Synthesis and Characterization of Cobalt Nano-Particles Through Microwave Polyol Process

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This article aims to synthesize and character cobalt nano-particles through microwave polyol process. At first, cobalt acetate is used as precursor to synthesize cobalt nano-particles by microwave assisted ethylene glycol in the presence of polyvinylpyrrolidone (PVP) as capping agent. As measured from ion-coupled plasma (ICP) and thermo-gravimetric analysis (TGA), the yields of as-synthesized cobalt particles in average diameters of 40 and 81 nm verified by transmission electronic microscopy (TEM), are 71 and 85%, respectively; and the structure of as-synthesized cobalt nano-particle is a face-center cubic structure analyzed by X-ray diffraction (XRD). Finally, the as-synthesized cobalt nano-particle modified by oleic acid is dispersed in kerosene to character magnetic property. As measured by vibration sample magnetometer (VSM), the saturation magnetisms of cobalt nano-particles with average diameters of 40 and 81 nm are 39.1 and 29.5 emu/g, respectively, in solution. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1383–1389, 2009

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Introduction

The research on the physical properties of magnetic nanocrystals is an important topic for nano-technology applications.[1] Magnetic nano-particles exhibit the different properties from the bulk materials due to the finite number of atoms and large percentage being located at the surface.[2] Some examples ascribed to the fine size of magnetic particles were giant magneto resistance, quantum tunneling of the magnetization, and superparamagnetism.[3–6]

Nanometer scale of magnetic particle has been prepared by various techniques including chemical precipitation from aqueous or organic solutions.[7,8] Particularly, an innovation was developed to fabricate metal particles using ethylene glycol,[9] which was called the polyol process. The polyol method was characterized by a low-temperature operation and environmentally because the reactions are carried out in the closed system. Furthermore, it was reported that microwave in combination with the polyol process, namely, the microwave-polyol (M-P) process, can be used to rapidly produce nanometer size of metal particles.[10] Microwave has the electromagnetic spectrum with frequencies ranging from 300 MHz to 300 GHz in wavelengths ranging from 1 m to 1 mm. The interaction of microwaves and fluid medium is dependent on dielectric constant and dielectric loss of fluid. When microwaves penetrate and propagate through a dielectric solution or suspension, the internal electric fields will induce translating motions of electrons or ions leading to dipoles. The resistance of motions resulting from inertial, elastic, and frictional forces induces losses and attenuates of the electric field producing volumetric heating.[11] With high dielectric constant and dielectric loss, ethylene glycol can be rapidly heated by microwave. In addition to the dipoles, the ionization of solution is also easily heated by microwave. In short, the advantages of the microwave-assisted chemical

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Table 1. Synthesis of Co Particles at 175 ± 10°C Under the Different Molar Ratios of Cobalt Acetate to PVP ($Co(Ac)_2$/PVP) and Conditions of Microwave

Samples	$[Co(Ac)_2]$ (M)	$[PdCl_2]$ (M)	$Co(Ac)_2$/ PVP (mol/mol)	Final Step of Heating Power (W)/Time (sec)*	Mean Particle Size (nm)†	Yield (%)‡
T61	0.1	0.00033	1/6	440/300	117	68.13
T62	0.1	0.00033	1/6	440/600	200	69.81
T63	0.1	0.00033	1/6	440/900	237	74.03
T91	0.1	0.00033	1/9	440/600	49	70.99
T92	0.1	0.00033	1/9	440/900	117	73.35
T93	0.1	0.00033	1/9	440/1200	172	82.63

*After heating at 800 W for 240 sec.

†Measured from dynamic laser light scattering particle analyzer.

‡Calculated by equation of (1 − concentration of Co^{2+} after reduction/concentration of Co^{2+} before reduction) × 100, where concentrations of Co^{2+} after and before reduction are measured by ion coupled plasma spectra.

reactions compared with conventional heating methods are summarized as follows: (a) saving energy due to fast heating, (b) increasing the rate of chemical reaction owing to more heat,[12] and (c) controlling selectivity of chemical reaction easily.[13]

Magnetic materials have many applications, such as, the magnetic field sensor, bio-sensors,[14] magnetic-storage media,[15] power generation, magnetic resonance imaging, tracers to radioactive materials, and so on. In where, magnetic fluid is made from single-domain magnetic particles dispersing in a carrier liquid. For the stabilization of magnetic fluid, an organic layer of dispersant is necessity to form a bridge between the carrier liquid and the magnetic particles.[16,17] The viscosity of magnetic fluid can be varied with applying magnetic field to retain the flow ability of liquid for the applications of sealing, louder speaker, inertia dampers, angular position sensors, inkjet printing, and the light switch.[18–20]

For magnetic particles per unit volume, the saturation magnetism is increased with reducing the diameter of magnetic particle. Wagener et al.[21] prepared magnetic material made from cobalt nano-particles by thermal decomposition to obtain 120 mT of saturation magnetism, but the employed metallic precursor is toxic and the as-synthesized magnetic nano-particle is easily oxidative. Accordingly, this paper attempts to rapidly synthesize cobalt nano-particles using microwave assisted ethylene glycol from cobalt acetate in the presence of polyvinylpyrrolidone as capping agent. Additionally, the vibration sample magnetometer (VSM) will be employed to character the magnetism of as-synthesized Co nano-particle dispersed in solution.

Experiment

Materials

Cobalt acetate (Co $(CH_3COO)_2 \cdot 4H_2O$), oleic acid, and sodium hydroxide were manufactured by SHOWA Co., Japan. Palladium chloride ($PdCl_2$) and polyacrylic acid (PAA, molecular weight = 100,000) were manufactured by Sigma-Aldrich Co., Taiwan. Polyvinylpyrrolidone (PVP, an average molecular weight of 10,000) was purchased from Sigma-Aldrich Co., Taiwan. Ethylene glycol and ethyl alcohol are both the products of Tedia Company Inc., U.S. Kerosene was supplied by Chinese Petroleum Corporation, Taiwan. All the materials were used as received without further treatment.

Preparation and characterization

The microwave assisted polyol syntheses is conducted to reduce cobalt acetate in the presence of PVP. A microwave oven (2.45 MHz, TAYUNG TMO-2050, Taiwan) was modified as follow: the water-cooled condenser is connected to a round flask in the microwave oven through a glass tube and a stirrer is equipped in the flask.

In synthesizing cobalt nano-particles, the cobalt acetate is mixed with ethylene glycol, polyvinylpyrrolidone and palladium chloride; and then heated at 175 ± 10°C with vigorous agitation in the glass round flask through a microwave. The adding amounts of chemicals and the time of reaction are listed in Tables 1–3. In where, Table 1 shows the different ratios of cobalt acetate to PVP as well as heating time of microwave for synthesis of Co particles at 175 ± 10°C. In

Table 2. Synthesis of Co Particles at 175 ± 10°C in Different Molar Ratios of Cobalt Acetate to Palladium Chloride ($Co(Ac)_2/PdCl_2$)

Sample	$[Co(Ac)_2]$ (M)	$Co(Ac)_2/PdCl_2$ (mol/mol)	$Co(Ac)_2$/ PVP (mol/mol)	Final Step of Heating Power (W)/Time (sec)*	Mean Particle Size (nm)†	Yield (%)‡
S1	0.1	375/1	1/12	440/900	52	63.58
S2	0.1	300/1	1/12	440/900	77	69.65
S3	0.1	225/1	1/12	440/900	122	70.66
S4	0.1	200/1	1/12	440/900	127	70.83

*After first step of heating at 800 W for 240 sec.

†Measured from dynamic laser light scattering particle analyzer.

‡Calculated by (1 − concentration of Co^{2+} after reduction/concentration of Co^{2+} before reduction) × 100, in which concentrations of Co^{2+} after and before reduction are measured from ion coupled plasma spectra.

Table 3. Synthesis of Co Metal Particles at 175 ± 10°C Under Different Concentrations of Cobalt Acetate

Sample	[Co(Ac)$_2$] (M)	Co(Ac)$_2$/PdCl$_2$ (mol/mol)	Co (Ac)$_2$/PVP (mol/mol)	Final Step of Heating Power (W)/Time (sec)*	Mean Particle Size (nm)[†]	Yield (%)[‡]
P1	0.075	300/1	1/12	440/900	71	73.77
P2	0.075	300/1	1/12	440/1200	83	84.65
P3	0.1	300/1	1/12	440/900	77	70.66
P4	0.1	300/1	1/12	440/1200	123	78.08
P5	0.125	300/1	1/12	440/900	115	70.07
P6	0.125	300:1	1/12	440/1200	163	76.34
P7	0.15	300:1	1/12	440/900	213	70.07
P8	0.15	300:1	1/12	440/1200	290	76.32

*After first step of heating at 800W for 240 sec.

[†] Measured from dynamic laser light scattering particle analyzer.

[‡] Calculated by (1 − concentration of Co^{2+} after reduction/concentration of Co^{2+} before reduction) $\times$ 100, in which concentrations of Co^{2+} after and before reduction are measured from ion coupled plasma spectra.

the initial stage, the microwave power at 800 W is applied for 240 sec to raise the temperature of solution at 180°C and then keep this condition until that a change in color from reddish to black is observed indicating the reduction of the cobalt salt into cobalt particles.

All the samples are examined by dynamic laser scattering particle analyzer (Brookhaven 90 Plus Particle Sizer, Germany) for the particle size and by transmission electron microscopy (TEM, JEOL-JEM 200CX, Japan) for the shape of particle. In where, in prior to TEM observation, the as-synthesized Co particles in solution are diluted with ethanol and dispersed by ultrasonic wave for 1200 sec followed by a small drop of the liquid placed and dried on a amorphous carbon-coated copper grid. In addition, taking 0.5 ml for dynamic laser scattering particle analysis and 3 ml for UV–visible analysis (Hitachi U-2000, Japan), respectively, from samples.

In this study, ion coupled plasma (ICP, LEEMAN DRE) and thermo-gravimetric analysis (TGA, Perkin Elemer Pyris 1) are employed to analyze the yield of as-synthesized cobalt particles from the reduction of cobalt acetate. The dispersion solution of as-synthesized cobalt particles is diluted with 100 times of de-ionic water for ICP analysis. After removing ethylene glycol through centrifuge (Boeco M-24, Germany) and vacuum drying at 200°C, the samples are analyzed by TGA from 200 to 900°C under nitrogen.

To characterize the structure of the synthesized cobalt particles, X-ray diffraction (XRD, Brucker AXS SMART-1000, Cu Kα radiation, $\lambda = 0.51418$ mm) is applied in this work. The samples are obtained by washing with ethanol and separating with centrifuge followed by vacuum drying at 600°C for 5400 sec.

Finally, the as-synthesized Co particles modified with oleic acid are dispersed in kerosene and vibrated with ultrasonic wave for measuring magnetization by vibrating sample magnetometer (VSM, ADE model 1660, American) with the external magnetic strengths ranging from $-13,500$ to 13,500 Oe at room temperature.

Results and Discussion

Syntheses of cobalt nano-particles

UV–visible spectrometry has been reported as an effective method to monitor the evolution of metal species in the synthesis of colloidal metal clusters because it could quantitatively measure the concentration of species in the solution based on their absorption spectrum.[22] As seen in Figure 1, the absorption peak at 520 nm disappears as the solution is heated by microwave at 440 W for 900 sec, which reveals that the cobalt acetate is entirely reduced into Co particle. The absorbance of UV–visible spectrum may be used to indicate that cobalt atoms are accumulated to form cobalt particles with increasing microwave heating time. The growth of cobalt particles is also found by the observations from ICP spectroscopy, which the yield of as-synthesized cobalt particles can be calculated by the equation of (1 − concentration of Co^{2+} after reduction/concentration of Co^{2+} before reduction) $\times$ 100, where concentrations of Co^{2+} after and before reduction are obtained by ion coupled plasma spectra

As shown in Table 1, as the molar ratio of cobalt acetate to PVP is 1/6, the yield and mean size of as-synthesized cobalt particles are increased with the heating time of

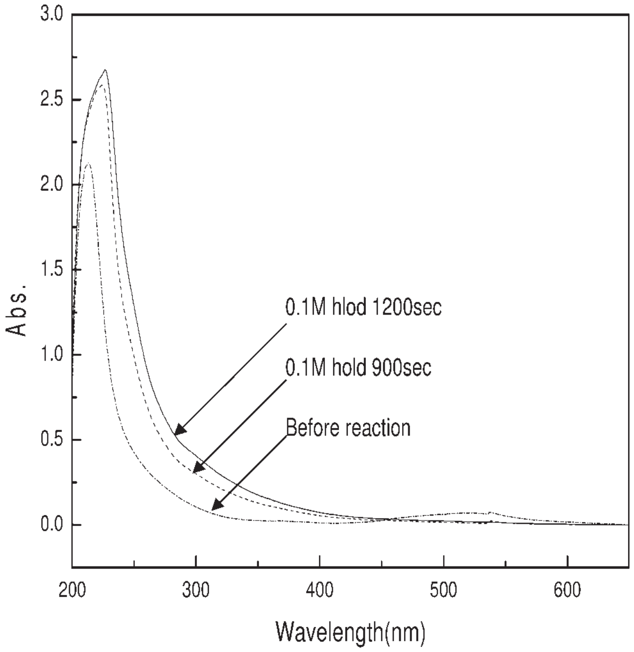


Figure 1. UV–visible spectrums of 0.1 M cobalt acetate in ethylene glycol before and after reaction under microwave at 440 W for 900 and 1200 sec, respectively.

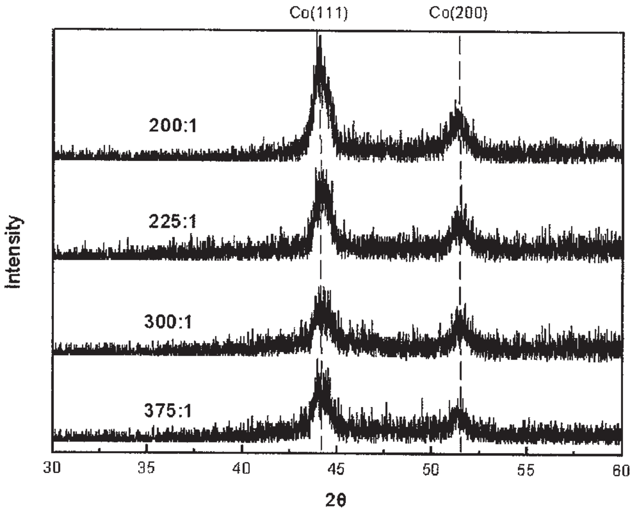


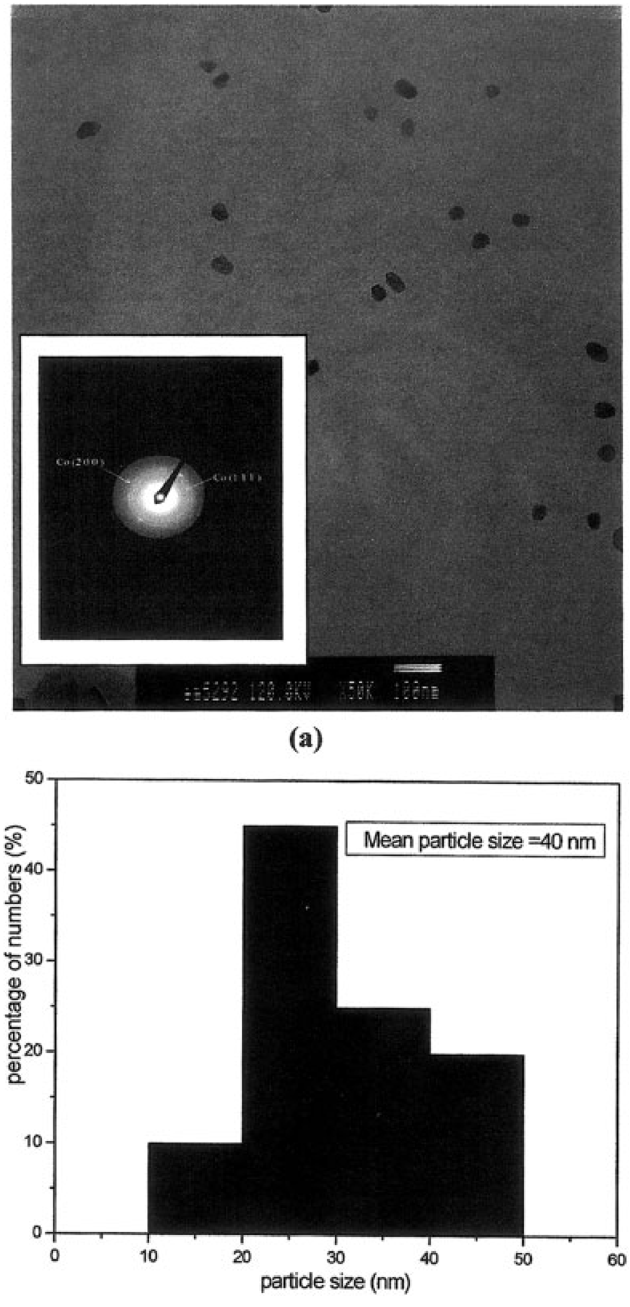
Figure 2. X-ray diffraction of as-synthesized cobalt particles with the molar ratios of cobalt acetate to palladium chloride: (a) 200:1, (b) 225:1, (c) 300:1, and (d) 375:1, where 2θ at 44.2° and 51.5° are, respectively, corresponding to Co (1 1 1) and Co (2 0 0) according to JCPDS card.

microwave at 440 W, while the average size of as-synthesized cobalt particles is reduced with decreasing the molar ratio of cobalt acetate to PVP ranging from 1/6 to 1/9 as the heating time of microwave is fixed. This result suggests that the amount of PVP dominates the yield and size of as-synthesized cobalt particle by means of microwave-assisted polyethylene glycol.

The use of the palladium salt forms the seeds of a heterogeneous nucleation to reduce cobalt salt into Co particles in the reaction system. Table 2 lists the different molar ratios of cobalt acetate to palladium chloride synthesizing cobalt particles at 175 ± 10°C. As shown in the table, the yield and the mean size of as-synthesized cobalt particles decreased and increased with increasing and decreasing the molar ratio of cobalt acetate to palladium chloride, respectively, ranging from 375/1 to 200/1. This is because as the concentration of palladium increases, nucleus sits per unit volume are increased leading to produce many fine cobalt particles and induce aggregation due to lack of capping agent, forming the larger cobalt particles in a heterogeneous nucleation process. For molar ratios of $Co(Ac)_2$ /$PdCl_2$ ranging from 375/1 to 200/1, as displayed in Figure 2, the X-ray diffraction patterns verify that the as-synthesized cobalt particles are the single phase of face centered cubic structure according to JCPDS card.

Table 3 shows the different concentrations of cobalt acetate to synthesize Co particles at 175 ± 10°C. Increasing concentrations of cobalt acetate from 0.075 to 0.15 M enlarges the particle size of as-synthesized Co from 71 to 213 nm and 77 to 290 nm of the mean sizes, through microwave-assisted polyol process under power at 440 W for 900 sec and 1200 sec, respectively, at 175±10°C. This reveals that the adding amount of cobalt acetate is a key factor to control the particle size of as-synthesized cobalt with ethylene glycol in microwave.

Figures 3–5 demonstrate the TEM images and electron diffraction patterns of as-synthesized cobalt particles. These



(a)

(b)

Figure 3. (a) TEM photography of cobalt particles synthesized from the 1/9 molar ratio of cobalt acetate to PVP and 0.1 M of the cobalt acetate under microwave at 440 W for 600 s, whose mean size of as-synthesized Co particle is about 40 nm and scale bar = 100 nm, as well as Inset: corresponding to electron diffraction pattern and (b) the size distribution of as-synthesized cobalt particle.

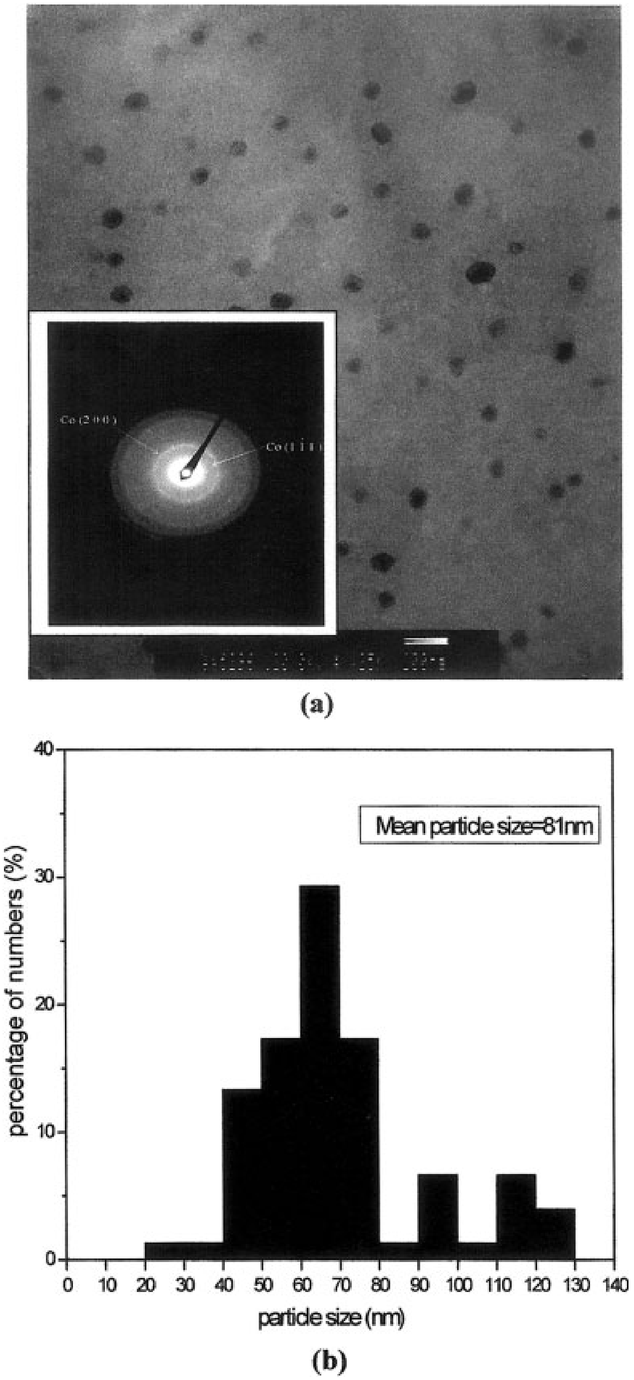


Figure 4. **(a) TEM photography of cobalt particles synthesized from 0.075 M of cobalt acetate under microwave at 440 W for 1200 s, whose mean size of as-synthesized Co particle is about 81 nm and scale bar = 100 nm as well as Inset: corresponding to electron diffraction pattern and (b) the size distribution of as-synthesized cobalt particle.**

figures show that samples consist of an-isometric particles and the plane distances of fringe patterns are 2.05 and 1.77 Å, corresponding to the lattices of (1 1 1) and (2 0 0) for cobalt crystal in face-centered cubic phase from JCPDS card. In particular, for the 1/9 molar ratio of cobalt acetate to PVP, under microwave at 440 W for 600 sec, the mean size of as-synthesized cobalt particles is about 40 nm, as depicted in Figure 3. Additionally, as shown in Figure 4, the mean particle size of as-synthesized cobalt is 81 nm as the

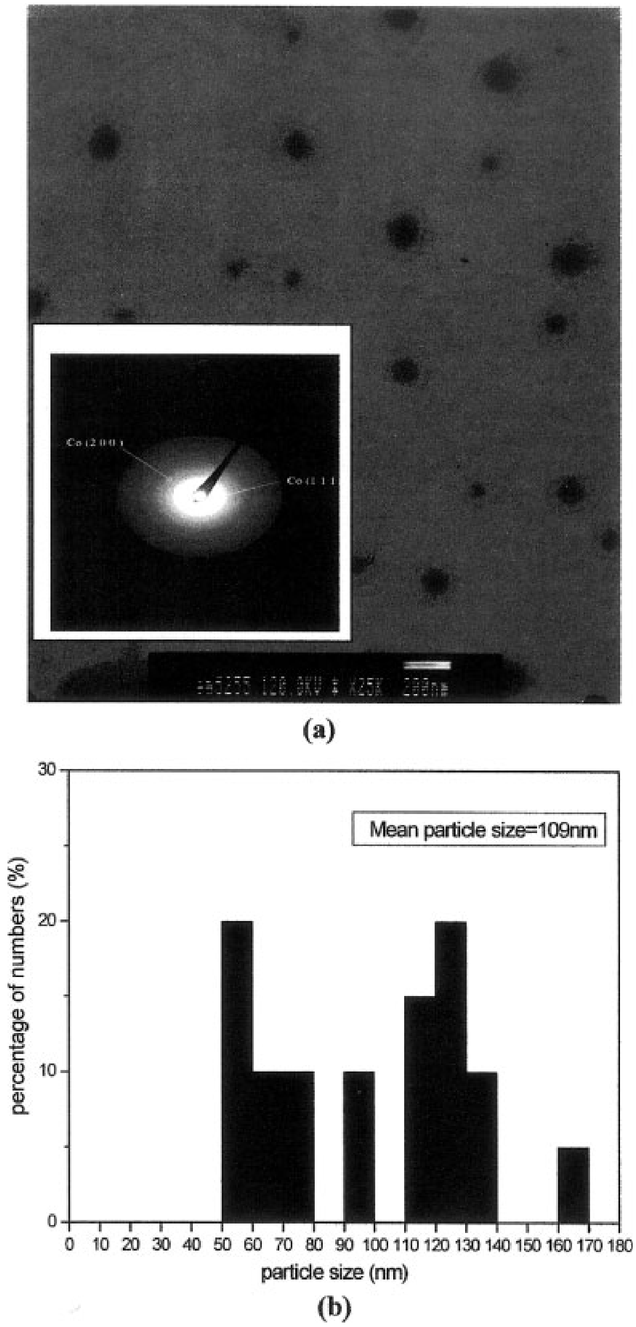
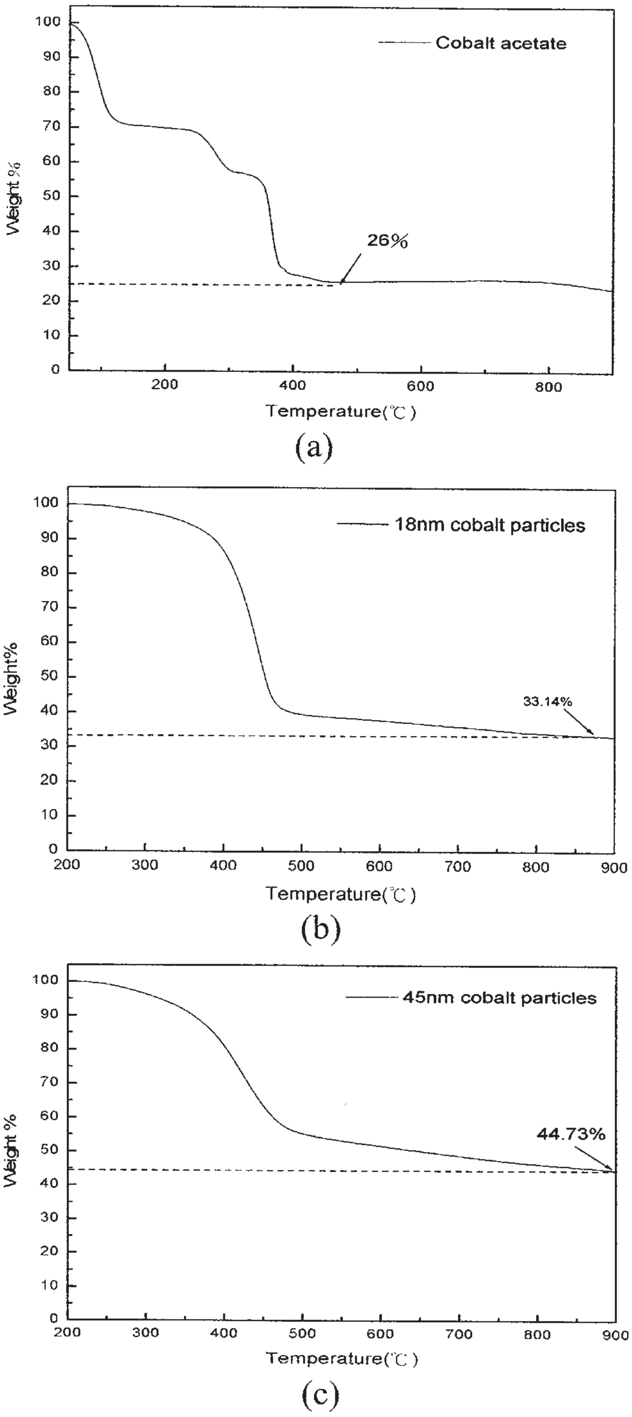


Figure 5. **(a) TEM photography of cobalt particles synthesized from the 1/9 molar ratio of cobalt acetate to PVP and 0.1 M of the cobalt acetate under microwave at 440 W for 1200 s, whose mean size of as-synthesized Co particle is about 109 nm and scale bar =200 nm as well as Inset: corresponding to electron diffraction pattern and (b) the size distribution of as-synthesized cobalt particle.**



(a)

(b)

(c)

Figure 6. TGA examinations of (a) cobalt acetate; (b) the as-synthesized cobalt particles in mean size of 40 nm; and (c) the as-synthesized cobalt particles in mean of 81 nm, in nitrogen.

cobalt acetate concentration is 0.075 M. In comparison, Figure 5 presents the average as-synthesized cobalt particle is about 109 nm. The above mean sizes of as-synthesized cobalt particle are estimated by TEM analysis, which is smaller than that measured by dynamic laser scattering particle analyzer, as listed in Tables 1–3, due to exclusion of polymeric protector. To exhibit the actual feature of particle, the TEM is used to indicate the mean size of as-synthesized cobalt particle in this work.

For further approving the yield of as-synthesized Co nanoparticles, Figure 6 presents the result of TGA measurement. As observed in Figure 6a, 26 wt % Co particle can be synthesized from the cobalt acetate; accordingly, 0.1 and 0.075 M of ionic cobalt in solution may be estimated as 0.9714 and 0.7286 m kg cobalt particles, respectively, after reducing cobalt acetate at 475°C. In addition, Figures 6b, c are TGA curves for as-synthesized cobalt nano-particles with PVP in mean size of 40 and 81 nm in nitrogen. As shown in the figures, the weight percentages are 33.14 and 44.73 wt %, respectively, corresponding to 0.7125 and 0.6262 m kg Co particles in mean sizes of 40 and 81 nm from reduction of 0.1 and 0.075 M of cobalt acetate through microwave-assisted polyol synthesis in the presence of PVP. The yields of as-synthesized cobalt nano-particles in the mean sizes of 18 and 45 nm are then 73.75 and 85.95%, respectively. This result is closed to ICP analysis, as shown in sample T91 of Table 1 and sample P2 of Table 3.

To sum up, through microwave-assisted polyol process, the maximum yields of as-synthesized cobalt nano-particles in mean sizes of 40 and 81 nm can be obtained as about 71 and 85%, respectively, in this work.

Magnetism of As-synthesized Co in Solution

The as-synthesized cobalt particle absorbed oleic acid is dispersed in kerosene and vibrated by ultrasonic bath for 3600 sec, and then analyzed by VSM for the property of magnetism at ambient temperature. As shown in Figure 7, the solution containing as-synthesized cobalt nano-particles in average diameters of 40 and 81 nm exhibits a super-paramagnetic behavior at room temperature, while the cobalt particles in average diameter of 109 nm shows a cohesive character. In addition, the saturation magnetization is increased with reducing the particle size of cobalt, such as, 39.1 and 29.5 emu/g

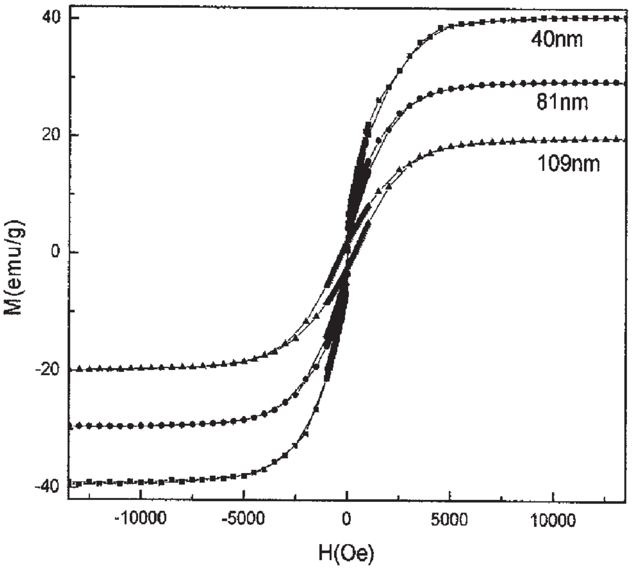


Figure 7. Magnetizations of the magnetic fluid varying with the mean size of as-synthesized cobalt particles at room temperature.

for the average diameters of 40 and 81 nm, respectively. This is because the total magnetic moment per atom in the Co particles is enhanced with decreasing particle size.[23]

Conclusion

In this work, through microwave-assisted polyol process, the yields of cobalt particles with average diameters of 40 and 81 nm can be obtained as 71 and 85%, respectively, in the presence of PVP and $PdCl_2$. Furthermore, the VSM was employed to identify the magnetism of as-synthesized cobalt particle in kerosene. As shown in the result, the saturation magnetisms of the solution with the average diameters 40 and 81 nm of as-synthesized cobalt are 39.1 and 29.5 emu/g, respectively.

Hopefully, these results will generate sufficient interest so that future studies can ascertain the nanometer scale of cobalt particles using microwave assisted ethylene glycol to rapidly manufacture the magnetic materials with high-saturation magnetisms for the applications of magnetic-field sensor, fast spurts ink printing and the light switch, and so on.

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