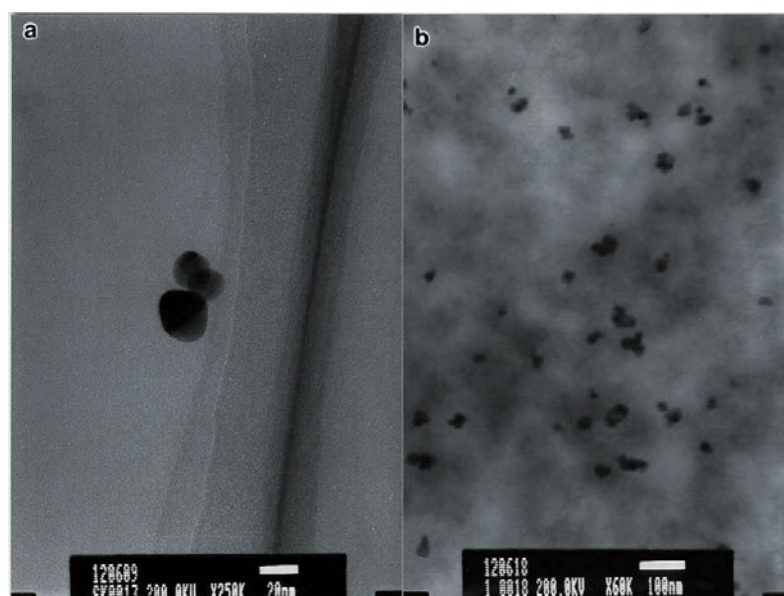


Figure 7. TEM pictures of Fe (a) and Ni (b) metal nanoparticles prepared by using Fe acetylacetonate and Ni acetate, respectively, in the presence of EG, PVP and DDA at 200 °C/15 min under MP conditions.

4. Conclusions

A variety of metal nanophases can be produced very rapidly using the novel MP process. Control of size and, in some cases, shape is possible by using different capping agents and different starting chemicals.

Acknowledgment

This research was financially supported by the Metals Program, Division of Materials Research, National Science Foundation under grant no DMR-0096527.

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