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The Graduate School
Intercollege Graduate Program in Materials

SYNTHESIS OF METAL NANOPARTICLES BY MICROWAVE-ASSISTED SOLVOTHERMAL TECHNIQUE

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ABSTRACT

Metal nanoparticles of Ag, Ni, Pd, and Pt were synthesized in this research work by microwave-assisted solvothermal technique. The microwave-assisted solvothermal technique was found to be faster than the conventional solvothermal process in the synthesis of all the metal nanoparticles investigated here. Ethylene glycol, methanol, and ethanol were used as both reducing agents and solvents. The particle size and morphology were observed using a transmission electron microscope (TEM). Particle size and size distribution were calculated by Image J softeware. Optical properties of synthesized metal nanoparticles were characterized by UV-Visible (UV-Vis) Spectrophotometer.

Silver nanoparticles of about 10 to 50 nm were synthesized with ethylene glycol as reducing agent. The morphology and particle size of Ag nanoparticle were controlled by varying the concentration of Ag metal source (AgNO$_3$), polyvinyl pyrrolidone (PVP) molecular weight, and the type of ligands. Furthermore, the growth rate was increased by adding NaOH in the system.

Well-dispersed Ni nanoparticles were synthesized with ethylene glycol as reducing agent in a binary protecting agent system of PVP and dodecylamine (DDA) with or without Pt seeding. By neutralizing the H$^+$ formed from the reductive reaction and coordinating with Ni particles, DDA added in the reaction system contributed to the morphology and size control and also led to the formation of Ni nanoparticles without Pt seeding.
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Chapter 1

Introduction

Metal nanoparticles are of great interest in the modern materials world due to special electronic, optical, and magnetic properties when compared to their bulk counterparts. The unique properties of metal nanoparticles result from their smallness and high surface to volume ratio compared to bulk metals and have been applied in various fields. The synthesis of metal nanoparticles is a key to their practical applications and has attracted much attention in the last decade. Many techniques have been developed to synthesize metal nanoparticles, including metal vaporization, chemical reduction, electrochemical reduction¹, and thermolysis method². Recently, new preparation methods have been developed such as sonochemical reactions³,⁴, photolytic⁵ and radiolytic reductions⁶,⁷, and microwave-assisted method⁸,⁹.

1.1 Previous work on synthesis of metal nanoparticles

The methods of synthesis of metal nanoparticles can be broadly classified into two categories: physical and chemical methods.

1.1.1 Physical methods

Metal vaporization is capable of synthesizing various metal nanoparticles including Mg, Cr, Mn, Fe, Co, Ni, Ga, Se, Ag, Cd, and Bi¹⁰. However, it is difficult to
prepare particles of rare elements, such as Nb, Mo, Rh, and Ir, since their melting
temperature is in excess of 2000ºC. Furthermore, the total yield is not very large and the
efficiency is less than 100% in contrast to the use of chemical methods. Therefore, the
high material cost may prohibit producing large quantities of particles of some rare
elements. Another drawback of this technique is the difficulty in the dispersion of the
particles.  

1.1.2 Chemical methods

Chemical reduction of metal salts in solution by reducing agents is the most
widely used method of generating colloidal suspensions of the metals. A wide range of
nanophase metals, from noble to transition, and their alloys have been synthesized.
Varying the reaction conditions can control size and shape of nanoparticles. Sun and Xia
(2002) have produced uniform silver nanocubes with controlled injection of AgNO₃ and
polyvinyl pyrrolidone (PVP) using the polyol process (using polyol such as ethylene
glycol as a reducing agent). The shape of silver nanocubes is strongly dependent on the
concentration of AgNO₃ and the ratio between AgNO₃ and PVP repeating unit.

Electrochemical reductions have been used to produce noble and transition metal
nanoparticles such as Ti, Fe, Co, Ni, Pd, Pt, Ag, and Au. The particle size can be
controlled by adjusting the current density; however, this electrochemical process needs
oxygen-free solvents and an argon atmosphere.  

Thermolysis of carbonyl-containing metal complexes has been used to produce
metal nanoparticles since many organometallic compounds of transition metals
decompose thermally to their respective metals under relatively mild conditions. Metals such as Rh, Ir, Ru, Os, Pd, and Pt have been synthesized; however, metal carbonyl pyrolysis is mostly used to produce Co, Fe, Ni, CoPt, and other magnetic particles. For example, Puntes et al., (2001)\(^2\) have synthesized magnetic cobalt nanorods and nanospheres with narrow size distributions and a high degree of shape control. The shape is controlled by the injection of an organometallic precursor into a hot surfactant mixture under inert atmosphere. Although many metal nanoparticles can be produced by this method, the metal carbonyl precursor is costly and the process can be complicated in obtaining well-controlled particle shape and size\(^2\).

Recently, developed techniques, such as sonochemical, photolytic, and radiolytic reductions, can be performed at ambient temperature with relatively low power. Various metals, such as Ag, Au, Pt, Pd, Fe, Co, and Ni, have been synthesized using these methods. These techniques, however, typically need a deaerated process or an argon atmosphere. For the synthesis of transitional metals, like Fe and Ni, expensive metal precursors such as metal carbonyls are used\(^{13,14}\).

A photo-induced method has been developed to successfully control particle shape and size through surface plasmon excitation. Jin et al., (2003)\(^{15}\) produced Ag nanoprisms (triangular silver nanocrystals) using this method. The size and shape were controlled by the wavelength of the irradiating light. However, this size and shape control process takes about 10 to 50 hours.

The above-mentioned methods are typically time-consuming and energy inefficient. For example, metal vaporization method requires a high vacuum and a high temperature due to the high melting point of the metals. For electrochemical reduction
and the recently developed methods such as sonochemical, photolytic, and radiolytic reductions, the synthesis process involves deaerated process or some type of inert (typically argon) atmosphere. Chemical reductive reactions have been widely used in hydrothermal systems, solvothermal systems, and reflux systems with controlled injection of reaction solutions. These methods can produce metal nanoparticles with controlled size and shape by varying the reaction conditions. Combined with microwave technique, the chemical reduction method is expected to provide a simple, fast, and energy efficient technique for the synthesis of metal nanoparticles.

1.1.3 Synthesis through microwave-assisted techniques

Microwave synthesis dramatically accelerates the reaction by changing the nature of the chemical synthesis and offering a new energy source that gives enough power to complete reactions in minutes. Moreover, microwave heating shifts chemical reactions from kinetic to thermodynamic control due to the high energy available, eliminating the metalstable products of some reactions. The applications of microwaves in the preparation of nanomaterials have been reported in recent years. Komarneni’s group developed a microwave-hydrothermal method to fabricate various inorganic materials such as mesoporous materials and ceramic powders (TiO$_2$, Fe$_2$O$_3$ and KNbO$_3$)\textsuperscript{16-19}. He et al., (2002)\textsuperscript{20} have synthesized a series of nanosized sulfide and oxide semiconductors via microwave-assisted chemical route. In recent years, synthesis of metal nanoparticles through microwave irradiation has been gaining popularity. Various metallic and bimetallic nanoparticles have been produced by microwave-assisted chemical reductions.
Harpeness and Gedandken (2004) reported microwave synthesis of core-shell Au/Pd bimetallic nanoparticles. In conjunction with a rapidly expanding applications base, microwave synthesis can be effectively applied to any reaction scheme, creating faster reactions, improving yields, producing cleaner chemistries, creating new phases, and leading to cost-effective reactions.

1.2 Hypothesis and objectives

The central hypothesis of this thesis research based on the above studies is that microwave-assisted reactions have advantages over conventional ones. The main objective of this research work is to synthesize metal nanoparticles with microwave-assisted reactions. The secondary objectives of this research are (a) to characterize the synthesized metal nanoparticles, (b) to study the optical properties of metal nanoparticles, and (c) to compare microwave-assisted technique with conventional method. This research work is outlined as follows:

- Synthesis of Ag nanoparticles with ethylene glycol and ethanol as reducing agents (Chapter 3)
- Synthesis of Ni nanoparticles with ethylene glycol as a reducing agent (Chapter 4)
- Synthesis of Pd nanoparticles with methanol and ethanol as reducing agents (Chapter 5)
- Synthesis of Pt nanoparticles with methanol and ethanol as reducing agents (Chapter 6)
In each chapter, factors controlling the morphology and particle size of metal nanoparticles have been studied. The optical properties of metal nanoparticles have been measured. Results with microwave-assisted methods have been compared with those of conventional method.
1.3 References


Chapter 2
Literature review

This chapter gives the literature review of properties and applications of metal nanoparticles, mechanism of producing nanoparticles by using protecting agents, and mechanism of microwave-assisted reactions.

Metal nanoparticles have attracted much attention due to their high surface area, special electronic, optical, and magnetic properties. These special properties have been applied in various fields ranging from microelectronics to biomedical science. A brief review of these properties and their corresponding applications is given below:

2.1 Properties and applications of metal nanoparticles

2.1.1 Electrical properties and the corresponding applications

The special electronic properties of the metal nanoparticles mainly result from the “quantum size effect”. With decreasing particle size, metal nanoparticles begin to show a discrete energy spectrum. As illustrated in Figure 2-1, the size of metal particles has a direct effect on their energy states. For a metal particle with bulk properties (Figure 2-1 a), there is no band gap in the electronic states and hence electrons can move freely in any direction. As the particles decrease in size, the energy states begin to exhibit a band gap (Figure 2-1 b). In the extreme case of a molecule formed by three atoms, there exists a wide band gap between the well-defined bonding and anti-bonding molecular orbitals
(Figure 2-1 c). Therefore, the size of metal particles determines how much the electrons can move around and consequently the possible energy levels of the electrons. Chen et al., (1998)\(^1\) reported that gold nanoparticles less than 5 nm exhibited Coulomb staircase responses (a series of steps on the current-voltage characteristic).

Figure 2-1: Illustration of the electronic states in (a) a metal particle with bulk properties and its typical band Structure, (b) a large cluster of cubic close packed atoms with a small band gap, and (c) a simple tri-atomic cluster with completely separated bonding and antibonding molecular orbitals.\(^2\)

Gold monolayer-protected metal clusters (MPCs) are also reported as nanometer-sized electrodes that have small capacitance\(^3\). The unusual electronic properties, such as the discrete energy spectrum, the smallness of the capacitance, and the possibility to manipulate single charges, may lead to new technologies and applications. Lent and
Porod (1995) found that by using a new computing scheme, it was possible to take advantage of the electron’s quantum nature to design switches and wires that are much smaller than the present ones and the main advantage is that they generate little heat.4

2.1.2 Optical properties and corresponding applications

Metal nanoparticles exhibit unusual optical properties due to the surface plasmon absorption that arises from the collective oscillations of the free conduction band electrons induced by the incident electromagnetic radiation. The surface plasmon resonance (SPR) frequencies are typically in the visible and near-infrared region of the spectrum. For example, spherical Ag and Au nanoparticles have strong surface plasmon bands around 400 and 520 nm, respectively. The surface plasmon absorption is dependent on the shape and size of the nanoparticles. For metal nanorods, two distinct plasmon absorption bands were observed corresponding to transverse and longitudinal plasmon resonance5,6. For example, gold nanorods with an aspect ratio of 3.3 exhibit two plasmon absorption bands at 525 and 740 nm. In the case of silver nanoparticles, a shift in the plasmon absorption band from 400 to 670 nm is observed as the particle shape changed from spherical to triangular prisms during visible light irradiation. In addition, plasmon absorption is also dependent on the size of metal particles. With decreasing size, the SPR absorption band is shifted to short wavelength. Small gold nanoparticles of <5 nm diameter do not show any plasmon absorption. Gold nanoparticles ranging from 5 to 50 nm show a sharp absorption band in the 520-530 nm region7. As the particles grow larger, the absorption band broadens and covers the visible range1,8. The plasmon
absorption of metal nanoparticles is sensitive to the surrounding environment because solvents change the refractive index surrounding gold nanoparticle or solvents complex with the gold surface.

The unique surface plasmon optical properties of nanoparticles are utilized in various applications, including gas sensors, optical filters as labels for biomacromolecules, intensity enhancement in Raman spectroscopy (SER), optical switching or optical limiting, and optical trapping (or “tweezers”). For example, Letsinger’s group reported a selective colorimetric polynucleotides detection method based on mercaptoalkyloligonucleotide-modified gold nanoparticle probes using the distance-dependent optical properties of gold nanoparticles.

2.1.3 Magnetic properties and corresponding applications

Transition metal nanoparticles show special magnetic properties. The large surface-to-volume ratio of these nanoparticles results in a different local environment for the surface atoms in their magnetic coupling/interaction with neighboring atoms, leading to the mixed volume and surface magnetic characteristics. Unlike bulk ferromagnetic materials, which usually have multiple magnetic domains, several small ferromagnetic particles could have only a single magnetic domain. In this case, superparamagnetism occurs; the magnetizations of the particles are randomly distributed and are aligned only under an applied magnetic field. Some important applications of magnetic nanoparticles include color imaging, bioprocessing, magnetic refrigeration, and ferrofluids. For instance, small FePt particles may be suitable for future ultrahigh-density magnetic

### 2.1.4 Additional applications

In addition to the above-mentioned applications, nanoparticles have been used for catalysis due to their large surface-to-volume ratio. The large percentage of surface atoms greatly increases surface activities. The ligand shell of nanoparticles makes them dispersed in liquids and thus suitable for homogeneous reactions. Ag, Au, Pt, Pd, Ni, and Co nanoparticles are able to catalyze a range of reactions: (1) hydrosilylation reactions, (2) oxidation reactions including oxidation of cyclohexane with Co, oxidation of cyclooctane, ethane, and glucose with Fe, Ru, and Ag colloids, and bimetallic Pd/Pt, (3) C-C coupling reaction with Ru, Pd, Pd/Ni nanoparticles, such as carbonylation of methanol, heck reactions, and Suzuki reactions, and (4) hydrogenation reactions with Pt, Ru, Pt/Co nanoparticles.

Nanoparticles have long been known to have special thermal and mechanical properties. It is well documented that the melting point of a solid material will be greatly reduced when it is processed as nanostuctures. For example, Jiang (2003) reported that Ag nanoparticles of around 2 nm have a melting point of 460 °C that is much lower than that of bulk silver (961 °C). This property is used for low temperature calcining in the sintering industry. The hardness and yield stress of a polycrystalline material typically increase with decreasing grain size on the micrometer scale. This property is used to increase hardness and toughness of coating materials.
The synthesis of metal nanoparticles is a key to their practical applications and has attracted much attention in the last decade. Many techniques have been developed to synthesize metal nanoparticles, as discussed in Chapter 1. These techniques can be categorized as physical and chemical methods. Through chemical method, nanoparticles can be well separated by using protecting agents, such as surfactants, polymers and sometimes ligands. These protecting agents prevent metal nanoparticles from growing to larger particles and stabilize colloidal metal nanoparticles from agglomeration.

2.2 Mechanism of stabilization of colloidal metal particles in liquids

At short interparticle distances, two particles would be attracted to each other by van der Waals forces. For colloidal particles of nanometer size, the attractive force becomes significant. Therefore, for the synthesis of nanoparticles, nanoparticles must be stabilized against aggregation into larger particles. Typically, there are two methods to stabilize nanoparticles: electrostatic stabilization and steric stabilization.

Electrostatic stabilization is generated by the adsorption of ions to the surface of electrophilic metal particles. This adsorption produces an electrical double layer. The electrical double layer generates a Coulombic repulsion force between particles and thus stabilizes particles against aggregation (shown in Figure 2-2).
Figure 2-2: Electrostatic stabilization of metal colloid particles. Ions adsorb onto the surface of the metal particles, producing an electrical double layer. This double layer provides Coulombic repulsion and thus stabilizes metal particles against aggregation.\textsuperscript{19}

Another method (mainly used in the synthesis of metal nanoparticles) to stabilize colloidal particles is by the adsorption of molecules such as polymers, surfactants, or ligands on the particle surface. Large molecules adsorbed on the surface of nanoparticles generate a steric barrier, which prevents the aggregation of nanoparticles (Figure 2-3). Those polymers, surfactants or ligands are defined as stabilizers/protecting agents/stabilizing agents. These protecting agents are often used in the synthesis of metal nanoparticles through chemical/electrochemical reductions, thermolysis method, sonochemical reactions, photolytic and radiolytic reductions, and microwave-assisted reactions\textsuperscript{7,20-25}. 
Microwave-assisted method is a simpler and cost-effective technique compared to conventional method because microwave heating is fast and energy efficient. The mechanism of microwave heating is discussed in the following section.

**2.3 Theory of microwave heating**

Microwaves are a form of electromagnetic energy. The frequency of microwaves ranges from 300 to about 300,000 megahertz (MHz). For microwave heating, 2450 MHz is preferred in the laboratory because it has the right penetration depth to interact with laboratory scale samples.
Microwave energy consists of an electric field and a magnetic field. During microwave irradiation, only the electric field transfers energy to heat a substance. The microwave photon energy (0.037 kcal/mole) is very low compared with the typical energy required to cleave molecular bonds (80-120 kcal/mole). Therefore, microwaves will only affect the molecular rotation but not the structure of the molecule.

2.3.1 Mechanism of microwave heating

Figure 2-4 shows the scheme of solution heating by conventional and microwave methods. For conventional heating, temperature is obtained through conductive heating with an external heat source. Thus, conventional heating results in a higher external temperature than the internal temperature. It takes time to achieve thermal equilibrium between the outside and inside of the solution. Therefore, conventional heating is inefficient and time-consuming. Microwaves heat reaction solutions through a different way. Microwaves couple directly with the molecules in the reaction solution through dipole rotation or ionic conduction. Dipole rotation and ionic conduction are two fundamental mechanisms for energy transfer from microwaves to the solution being heated.
Dipole rotation is an interaction in which polar molecules align themselves with the changing electric field of the microwaves. The rotational motion of the molecule leads to energy transfer. The coupling ability of dipole rotation is dependent on the polarity of the molecules. The higher the polarity of the molecule, the greater is its ability to couple with the microwave energy. Ionic conduction is due to free ions or ionic species in the reaction solution being heated. Through ionic conduction mechanism, the electric field leads to ionic motion as the molecules orient themselves to the changing electric field of the microwaves. By these two mechanisms, microwaves transfer energy in $10^{-9}$ seconds (with a frequency of $10^9$Hz) with each cycle of electromagnetic energy. The kinetic molecular relaxation from this energy is approximately $10^{-5}$ seconds. Therefore, the energy transfers faster than the molecules can relax, resulting in the non-equilibrium...
condition and high instantaneous temperatures. Through microwave heating, reaction rate can also be increased.

Arrhenius reaction rate equation (Equation 2-1) is given as follows:

$$k = A e^{-\frac{E_a}{RT}}$$  \hspace{1cm} \text{Equation 2-1}

Where $k$ is reaction rate coefficient, $A$ is a constant (affected by the collision frequency between molecules and by the fraction of those molecules that have the minimum energy required to overcome the barrier of the activation energy), $E_a$ is the activation energy (energy difference between energy level of reactants and a higher transition state energy level), $R$ is the universal gas constant ($R = 8.314 \times 10^{-3} \text{kJ mol}^{-1}\text{K}^{-1}$), and $T$ is temperature (in degrees Kelvin).

Microwave irradiation does not affect the activation energy. Due to the high instantaneous heating by microwave irradiation, energetic collisions are generated much faster than by conventional heating. Therefore, reaction rates can be increased. The efficiency of microwave heating depends on the solvents of the reactions. The following section discusses the theory of how the physical constants relate to the energy transfer and how to choose the solvents.

\subsection*{2.3.2 Selection of solvents used in microwave-assisted techniques}

With microwave heating, solvents play an important role in solution reactions. The more efficiently a solvent couples with the microwave energy, the faster the increase in temperature of the reaction solution. The polarity of a solvent plays a significant role.
The higher the polarity value of the solvent, the greater is its ability to couple with the microwave energy.

2.3.2.1 Theory

Many factors affect the polarity of a solvent, such as the dielectric constant, dielectric loss, and tangent delta. These constants contribute to the solvent’s absorbing ability. The dielectric constant (ε’) is the ratio of the electrical capacity of a capacitor filled with the solvent to the electrical capacity of the evacuated capacitor (ε’ = C_{filled}/C_{evacuated}). Tangent delta (tan δ = ε”/ε’) is the dissipation factor. ε” is the dielectric loss (the amount of input microwave energy that is dissipated as heat to the sample).

The three dielectric parameters (tangent delta, dielectric constant, and dielectric loss) are related to the ability of a solvent to absorb microwave energy. The dielectric loss is the most indicative factor. The higher the dielectric loss value of the solvent, the more efficiently the solvent converts microwave energy into thermal energy, and the faster the temperature of the solvent can be increased. Table 2-1 presents values of the dielectric constant, tangent delta, and dielectric loss for thirty common solvents, measured at room temperature and at a frequency of 2450MHz.
Table 2-1: Dielectric constant ($\varepsilon'$), tan$\delta$, and dielectric loss ($\varepsilon''$) for 30 common solvents (measured at room temperature and 2450 MHz)$^{27}$

<table>
<thead>
<tr>
<th>Solvent (bp °C)</th>
<th>Dielectric Constant</th>
<th>Tan$\delta$</th>
<th>Dielectric Loss ($\varepsilon''$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol (197)</td>
<td>37.0</td>
<td>1.350</td>
<td>49.950</td>
</tr>
<tr>
<td>Formic Acid (100)</td>
<td>58.5</td>
<td>0.722</td>
<td>42.237</td>
</tr>
<tr>
<td>DMSO (189)</td>
<td>45.0</td>
<td>0.825</td>
<td>37.125</td>
</tr>
<tr>
<td>Ethanol (78)</td>
<td>24.3</td>
<td>0.941</td>
<td>22.866</td>
</tr>
<tr>
<td>Methanol (65)</td>
<td>32.6</td>
<td>0.659</td>
<td>21.483</td>
</tr>
<tr>
<td>Nitrobenzene (202)</td>
<td>34.8</td>
<td>0.589</td>
<td>20.497</td>
</tr>
<tr>
<td>1-Propanol (97)</td>
<td>20.1</td>
<td>0.757</td>
<td>15.216</td>
</tr>
<tr>
<td>2-Propanol (82)</td>
<td>18.3</td>
<td>0.799</td>
<td>14.622</td>
</tr>
<tr>
<td>Water (100)</td>
<td>80.4</td>
<td>0.123</td>
<td>9.889</td>
</tr>
<tr>
<td>1-Butanol (118)</td>
<td>17.1</td>
<td>0.571</td>
<td>9.764</td>
</tr>
<tr>
<td>NMP (215)</td>
<td>32.2</td>
<td>0.275</td>
<td>8.855</td>
</tr>
<tr>
<td>Isobutanol (108)</td>
<td>15.8</td>
<td>0.522</td>
<td>8.248</td>
</tr>
<tr>
<td>2-Butanol (100)</td>
<td>15.8</td>
<td>0.447</td>
<td>7.063</td>
</tr>
<tr>
<td>2-Methoxyethanol (124)</td>
<td>16.9</td>
<td>0.410</td>
<td>6.929</td>
</tr>
<tr>
<td>DMF (153)</td>
<td>37.7</td>
<td>0.161</td>
<td>6.070</td>
</tr>
<tr>
<td>o-Dichlorobenzene (180)</td>
<td>9.90</td>
<td>0.280</td>
<td>2.772</td>
</tr>
<tr>
<td>Acetonitrile (82)</td>
<td>37.5</td>
<td>0.062</td>
<td>2.325</td>
</tr>
<tr>
<td>Nitromethane (101)</td>
<td>36.0</td>
<td>0.064</td>
<td>2.304</td>
</tr>
<tr>
<td>MEK (80)</td>
<td>18.5</td>
<td>0.079</td>
<td>1.462</td>
</tr>
<tr>
<td>1,2-Dichloroethane (83)</td>
<td>10.4</td>
<td>0.127</td>
<td>1.321</td>
</tr>
<tr>
<td>Acetone (56)</td>
<td>20.7</td>
<td>0.054</td>
<td>1.118</td>
</tr>
<tr>
<td>Acetic acid (113)</td>
<td>6.20</td>
<td>0.174</td>
<td>1.079</td>
</tr>
<tr>
<td>Chloroform (61)</td>
<td>4.80</td>
<td>0.091</td>
<td>0.437</td>
</tr>
<tr>
<td>Dichloromethane (40)</td>
<td>9.10</td>
<td>0.042</td>
<td>0.382</td>
</tr>
<tr>
<td>Ethyl Acetate (77)</td>
<td>6.00</td>
<td>0.059</td>
<td>0.354</td>
</tr>
<tr>
<td>THF (66)</td>
<td>7.40</td>
<td>0.047</td>
<td>0.348</td>
</tr>
<tr>
<td>Chlorobenzene (132)</td>
<td>2.60</td>
<td>0.101</td>
<td>0.263</td>
</tr>
<tr>
<td>Toluene (111)</td>
<td>2.40</td>
<td>0.040</td>
<td>0.096</td>
</tr>
<tr>
<td>o-Xylene (144)</td>
<td>2.60</td>
<td>0.018</td>
<td>0.047</td>
</tr>
<tr>
<td>Hexane (69)</td>
<td>1.90</td>
<td>0.020</td>
<td>0.038</td>
</tr>
</tbody>
</table>

DMSO: Dimethylsulfoxide  
NMP: N-Methyl-2-Pyrrolidone  
DMF: N,N-Dimethylformamide  
MEK: Methy ethyl ketone  
THF: Tetrahydrofuran
2.3.2.2 Choosing a solvent

According to dielectric loss value, the thirty common solvents can be categorized into three different groups: high, medium, and low absorbing solvents\textsuperscript{27} (Table 2-2). High absorbing solvents have dielectric loss values ranging from 14 to 50. Medium absorbers generally have dielectric loss values between 1.00 and 13.99. The low absorbing molecules have dielectric loss values less than 1.00. Small chain alcohols, like ethanol, methanol, and ethylene glycol, are high absorbers, heating very quickly and efficiently. Therefore, they are good solvents for reactions by microwave heating. For medium absorbers (like dichlorobenzene, water, dimethylformamide (DMF)), they also heat efficiently, but it takes more time to reach desired temperature. Nonpolar solvents (such as hexane, benzene, and toluene) are low absorbers. Low absorbers can be heated above their boiling point, but much longer time is needed to reach the boiling point.

Choosing the correct solvent is an important factor for reactions that use microwave heating for the formation of metal nanoparticles. High and medium absorbers are normally used as solvents in microwave-assisted reaction due to their efficient and fast heating. Low absorbers (nonpolar solvents) are not normally used in microwave-assisted reactions.

Based on the above theory, ethylene glycol, methanol, and ethanol (which are all high absorbers) are good solvents for chemical reactions under microwave irradiation. These three solvents also serve as reducing agents. Therefore, ethylene glycol, methanol, and ethanol were chosen to serve as both solvents and reducing agents in this research work.
Table 2-2: The category of solvents: high, medium, and low absorbers according to their dielectric loss value.

<table>
<thead>
<tr>
<th>Absorbance Level</th>
<th>Solvents</th>
<th>Dielectric Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High</strong></td>
<td>Ethylene Glycol</td>
<td>49.95</td>
</tr>
<tr>
<td></td>
<td>Formic Acid</td>
<td>42.237</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>37.125</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>22.866</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>21.483</td>
</tr>
<tr>
<td></td>
<td>Nitrobenzen</td>
<td>20.497</td>
</tr>
<tr>
<td></td>
<td>1-Propanol</td>
<td>15.216</td>
</tr>
<tr>
<td></td>
<td>2-Propanol</td>
<td>14.622</td>
</tr>
<tr>
<td><strong>Medium</strong></td>
<td>Water</td>
<td>9.889</td>
</tr>
<tr>
<td></td>
<td>1-Butanol</td>
<td>9.764</td>
</tr>
<tr>
<td></td>
<td>NMP</td>
<td>8.855</td>
</tr>
<tr>
<td></td>
<td>Isobutanol</td>
<td>8.248</td>
</tr>
<tr>
<td></td>
<td>2-Butanol</td>
<td>7.063</td>
</tr>
<tr>
<td></td>
<td>2-Methoxyethanol</td>
<td>6.929</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>6.07</td>
</tr>
<tr>
<td></td>
<td>o-Dichlorobenzene</td>
<td>2.772</td>
</tr>
<tr>
<td></td>
<td>Acetonitrile</td>
<td>2.325</td>
</tr>
<tr>
<td></td>
<td>Nitromethane</td>
<td>2.304</td>
</tr>
<tr>
<td></td>
<td>MEK</td>
<td>1.462</td>
</tr>
<tr>
<td></td>
<td>1,2-Dichloroethane</td>
<td>1.321</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>1.118</td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td>1.079</td>
</tr>
<tr>
<td><strong>Low</strong></td>
<td>Chloroform</td>
<td>0.437</td>
</tr>
<tr>
<td></td>
<td>Dichloromethane</td>
<td>0.382</td>
</tr>
<tr>
<td></td>
<td>Ethyl Acetate</td>
<td>0.354</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>0.348</td>
</tr>
<tr>
<td></td>
<td>Chlorobenzene</td>
<td>0.263</td>
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<tr>
<td></td>
<td>Toluene</td>
<td>0.096</td>
</tr>
<tr>
<td></td>
<td>o-Xylene</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
<td>0.038</td>
</tr>
</tbody>
</table>
2.4 References


3.1 Introduction

Silver nanoparticles are widely investigated because they exhibit special optical, electronic and chemical properties. Nanosilver-containing antibacterial and antifungal granules ("NAGs") were invented for medical applications\(^1\). The NAGs can be used in a variety of healthcare and industrial products. Healthcare products include: ointments or lotions to treat skin trauma, soaking solutions or cleansing solutions for dental or feminine hygiene, medications for treating gastrointestinal bacteria infections, and eye diseases. Industrial products include: food preservatives, water disinfectants, paper disinfectants, construction filling materials (to prevent mold formation)\(^1\). Based on the optical property of surface plasmon resonance absorption, Ag nanoparticles can also be used in biosensor, a solution immunoassay, medical diagnostics, biomedical research, and environmental science\(^2,3\). These properties of silver nanoparticles depend on the size and shape of nanoparticles. Silver nanoparticles have been synthesized and particle size and shape can be controlled through many methods. Silver nanoparticles with spherical\(^4\), cubic\(^5\), disk\(^6\), triangular prism\(^7,8\), wire\(^9\) shapes have been manufactured. Seeding or stepwise methods\(^5,10\) and controlling the ratio of protecting agents to metal cations\(^11\), the reaction pH or temperature have been used to control the size and shape of metal particles. Sun and Xia (2002)\(^5\) have produced uniform silver nanocubes with controlled
injection of AgNO₃ and polyvinyl pyrrolidone (PVP) by polyol process (using polyol such as ethylene glycol as a reducing agent). The shape of silver nanocubes is strongly dependent on the concentration of AgNO₃ and the ratio between AgNO₃ and PVP repeating unit.

Silver nanoparticles absorb light significantly due to surface plasmon absorption and their UV/Vis spectrum shows an intense absorption peak. The UV/Vis spectrum is sensitive to the shape, size, surrounding medium, aggregation, and geometric arrangements of nanoparticles. Jin et al., (2003) synthesized shape and size controlled Ag nanoprism and reported the shape and size dependent surface plasmon absorption ranging from 390 nm to 1100 nm. In this work, Ag nanoparticles with controlled size and shape were synthesized by microwave-polyol process and the optical properties were studied.

3.2 Experimental

Materials used in the synthesis are listed in Table 3-1. In the synthetic experiments silver nitrate was used as Ag metal precursor. PVP, (C₆H₉NO)ₙ, was used as a protecting agent to prevent particles from agglomerating and increasing in size. PVP polymers of different molecular weights were used to study the effects of molecular weight on the morphology and size of nanoparticles. n-dodecylamine (DDA, CH₃(CH₂)₁₁NH₃) was used as a second protecting agent when ethanol was used as a reducing agent. Ligands such as ethylenediaminetetraacetic acid (EDTA, (HOCOCH₂)₂N(CH₂)₂N(HOCOCH₂)₂) was used in the synthesis to control the growth of
Ag nanoparticles. Ammonium hydrogen fluoride (NH₄F) was also used in the synthesis because F⁻ can coordinate with Ag⁺, and then release Ag⁺ gradually, which can be used to control the growth of Ag nanoparticles. Sodium hydroxide was used to investigate the effect on the morphology of particles.

Table 3-1: List of chemical name, company, and purity of materials used in the synthesis

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Company</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal precursor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>Alfa Aesar A Johnson Matthey Company</td>
<td>ACS 99.9% (metal basis)</td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVP)</td>
<td>Aldrich Chemical Company, Inc</td>
<td>---- ----</td>
</tr>
<tr>
<td>(M W 8K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVP)</td>
<td>Aldrich Chemical Company, Inc</td>
<td>---- ----</td>
</tr>
<tr>
<td>(M W 10K) from Aldrich Chemical Company, Inc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVP)</td>
<td>Aldrich Chemical Company, Inc</td>
<td>---- ----</td>
</tr>
<tr>
<td>(M W 40K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVP)</td>
<td>Alfa Aesar a Johnson Matthey Company</td>
<td>---- ----</td>
</tr>
<tr>
<td>(M W 630K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVP)</td>
<td>Alfa Aesar a Johnson Matthey Company</td>
<td>---- ----</td>
</tr>
<tr>
<td>(M W 1300K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-dodecylamine (DDA)</td>
<td>Avocado Research Chemicals Ltd</td>
<td>98%</td>
</tr>
<tr>
<td>Protecting agents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reducing agents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol, anhydrous</td>
<td>Sigma-Aldrich Inc</td>
<td>99.8%</td>
</tr>
<tr>
<td>Ethanol 200proof anhydrous</td>
<td>Aldrich Chemical Company</td>
<td>99.5%</td>
</tr>
<tr>
<td>Ligands</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium hydrogen fluoride</td>
<td>Alfa Aesar a Johnson Matthey Company</td>
<td>---- ----</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid</td>
<td>Fisher Scientific company</td>
<td>---- ----</td>
</tr>
<tr>
<td>Sodium hydroxide anhydrous</td>
<td>Alfa Aesar a Johnson Matthey Company</td>
<td>97.0%</td>
</tr>
</tbody>
</table>
The metal precursors were mixed with ethylene glycol (HOCH₂CH₂OH) and PVP, with or without NaOH, and treated at 150 °C for 15 min in double-walled digestion vessels using a MARS5 microwave digestion system, (CEM Corp. Matthews, NC). The system operates at a frequency of 2.45GHz with a maximum power of 1200 ± 50W. The particle size and morphology were observed using TEM (2010 JEOL, Tokyo, Japan or Philips 420). Particle size and size distribution were calculated by Image J™ software. Particle size was calculated by collecting around 100 - 200 nanoparticles and based on the assumption that particles are spherical in shape. Particle size was determined by 95% confidence interval. Optical properties of synthesized Ag nanoparticles (dispersed with protecting agent in ethylene glycol) were characterized by Agilent UV-Visible (UV-Vis) Spectrophotometer at 25 °C, in the spectral range of 250 –1100 nm, in 1 cm cuvettes.

3.3 Results and discussion

3.3.1 Synthesis of Ag nanoparticles with ethylene glycol as a reducing agent

3.3.1.1 Effects of PVP molecular weight

In order to investigate the effect of PVP molecular weight on the morphology and particle size (here particle size has the same meaning as particle diameter) of synthesized Ag nanoparticles, different PVP molecular weights were used in the synthesis of Ag nanoparticles. Table 3-2 lists the PVPs of different molecular weights, quantities of
chemicals, and volume of ethylene glycol used in Ag nanoparticle synthesis at 150°C for 15 min.

Table 3-2: List of PVPs of different molecular weights, quantities of chemicals, volume of ethylene glycol used in Ag nanoparticle synthesis at 150°C for 15 min, and particle sizes of obtained Ag nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>AgNO₃ (g)</th>
<th>PVP molecular weight (0.5g)</th>
<th>EG (ml)</th>
<th>NaOH (g)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>072208</td>
<td>0.015</td>
<td>8K</td>
<td>100ml</td>
<td>--------</td>
<td>26 ± 1</td>
</tr>
<tr>
<td>072207</td>
<td>0.015</td>
<td>10K</td>
<td>100ml</td>
<td>--------</td>
<td>27 ± 2</td>
</tr>
<tr>
<td>072206</td>
<td>0.015</td>
<td>40K</td>
<td>100ml</td>
<td>--------</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>072205</td>
<td>0.015</td>
<td>630K</td>
<td>100ml</td>
<td>--------</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>072204</td>
<td>0.015</td>
<td>1300K</td>
<td>100ml</td>
<td>--------</td>
<td>28 ± 2</td>
</tr>
<tr>
<td>022806</td>
<td>0.015</td>
<td>40K</td>
<td>100ml</td>
<td>0.016</td>
<td>------</td>
</tr>
</tbody>
</table>

Ag nanoparticles with different particle sizes were synthesized by using different PVP molecular weights. Figures 3-1 and 3-2 show the TEM images and size distributions of Ag nanoparticles synthesized with different PVP molecular weights of 8K, and 630K, respectively. Particle sizes of synthesized Ag nanoparticles are about 26, 27, 29, 10, and 28 nm on the average with PVP molecular weight of 8K, 10K, 40K, 630K, and 1300K, respectively (Table 3-2).
Figure 3-1: TEM image and particle size distribution of Ag nanoparticles (sample 072208) synthesized with PVP molecular weight of 8K.

Figure 3-2: TEM image and particle size distribution of Ag nanoparticles (sample 072205) synthesized with PVP molecular weight of 630K.

Figure 3-3 shows the dependence of Ag nanoparticle size on PVP molecular weight. When PVP with molecular weights of 8K, 10K, and 40K were used in the synthesis, average particle sizes of produced Ag nanoparticles are similar and around 27
nm because the molecular weights of PVP did not change enough to affect the particle size. When PVP with molecular weight of 630K was used, particle size decreased and average particle size is about 10 nm. This is due to the bigger barrier formed from PVP with the higher molecular weight, which prevents the growth of Ag nanoparticles. With PVP molecular weight of 1300K, the average particle size of obtained Ag nanoparticles is approximately 28 nm. This might be due to the low solubility of PVP with molecular weight of 1300K. When PVP with molecular weight of 1300K was used, the reaction solution was stickier than that with PVP of low molecular weight. This high molecular weight PVP did not dissolve well in ethylene glycol. Therefore, PVP of molecular weight of 1300K cannot form efficient protecting barrier for the growth of Ag nanoparticles, thus resulted in larger particles than with PVP of molecular weight, 630K.

Figure 3-3: Relationship between PVP molecular weight and average particle diameter of synthesized Ag nanoparticles.
3.3.1.2 Effects of concentration of metal precursor

The concentration of AgNO$_3$, which provides the metal source for the nuclei and growth of Ag nanoparticles, is a key factor for controlling the particle size. Table 3-3 lists the particle sizes of Ag nanoparticles synthesized with different concentrations of metal source.

Table 3-3: List of weights of chemicals, volumes of ethylene glycol used in the synthesis of Ag nanoparticle at 150ºC for 15 min, and particle sizes of synthesized Ag nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>AgNO$_3$ (g)</th>
<th>Weight of PVP (MW 40K) (g)</th>
<th>EG (ml)</th>
<th>Concentration of Ag$^+$ ion (mM)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>081204</td>
<td>0.015</td>
<td>0.5</td>
<td>150</td>
<td>0.59</td>
<td>24 ± 2</td>
</tr>
<tr>
<td>072206</td>
<td>0.015</td>
<td>0.5</td>
<td>100</td>
<td>0.88</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>081208</td>
<td>0.015</td>
<td>0.5</td>
<td>67</td>
<td>1.3</td>
<td>34 ± 2</td>
</tr>
<tr>
<td>081205</td>
<td>0.015</td>
<td>0.5</td>
<td>50</td>
<td>1.76</td>
<td>36 ± 3</td>
</tr>
<tr>
<td>081218</td>
<td>0.015</td>
<td>0.5</td>
<td>25</td>
<td>3.52</td>
<td>27 ± 3</td>
</tr>
<tr>
<td>080211</td>
<td>0.015</td>
<td>0.5</td>
<td>8</td>
<td>10.56</td>
<td>19 ± 1</td>
</tr>
</tbody>
</table>

Figure 3-4 gives the TEM images and particle size distributions of Ag nanoparticles synthesized at different Ag$^+$ concentrations of 0.59, 0.88, and 1.3mM. Figure 3-5 shows the TEM images and particle size distributions of Ag nanoparticles obtained at various Ag$^+$ concentrations of 1.76, 3.52, and 10.56 mM. By increasing the concentration of Ag metal source, particle size increased. Figure 3-4 a, b, c, and Figure 3-5 a give the TEM images and particle size distributions of Ag nanoparticles, which showed that the average Ag nanoparticle size increased from about 24 nm to 36 nm with concentration increasing from 0.59 mM to 1.76 mM. This is because high concentration of Ag$^+$ provides more Ag metal source for the growth of Ag nanoparticles. However, with a further increase in the concentration of Ag$^+$ ions to 3.52 mM or 10.56mM, particle
size decreased (Figure 3-5 b and c) This is probably because excess Ag$^+$ ions produce more nuclei during the nucleation period, thus led to the formation of smaller nanoparticles. Figure 3-6 illustrates the relationship of Ag nanoparticle size and the concentration of Ag$^+$. 
Figure 3-4: TEM images of Ag nanoparticles synthesized with PVP molecular weight of 40k at different concentrations of Ag metal source, a, sample 081204, 0.59 mM; b, sample 072206, 0.88 mM; c, sample 081208, 1.3 mM.
Figure 3-5: TEM images of Ag nanoparticles synthesized with PVP molecular weight of 40k at different concentrations of Ag metal source, a, sample 081205, 1.76 mM; b, sample 081218, 3.52 mM; c, sample 080211, 10.56 mM.
3.3.1.3 Effects of ligands

In order to control the growth of Ag nanoparticles, ligands (F⁻ and EDTA) were added in the reaction system. The complexes formed with the metal ions and ligands release the metal source gradually, thus controlling the growth rate. Table 3-4 gives the morphology of obtained Ag nanoparticles and the reaction conditions in the synthesis.
**Table 3-4**: Quantities of chemicals, ratios of ligands to AgNO₃, concentrations of AgNO₃, the volumes of ethylene glycol used in the synthesis, and morphology of synthesized Ag nanoparticles at 150°C for 15 min.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>AgNO₃ (g)</th>
<th>PVP M.W. 1300K (g)</th>
<th>NH₄F (g)</th>
<th>EDTA (g)</th>
<th>Ratio</th>
<th>Cₐg⁺ (mM)</th>
<th>EG (ml)</th>
<th>Morphology of Ag nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>092504</td>
<td>0.225</td>
<td>0.2</td>
<td>---------</td>
<td>0.438</td>
<td>1</td>
<td>26.5</td>
<td>50</td>
<td>Skeleton structure Ag powder</td>
</tr>
<tr>
<td>092509</td>
<td>0.225</td>
<td>0.2</td>
<td>---------</td>
<td>0.109</td>
<td>0.25</td>
<td>6.6</td>
<td>50</td>
<td>Skeleton structure Ag powder</td>
</tr>
<tr>
<td>092612</td>
<td>0.225</td>
<td>0.2</td>
<td>---------</td>
<td>0.438</td>
<td>1</td>
<td>13.3</td>
<td>100</td>
<td>Skeleton structure Ag powder</td>
</tr>
<tr>
<td>092616</td>
<td>0.225</td>
<td>0.2</td>
<td>---------</td>
<td>0.109</td>
<td>0.25</td>
<td>3.3</td>
<td>100</td>
<td>Ag particles with different shapes</td>
</tr>
<tr>
<td>04031103</td>
<td>0.225</td>
<td>0.2</td>
<td>0.167</td>
<td>---------</td>
<td>3</td>
<td>26.5</td>
<td>50</td>
<td>Ag nanoparticles with few nanorods</td>
</tr>
<tr>
<td>04031104</td>
<td>0.225</td>
<td>0.2</td>
<td>0.333</td>
<td>---------</td>
<td>6</td>
<td>26.5</td>
<td>50</td>
<td>Ag nanoparticles and nanowires</td>
</tr>
<tr>
<td>04031307</td>
<td>0.225</td>
<td>0.2</td>
<td>0.167</td>
<td>0.263</td>
<td>------</td>
<td>26.5</td>
<td>50</td>
<td>Ag nanospheres</td>
</tr>
</tbody>
</table>

EDTA: ethylenediaminetetraacetic acid
EG: ethylene glycol
Ratio: Molar ratio of Ligand/Ag⁺
C: Concentration

In the synthesis of Ag nanoparticles, PVP served as a protecting agent. NH₄F and EDTA (H₄Y) are used to bond with Ag ions forming metal ion complexes. The reactions of NH₄F and EDTA with Ag⁺ are shown as follows:

\[
Ag^+ + nF^- \rightarrow AgF_n^{1-n} \quad (n = 1-6)
\]
\[ \text{Ag}^+ + \text{Y}^- \rightarrow \text{AgY}^{3-} \]

F\(^-\) ions can complex Ag ions with the formation of AgF\(_n\)^{1-n}. EDTA has the ability to chelate metal ions in 1:1 metal-to-EDTA complexes. The fully deprotonated form (all acidic hydrogens removed) of EDTA binds to the metal ion. The stability or equilibrium constants for different metals are different. The release rate of metal source depends on the stabilities of the complexes. Therefore, the growth rate of nanoparticles can be controlled by selecting different ligands or varying the ratio of ligands to metal source. The ligands of F\(^-\) or EDTA may also affect the morphology of synthesized metal nanoparticles.

Due to the formation of metal ion complexes, there were less free Ag ions in the reaction solution, leading to fewer nuclei formed. The complexes can release the metal source (Ag\(^+\)) gradually during the reducing reaction. Therefore, Ag nanoparticles of larger particle size can be obtained by adding ligands.

At higher Ag\(^+\) concentration (for sample 092504 and sample 092509), Ag powders with skeleton structure were produced with EDTA to AgNO\(_3\) ratio of 1 and 0.25. Figure 3-7 shows the scanning electron microscope (SEM) images of Ag particles (sample 092504) obtained with EDTA to Ag\(^+\) ratio of 1. At low Ag\(^+\) concentration, Ag particles (sample 092616) were synthesized with low EDTA to AgNO\(_3\) ratio of 0.25 (shown in Figure 3-8) and the particle size is above 1 µm. With high EDTA to AgNO\(_3\) ratio of 1 (for sample 092612), synthesized Ag powders also have skeleton structure.
Figure 3-7: SEM image of Ag nanoparticles (sample 092504) synthesized with EDTA to Ag+ ratio of 1 at high concentration of 26.5 mM at 150°C for 15 min.

Figure 3-8: SEM image of obtained Ag nanoparticles (sample 092516) with EDTA to Ag+ ratio of 0.25 at low concentration of 3.3 mM at 150°C for 15 min.
Figure 3-9 shows the TEM images of Ag nanoparticles synthesized with PVP as stabilizer and NH$_4$F as a ligand at 150ºC 15 min. With NH$_4$F to AgNO$_3$ ratio of 3, Ag nanoparticles with small amount of Ag rods were synthesized (shown in Figure 3-9 a). Particle size is approximately 71 nm on the average. With higher NH$_4$F to AgNO$_3$ ratio of 6, Ag nanoparticles with some Ag nanoparticles and wires were obtained (shown in Figure 3-9 b). Average particle size of Ag nanoparticles is about 83 nm. The length of Ag nanowires ranges from 150 nm to 1µm and the minor axis of Ag nanowires is approximately 40 nm on the average.

By adding EDTA along with NH$_4$F in the synthesis system, the Ag nanorods and wires were eliminated from the produced Ag particles (shown in Figure 3-10). This is probably because EDTA does not favor the growth along the direction of nanorods or wires. Synthesized Ag nanospheres are approximately 45 nm. Particle size distribution is shown in Figure 3-11.
Figure 3-9: TEM images of Ag nanoparticles synthesized with PVP as stabilizer and NH$_4$F as ligand at 150°C 15 min. (a, ratio of NH$_4$F to AgNO$_3$ is 3, sample 04031103; b, ratio of NH$_4$F to AgNO$_3$ is 6, sample 04031104).

Figure 3-10: Low (left) and high (right) magnification TEM images of silver nanoparticles synthesized with PVP and EDTA as protecting agents at 150°C 15 min. (sample 04031307 with NH$_4$F to EDTA ratio of 2)
3.3.1.4 Effects of NaOH

Yang et al., (2004)\textsuperscript{18} reported the mechanism of polyol reduction of Ru\textsuperscript{3+}. Accordingly, the mechanism of reduction of Ag\textsuperscript{+} by ethylene glycol is provided as follows:

\[
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \\
\text{CH}_3\text{CHO} + 2\text{Ag}^+ + 3\text{OH}^- & \rightarrow \text{CH}_3\text{COO}^- + \text{Ag} + 2\text{H}_2\text{O}
\end{align*}
\]

Therefore, adding NaOH increases the reaction rate. By adding NaOH in the reaction solution, silver strings were produced as shown in Figure 3-12 instead of nanoparticles.
3.3.2 Synthesis of Ag nanoparticles with ethanol as a reducing agent

Silver nanoparticles were synthesized with PVP or DDA as protecting agents when ethanol was used as a reducing agent. Table 3-5 lists the particle sizes of Ag nanoparticles synthesized under different reaction conditions at 150 °C for 15 min.
Table 3-5: Lists of particle sizes of Ag nanoparticles synthesized under different reaction conditions.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>AgNO$_3$ (g)</th>
<th>Weight of PVP (MW 40K) (g)</th>
<th>EG (ml)</th>
<th>Weight of DDA (mg)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>04081709</td>
<td>0.015</td>
<td>0.17</td>
<td>10</td>
<td>----</td>
<td>11.5 ± 1.4</td>
</tr>
<tr>
<td>05021401</td>
<td>0.022</td>
<td>0.12</td>
<td>20</td>
<td>5</td>
<td>8.4 ± 0.1</td>
</tr>
<tr>
<td>05021409</td>
<td>0.022</td>
<td>0.12</td>
<td>20</td>
<td>100</td>
<td>19.8 ± 2.2</td>
</tr>
<tr>
<td>05021414</td>
<td>0.022</td>
<td>----</td>
<td>20</td>
<td>100</td>
<td>&gt;200</td>
</tr>
</tbody>
</table>

When PVP was used as a protecting agent, the obtained Ag nanoparticles had irregular shape and had a very broad size distribution as shown in Figure 3-13.

![Figure 3-13: TEM image and particle size distribution of Ag nanoparticles (sample 04081709) synthesized with PVP alone as a protecting agent.](image)

When a small amount of DDA (5 mg) was added in the reaction solutions, monodispersed Ag nanoparticles were synthesized. The average particle size is approximately 8 nm. TEM image and particle size distribution is shown in Figure 3-14 a. Increase the amount of DDA (up to 100 mg) led to larger nanoparticles and a bimodal particle size distribution (shown in Figure 3-14 b). The average particle size is
approximately 20 nm. However, these Ag nanoparticles had defined shape compared with those synthesized with PVP alone as a protecting agent.

Figure 3-14: TEM images and particle size distributions of Ag nanoparticles synthesized by using ethanol as a reducing agent with the same amounts of PVP and different amounts of DDA as protecting agents. (a) sample 05021401, 5 mg DDA; (b) sample 05021409, 100 mg DDA)

The amine group of DDA can coordinate with Ag atoms on the surface of nanoparticles. Therefore, as a surfactant, DDA can prevent the growth of nanoparticles. When DDA was added in the reaction solution, monodispersed Ag nanoparticles were obtained. The amine group of DDA reacts with H$^+$ formed from the reduction reaction
with the formation of $\text{CH}_3\text{C}_11\text{H}_{22}\text{NH}_3^+$. The reduction rate can be effectively increased due to the decreased amount of $\text{H}^+$ when the amount of DDA is large enough. Consequently, the particle size was increased by adding a large amount of DDA.

In the synthesis, PVP is also a key factor. Without PVP, Ag particles larger than 200 nm were obtained (shown in Figure 3-15).

![TEM image of Ag nanoparticles](image)

**Figure 3-15:** TEM image of Ag nanoparticles (sample 05021414) synthesized with DDA alone as a protecting agent.

### 3.3.3 Optical properties of Ag nanoparticles

Ag nanoparticles exhibit optical properties due to the surface plasmon absorption arising from the collective oscillations of the free conduction band electrons induced by the incident electromagnetic radiation. Ag nanospheres of about 4.8 nm show UV-Vis absorption at 394 nm$^{12}$. The plasmon absorption of Ag nanoparticles is dependent on the
particle size and sensitive to the surrounding environment due to solvents altering the refractive index surrounding nanoparticles or solvents and protecting agents’ complexing with the metal surface\textsuperscript{19}. As the particles grow bigger, the absorption band broadens and covers the visible range\textsuperscript{20}. According to Mie’s theory, the extinction coefficient, $K$, for small particles, is approximately calculated by the following equation (Equation 3-1)\textsuperscript{21}:

$$K = \frac{18\pi NVn^{3/2}/\lambda}{\epsilon_2/[(\epsilon_1 + 2n^2)^2 + \epsilon_2^2]}$$  \hspace{1cm} \text{Equation 3-1}$$

where $N$ is the particle concentration, $V$ is the volume of the particles, $n$ is the index of refraction of the dielectric medium, $\lambda$ is the wavelength of incident light, and $\epsilon_1$ and $\epsilon_2$ are the real and imaginary parts of the complex dielectric constant of the particles, respectively. This equation is based on the assumptions that $N$ is low, the particles have uniform sizes and spherical shapes, and particle size ranges from of 3 to 20 nm. Based on this theory, Creighton and Eadon (1991)\textsuperscript{22} have reported the calculated optical spectrum of various metal nanoparticles in water and in vacuum. $K/NV$ was calculated according to Equation 3-1. The wavelength of incident light was chosen from 200 to 1200 nm. The index of refraction of ethylene glycol is 1.46. The dielectric constants as a function of wavelength for the bulk metal (Ag) were obtained from the book of Weaver \textit{et al.},\textsuperscript{23} used here for the calculation of UV-Vis spectrum of Ag nanoparticles. Figure 3-16 presents the calculated optical (UV-Vis) spectrum of Ag nanoparticles in ethylene glycol based on the, showing that the SPR absorption is at around 400 nm.
Figure 3-16: Calculated UV-Vis spectrum of Ag nanoparticles of less than 20 nm in ethylene glycol

Figure 3-17 shows the UV-Vis spectrum of synthesized Ag nanoparticles with different average particle sizes ranging from 19 to 36 nm. The UV-Vis absorptions are around 420 nm. Figure 3-18 shows the relationship between of average Ag nanoparticle size and UV-Vis absorption position. The UV-Vis absorptions slightly blue shifted from 424 nm to 417 nm with the average particle size decreasing from 36 nm to 19 nm.
Figure 3-17: UV-Vis spectra of synthesized Ag nanoparticles with different particle size ranging from 19 to 36 nm. The UV-Vis absorptions are around 420 nm. The UV-Vis absorptions have slight blue shift with decreasing particle size. Legend in this Figure gives the corresponding sample codes and average particle sizes.

Figure 3-18: Dependence of particle size on optical property of Ag nanoparticles. The UV-Vis absorptions are around 420 nm. The UV-Vis absorptions slightly blue shifted from 424 nm to 417 nm with the average particle size decreasing from 36 nm to 19 nm.
3.3.4 Comparison of microwave-assisted technique with conventional method

For comparison with microwave-hydrothermal method, Ag nanoparticles were synthesized by conventional-hydrothermal (C-H) method in an oven using Parr bombs. PVP of MW 40K was used in the C-H synthesis. Table 3-6 lists the particle sizes and morphology of synthesized Ag nanoparticles by C-H method and the details of the reaction conditions used in the synthesis.

Table 3-6: Quantities of chemicals used in the synthesis, the reaction time, and the particle sizes and morphology of synthesized Ag nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>AgNO3 (g)</th>
<th>PVP (g) (MW 40K)</th>
<th>EG (ml)</th>
<th>Reaction time (h)</th>
<th>Particle size (nm)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>05021304</td>
<td>0.015</td>
<td>0.5</td>
<td>100</td>
<td>1</td>
<td>16 ± 1</td>
<td>Nanospheres</td>
</tr>
<tr>
<td>05021305</td>
<td>0.015</td>
<td>0.5</td>
<td>100</td>
<td>2</td>
<td>35 ± 2</td>
<td>Nanosphere with a few nanorods</td>
</tr>
<tr>
<td>05021306</td>
<td>0.015</td>
<td>0.5</td>
<td>100</td>
<td>5</td>
<td>&gt;200</td>
<td>Bulk power with a few nanospheres</td>
</tr>
</tbody>
</table>

Figure 3-19 gives the TEM images of Ag nanoparticles synthesized in an oven at 150°C for 1, 2, and 5 hours. Nanoparticles of Ag synthesized with 1 h are spherical in shape and about 16 nm in size on the average (Figure 3-19 a), which is smaller than Ag nanoparticles (about 29 nm) synthesized with microwave heating for 15 min. Nanoparticles synthesized in an oven for 2 hours have similar shapes and particle size (35 nm) (shown in Figure 3-19 b) as nanoparticles synthesized with microwave-assisted method for 15 min. With longer time of 5 h, Ag particles larger than 200 nm (Figure 3-19 c) were obtained. Silver nanoparticles with similar shapes and sizes can be obtained with conventional method, though longer time is needed compared with microwave-
assisted method. Since Ag ions are easily reduced the only advantage of microwave-assisted method is time efficiency.

Figure 3-19. TEM images of Ag nanoparticles synthesized in an oven at 150°C for a, 1 h (sample 05021304); b, 2h (sample 05021305); and c, 5 h (sample 05021306).
3.4 Conclusion

Silver nanoparticles of about 10 nm to 1 µm have been synthesized with ethylene glycol as a reducing agent. The morphology and particle size of Ag nanoparticles were controlled by varying the concentration of Ag metal source (AgNO₃), PVP molecular weight, and ligands.

With different concentrations of Ag metal source, particle size of Ag nanoparticles was controlled and the average particle size ranged from 10 to 30 nm. Particle size increased initially up to a concentration of 1.76 mM AgNO₃ due to the availability of more Ag metal source for the growth of Ag nanoparticles. However, further increase of AgNO₃ concentration led to the decrease of Ag nanoparticle size probably because of large number of nuclei.

The particle size of synthesized Ag nanoparticles was also found to be dependent on the PVP molecular weight. When PVP with low molecular weight (8K, 10K, and 40K) were used in the synthesis, particle sizes of Ag nanoparticles synthesized were similar and average particle sizes were around 27 nm. When higher PVP molecular weight of 630K was used as a protecting agent, the average particle size decreased to about 10 nm. This is because PVP with higher molecular weight formed the stronger barrier surrounding Ag nanoparticles, thus prevented the growth of Ag nanoparticles. When PVP with molecular weight of 1300K was used, particle size was about 28 nm on the average. This is probably because PVP is too bulky to dissolve well in ethylene glycol and therefore there was not enough supply of this PVP to prevent growth.
On the other hand, the growth of Ag nanoparticles can be controlled by adding ligands in the reaction solutions. By binding Ag$^+$ ions with ligands, Ag nanoparticles with larger particle sizes were obtained. Adding ligands can also control the morphology of synthesized Ag nanoparticles. Furthermore, the growth rate of Ag particles was found to increase by adding NaOH in the system. Microwave-assisted method led to faster formation of Ag nanoparticles compared to the conventional method.

UV-Vis spectra show that Ag nanoparticles have absorption band around 400 nm and the absorption bands blue shifted when particle size decreased.
3.5 References


Chapter 4

Synthesis of Ni nanoparticles by using ethylene glycol as a reducing agent

4.1 Introduction

Magnetic nanoparticles, such as Fe, Co, and Ni, have attracted much attention due to their unique properties and applications in various fields. Ni nanoparticles have been used as electrode materials in multilayer ceramic capacitors, and catalysts\(^1,2\). Ni nanoparticles have been synthesized through many methods, such as chemical/electrochemical methods, sonochemical method\(^3\), microwave plasma deposition\(^4\), conventional polyol process\(^5\), and spray-pyrolysis method\(^4,6\) with various reducing agents. In order to get dispersed nanoparticles, Ni nanoparticles have also been synthesized and dispersed in Al\(_2\)O\(_3\) matrix, Al-MCM41 host, or in polymer matrix \(^7-9\). However, Ni nanoparticles with controlled morphology were obtained with limited success. Binary protecting agent systems were used by some researchers\(^10,11\) to control particle shape in the synthesis of CdSe and Co nanoparticles. Manna et al., (2000)\(^10\) reported the synthesis of shape controlled CdSe nanoparticles with a binary surfactant system containing tri-n-octylphosphine oxide (TOPO) and hexylphosphonic acid (HPA). Puntes et al., (2001)\(^11\) synthesized magnetic cobalt nanorods and nanospheres with narrow size distributions and a high degree of shape control by the injection of an organometallic precursor into a hot surfactant mixture of TOPO and oleic acid under inert atmosphere.
Hedge et al., (1996)\textsuperscript{12} have reported the synthesis of Ni powder of 135 nm according to the polylol process using polyvinylpyrrolidone (PVP) as a protective agent. Smaller size Ni powders (30 nm) have been obtained from Ni(OH)\textsubscript{2} in ethylene glycol (EG) and PVP using Pd or Pt as nucleating agents. In the above studies the particles are either larger or not well dispersed. In this work, microwave-assisted polylol method (M-P process) is reported for the synthesis of well-dispersed Ni nanoparticles with or without Pt seeding. Reducing reaction was carried out in a binary protecting agent system with polyvinyl pyrrolidone (PVP) and dodecylamine (DDA). Ni nanoparticles with controlled morphology and size were synthesized using this method. This technique is expected to be more cost-effective for large-scale production because it is simpler, for example, compared with the procedure of injection of an organometallic precursor into a hot surfactant mixture\textsuperscript{11}.

### 4.2 Experimental

Table 4-1 lists the materials used in the synthesis. Nickel acetate tetrahydrate was used as a metal precursor in all experiments. Ethylene glycol and PVP were used as a reducing agent and a protecting agent, respectively. DDA was used as a second protecting agent, which could coordinate with Ni ion precursor to affect the morphology of nanoparticles. Protecting agents, PVP and DDA, were dissolved in ethylene glycol. The metal precursor was mixed with the reducing agent and protecting agents. H\textsubscript{2}PtCl\textsubscript{6} was added in some cases to form the seeds for the synthesis of Ni nanoparticles in some experiments. The mixed solution was treated using a microwave digestion system
The microwave-assisted polyol (M-P) reactions were carried out at 195°C for 45 min. Conventional-polyol (C-P) experiments were carried out in Parr bombs heated in an oven in all cases and the C-P reactions were carried out for 2-17 hours. Structure of synthesized Ni nanoparticles was characterized by X-Ray Diffraction instrument (Scintag Pad V, q / 2-q vertical goniometer). The size and morphology of synthesized particles were determined using Transmission Electron Microscope, TEM (Philips 420, Tungsten based 120KeV). Size distribution histograms of synthesized Ni nanoparticles were calculated by Image J™ software based on the assumption that particles are spherical in size. Particle size was calculated with randomly choosing around 100 to 200 nanoparticles and based on 95% confidence interval. The EDS (Energy dispersive spectrometry) analysis was carried out with Cresham Sirius 30 Si (Li) X-ray detector attached to the Philip 420 TEM. The UV-Vis spectra were recorded on Agilent UV-Visible (UV-Vis) Spectrophotometer at 25°C, in the spectral range of 250 – 1100 nm, in 1 cm cuvettes.

Table 4-1: List of materials used in the synthesis

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Chemical name</th>
<th>Company</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal precursor</td>
<td>Nickel (II) acetate tetrahydrate</td>
<td>Aldrich Chemical Co., Inc</td>
<td>98%</td>
</tr>
<tr>
<td>Protecting agents</td>
<td>Polyvinyl pyrrolidone (PVP) (M W 40K)</td>
<td>Aldrich Chemical Company, Inc</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>n-Dodecylamine (DDA)</td>
<td>Avocado Research Chemicals Ltd</td>
<td>98%</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>Ethylene glycol, anhydrous</td>
<td>Sigma-Aldrich Inc</td>
<td>99.8%</td>
</tr>
</tbody>
</table>
4.3 Theoretical basis

For the synthesis of magnetic metal nanoparticles such as Ni and Co, it is difficult to make isolated magnetic nanoparticles, partially because the forces between the particles are large. These forces are due to the high electron affinity and the high surface tension arising from the partially filled d-orbital, from the van der Waals forces between polarizable metal particles, and from magnetic dipole interactions. The presence of PVP alone in ethylene glycol did not lead to the formation of well-dispersed Ni nanoparticles. With PVP as a protecting agent, large agglomerated Ni nanoparticles were obtained probably because the interaction between PVP and Ni metal particles was not strong enough to prevent the growth and agglomeration of metal particles. Therefore, introducing a second protecting agent that has stronger interaction with metal particles in the reaction system was considered for the synthesis of Ni nanoparticles. We selected DDA as a second protective agent. The effect of DDA added in the reaction solution was discussed briefly in chapter 3. In this chapter, the details of the contribution of DDA to the synthesis of Ni nanoparticles will be discussed.

The interaction between DDA and Ni ions appears to be stronger, and well-dispersed Ni nanoparticles could be obtained in the presence of DDA. The interaction between PVP and Ni metal may either be attributed to the donation of a pair of electrons from the carbonyl oxygen to the Ni ions or to the complex formation of the nitrogen on five-membered nitrogen-containing heterocycles with the Ni ions. Compared with DDA, PVP leads to weaker interaction due to the steric hindrance from the five-membered heterocycles. DDA provides a pair of electrons from the nitrogen at the end of
twelve-carbon chain. The steric hindrance from the twelve-carbon chain is smaller than that from five-membered heterocycles. From the UV-Vis absorptions of Ni$^{2+}$–PVP and Ni$^{2+}$–DDA–PVP (which will be discussed in the section 4.4.3 of optical properties), the blue shift of the absorption from Ni$^{2+}$–DDA–PVP solution also indicates that DDA has stronger interaction with Ni ions. Therefore, DDA, which has stronger binding with Ni or Ni ions, serves as a second protecting agent to prevent the growth and agglomeration of Ni nanoparticles.

Furthermore, according to the reduction mechanism, DDA can also increase the reaction rate and lead to the formation of Ni nanoparticles. Yang et al., (2004) and Horiuchi et al., (2003)\textsuperscript{14,15} reported the mechanism of polyol reduction of metal ions. Accordingly, the mechanism of reduction of Ni$^{2+}$ by ethylene glycol is provided as follows:

\[
\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CHO} + \text{Ni}^{2+} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + \text{Ni} + 3\text{H}^+
\]

The amine group of DDA reacts with H$^+$ formed from the reduction reaction with the formation of CH$_3$C$_{11}$H$_{22}$NH$_3^+$. The reduction rate can be effectively increased due to the decreased amount of H$^+$ when the amount of DDA is large enough.

Therefore, DDA can prevent the growth and agglomeration of Ni nanoparticles, due to stronger binding with Ni metal. On the other hand, DDA also increases the reduction reaction rate, therefore, leads to the formation of Ni nanoparticles. When both DDA and PVP are used in the system, the effects on Ni nanoparticle formation depend on the PVP molecular weight and the amount of DDA added in the reaction system.
4.4 Results and discussion

4.4.1 Effects of the amount of DDA added in the reduction reaction system

4.4.1.1 Effects on morphology of synthesized Ni nanoparticles

Ni metal nanoparticles were synthesized with Pt as seeds which will accelerate the nucleation rate. Table 4-2 lists the quantities of various chemicals and volumes of ethylene glycol used in the microwave-polyol synthesis of Ni nanoparticles of different sizes.
Table 4-2: List of different amounts of DDA added, quantities of various chemicals, volumes of ethylene glycol used in the Microwave-Polyol experiments at 195°C/45 min for low concentration of metal source, and the morphology and particle size of synthesized Ni nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Metal precursor (mg)</th>
<th>Weight of PVP (mg)</th>
<th>Weight of DDA (mg)</th>
<th>Volume of ethylene glycol (mL)</th>
<th>Amount of H₂PtCl₆ (mg)</th>
<th>Particle size (nm)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nickel acetate tetrahydrate</td>
<td>MW 630K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>04062707</td>
<td>7.8</td>
<td>120</td>
<td>----</td>
<td>20</td>
<td>0.98</td>
<td>&gt;100</td>
<td>Agglomerated particles</td>
</tr>
<tr>
<td>04080204</td>
<td>7.8</td>
<td>120</td>
<td>1</td>
<td>20</td>
<td>0.98</td>
<td>&gt;100</td>
<td>Agglomerated particles with a few nanoparticles and strings</td>
</tr>
<tr>
<td>04072804</td>
<td>7.8</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
<td>63 ± 2</td>
<td>Nanoparticles with polygon shape</td>
</tr>
<tr>
<td>04071216</td>
<td>7.8</td>
<td>120</td>
<td>20</td>
<td>20</td>
<td>0.98</td>
<td>56 ± 6</td>
<td>Nanoparticles with irregular shape</td>
</tr>
<tr>
<td>04070806</td>
<td>7.8</td>
<td>120</td>
<td>1000</td>
<td>20</td>
<td>0.98</td>
<td>37 ± 2</td>
<td>Nanoparticles with irregular shape</td>
</tr>
</tbody>
</table>

Figure 4-1 shows the X-ray diffraction (XRD) pattern of Ni nanoparticles synthesized with different amounts of DDA added in the reaction solutions (Figure 4-1 a, sample 04062707 without DDA; Figure 4-1 b, sample 04072804 with 5 mg DDA; Figure 4-1 c, sample 04071216 with 20 mg DDA). XRD patterns (Figure 4-1) prove the formation of Ni metal particles. Without or with small amount of DDA (5 mg) in the synthesis system, Ni particles with FCC (face centered cubic) structure were synthesized (Figure 4-1 a and b). With 20 mg DDA added in the synthesis system, Ni particles with both FCC and Hexagonal structure were synthesized. The intensity of XRD pattern
decreases by increasing the amount of DDA, indicating the particle size decreases. Increasing the amount of DDA leads to two polymorphs of Ni metal as can be seen from the inset in Figure 4-1. The inset shows the two small peaks of hexagonal structure (010 and 002) and one peak of FCC structure (111) as shown in Figure 4-1 c.

![X-ray diffraction (XRD) patterns](image)

**Figure 4-1:** X-ray diffraction (XRD) patterns of Ni nanoparticles synthesized with different amount of DDA added in the reaction solutions. (a, sample 04062707 without DDA; b, sample 04072804 with 5 mg DDA; c, sample 04071216 with 20 mg DDA). Inset shows the two small peaks of hexagonal structure (010 and 002) and one peak of FCC structure (111) of sample c, 04071216.

**Figure 4-2** (a-e) shows the morphologies of Ni particles formed by M-P process with PVP of molecular weight 630K, with or without DDA. Agglomerated large Ni metal
particles (larger than 100 nm) were formed without adding DDA (shown in Figure 4-2 a).
The presence of PVP alone in ethylene glycol did not give rise to the formation of well-dispersed Ni nanoparticles, which indicates that the interaction between PVP and Ni ion might not be strong enough to prevent the growth and agglomeration of Ni particles. Therefore, adding a second protecting agent to interact with Ni is a possible method to prevent the growth and agglomeration of Ni particles. The interaction between DDA and Ni appears to be stronger, and well-dispersed Ni nanoparticles could be obtained. The morphology of Ni metal was changed by adding DDA as a second protecting agent apparently because of the interaction with Ni. By adding 1mg amount of DDA, a small amount of Ni nanoparticles in the form of strings was obtained. (shown in Figure 4-2 b). Well-dispersed Ni nanoparticles of 63 ± 2 nm (based on 95% confidence interval) were obtained with an apparently optimum amount of DDA (5 mg), as shown in Figure 4-2 c. These nanoparticles have a tendency to form chain-like organization. With increasing amount of the DDA, the size and arrangement of Ni nanoparticles changed. By further increasing the amount of DDA (20 mg), these Ni nanoparticles had different morphology with irregular shapes and the average particle size is 56 ± 6 nm. (TEM image is shown in Figure 4-2 d). When the amount of added DDA reached 1000mg, particle size further decreased to 37 ± 2 nm and particles had irregular shapes (shown in Figure 4-2 e).
Figure 4-2: TEM images of Ni particles formed by M-P process with PVP of molecular weight 630K (a, sample 04062707, without DDA; b-e, sample 04080204, with 1mg; sample 04072804, with 5mg; sample 04071216, 20mg; and sample 04070806, 1000mg DDA, respectively)
Selected area electron diffraction (SAED) pattern (Figure 4-3) verifies formation of crystallized Ni particles (in Figure 4-2 c) with FCC structure. The SAED pattern shows Debye rings assigned to \{111\} (d1=2.07Å), \{200\} (d2=1.79Å), \{220\} (d3=1.24Å), and \{311\} (d4 = 1.08Å) (The d values were calculated from SAED pattern.). Figure 4-4 presents SAED pattern of Ni nanoparticle synthesized with 20 mg DDA (sample 04071216), showing the synthesized Ni nanoparticles with 20 mg DDA have two different structures i.e., FCC and hexagonal structures. Energy dispersive spectrometries further prove the formation of Ni nanoparticles. Figure 4-5 presents the EDS spectrum of Ni nanoparticles given in Figure 4-2 c proving the formation of Ni metal nanoparticles. Peaks corresponding to Cu and C in the EDS spectrum resulted from the copper grid with carbon film. In this spectrum, a very small oxygen peak also appeared. This might be due to the surface oxidation of Ni nanoparticles or more likely due to the residue of surfactant around the nanoparticles.
Figure 4-3: Selected area electron diffraction (SAED) pattern of Ni nanoparticles in Figure 4-2 c. This pattern verifies formation of crystallized Ni particles (in Figure 4-2 c) with FCC structure. Debye rings are assigned to \(\{111\}\) (d1=2.07Å), \(\{200\}\) (d2=1.79Å), \(\{220\}\) (d3=1.24Å), and \(\{311\}\) (d4 = 1.08Å).

Figure 4-4: Selected area electron diffraction (SAED) pattern of Ni nanoparticles in Figure 4-2 d. This pattern verifies the formation of crystallized Ni particles with FCC structure and hexagonal structure.
Figure 4-5: Energy dispersive spectrometry of Ni nanoparticles synthesized with different amounts of DDA added (1 mg, sample 04080204 in Figure 4-2 b; 5 mg, sample 04072804 in Figure 4-2 c; and 20 mg, sample 04071216 in Figure 4-2 d). The EDS spectrum further proves the formation of Ni metal nanoparticles.

4.4.1.2 Effect on the particle size of synthesized Ni nanoparticles

Table 4-3 lists the different amounts of DDA added and particle size of Ni nanoparticles synthesized with different PVP molecular weights.
Table 4-3: List of different amounts of DDA added, different molecular weights of PVP used, quantities of various chemicals used in the Microwave-Polyol experiments at 195°C/45 min for low concentration of metal source, and the particle size of resulted Ni nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Metal precursors, mg</th>
<th>Weight of PVP, mg</th>
<th>Weight of DDA, mg</th>
<th>Volume of ethylene glycol, mL</th>
<th>Amount of H$_2$PtCl$_6$, mg</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nickel acetate tetrahydrate</td>
<td>MW 1300K</td>
<td>MW 630K</td>
<td>MW 40K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>04080201</td>
<td>7.8</td>
<td>120</td>
<td>1</td>
<td>20</td>
<td>0.98</td>
<td>51</td>
</tr>
<tr>
<td>04080204</td>
<td>7.8</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
<td>83</td>
</tr>
<tr>
<td>05012501</td>
<td>7.8</td>
<td>120</td>
<td>10</td>
<td>20</td>
<td>0.98</td>
<td>0</td>
</tr>
<tr>
<td>04072804</td>
<td>7.8</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
<td>63</td>
</tr>
<tr>
<td>05012501</td>
<td>7.8</td>
<td>120</td>
<td>10</td>
<td>20</td>
<td>0.98</td>
<td>107</td>
</tr>
<tr>
<td>04071216</td>
<td>7.8</td>
<td>120</td>
<td>20</td>
<td>20</td>
<td>0.98</td>
<td>56</td>
</tr>
<tr>
<td>05013109</td>
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<td>100</td>
<td>10</td>
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<td>32</td>
</tr>
<tr>
<td>04072806</td>
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<td>20</td>
<td>0.98</td>
<td>61</td>
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<tr>
<td>04080901</td>
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<td>0.98</td>
<td>68</td>
</tr>
<tr>
<td>04071217</td>
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<td>120</td>
<td>20</td>
<td>20</td>
<td>0.98</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 4-6 presents the relationship of particle size and the amount of DDA added. Initially, particle size increased with a small increase in the amount. With a further increase in the amount of DDA, particle size decreased (Figure 4-6). In the case of PVP molecular weight of 1300K, Ni nanoparticles did not form. The possible mechanism is as follows:

With small amount of DDA, DDA interacts with Ni metal particles first and prevents the growth and agglomeration. With a small increase of DDA, the extra amount of DDA interacts with H$^+$ formed by this reduction reaction, thus increases the reaction rate. Therefore, particle size increased. By further increasing the amount of DDA, due to large amount of excessive DDA surrounding growing Ni particles, the barrier formed by DDA prevents the growth of Ni nanoparticles. When PVP of molecular weight 1300K
was used, Ni nanoparticles did not form with small amount of DDA (10 mg) because of the stronger steric hindrance of higher molecular weight.

Figure 4-6: Relationship of amount of DDA added in 20 ml ethylene glycol and particle size of Ni nanoparticles synthesized with PVP of different molecular weight. With a small amount of increase of DDA, particle size increases. With further increase of DDA amount, particle size decreases.

**4.4.1.3 Effect on the formation of Ni nanoparticles**

Besides its contribution to the control of Ni nanoparticle morphology and size, DDA can also be helpful in the formation of Ni nanoparticles when Pt metal source is not used to form seeds for the formation of Ni nanoparticles. At high concentration of metal source and PVP, as listed in Table 4-4. Ni metal particles can not be produced without adding DDA or with a small amount of DDA.
Table 4-4: Quantities of various chemicals and volumes of ethylene glycol used in the microwave-polyol experiments at 200ºC/60 min for high concentration of metal source, PVP, and DDA.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Metal precursors (mg)</th>
<th>Weight of PVP (mg)</th>
<th>Weight of DDA (mg)</th>
<th>Volume of ethylene glycol (mL)</th>
<th>Molar ratio of DDA to PVP repeating unit</th>
<th>Formation of Ni nanoparticles</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>04030201</td>
<td>Nickel acetate tetrahydrate</td>
<td>600</td>
<td>------</td>
<td>20</td>
<td>0</td>
<td>No</td>
<td>---</td>
</tr>
<tr>
<td>04030204</td>
<td>99.2</td>
<td>600</td>
<td>20</td>
<td>20</td>
<td>0.02</td>
<td>No</td>
<td>---</td>
</tr>
<tr>
<td>04030207</td>
<td>99.2</td>
<td>600</td>
<td>40</td>
<td>20</td>
<td>0.04</td>
<td>Yes</td>
<td>72 ± 5</td>
</tr>
<tr>
<td>04030208</td>
<td>99.2</td>
<td>600</td>
<td>1000</td>
<td>20</td>
<td>1</td>
<td>Yes</td>
<td>106 ± 3</td>
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<tr>
<td>04030209</td>
<td>99.2</td>
<td>600</td>
<td>2000</td>
<td>20</td>
<td>2</td>
<td>Yes</td>
<td>74 ± 6</td>
</tr>
</tbody>
</table>

With high concentration of PVP, the steric hindrance of PVP around Ni ions prevents the nucleation and growth of Ni particles. By increasing the amount of DDA, Ni nanoparticles were synthesized. The particle size and size distribution were changed by further increasing the amount of DDA. Figure 4-7 (a-c) shows the TEM images of Ni nanoparticles (sample 04030207, 04030208, and 04030209, respectively) synthesized with different ratios of DDA to PVP repeating unit. At DDA to PVP repeating unit ratio of 0.04, nonuniform Ni nanoparticles were produced. The particle size is approximately 72 ± 5 nm and particle size distribution is broad ranging from about 20 to 140 nm. Uniform Ni nanoparticles of about 106 nm on average were synthesized with a DDA to PVP repeating unit ratio of 1. Particle size ranges mainly from 100 to 120 nm. At DDA to PVP repeating unit ratio of 2, Ni nanoparticles with bimodal size (about 60 and 100 nm) distribution were obtained and particle size is 74 ± 6 nm.
Figure 4-7: TEM images and particle size distributions of Ni nanoparticles synthesized with different DDA amounts of a, (sample 04030207) 0.04g; b, (sample 04030208) 1g; and c, (sample 04030209) 2g.
4.4.2 Effects of PVP on the morphology and particle size of synthesized Ni nanoparticles

4.4.2.1 Effect of PVP on the morphology of synthesized Ni nanoparticles

Ni nanoparticles were also synthesized without PVP. Figure 4-8 shows the TEM image of Ni nanoparticles synthesized with DDA alone as a protecting agent. The other reaction condition and quantities of chemicals used in reaction solution are exactly the same as those of sample 04072804 in Figure 4-2 c. The TEM image shows that the synthesized Ni nanoparticles agglomerate and particle size is not uniform, indicating that both PVP and DDA contribute to the formation of well-dispersed Ni nanoparticles.

Figure 4-8: TEM image of Ni nanoparticles synthesized without PVP and with the other reaction conditions being the same as sample 04072804 in Figure 4-2 c.
4.4.2.2 Effects of PVP molecular weight on the morphology and particle size of synthesized Ni nanoparticles

PVP molecular weight is another important factor controlling the size and shape of synthesized Ni nanoparticles. Table 4-5 lists the different PVP molecular weights used in the synthesis of Ni nanoparticles when the amounts of DDA added in the reaction solution are kept constant.

Table 4-5: List of different PVP molecular weight used, quantities of various chemicals, volumes of ethylene glycol used in the Microwave-Polyol experiments at 195ºC/45 min for low concentration of metal source, and morphology of synthesized Ni nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Metal precursors (mg)</th>
<th>Molecular weight of PVP (0.12g)</th>
<th>Weight of DDA (mg)</th>
<th>Volume of ethylene glycol (mL)</th>
<th>Amount of H$_2$PtCl$_6$ (mg)</th>
<th>Morphology</th>
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<tr>
<td>04080307</td>
<td>7.8</td>
<td>10K</td>
<td>1</td>
<td>20</td>
<td>0.98</td>
<td>Larger particles</td>
</tr>
<tr>
<td>04080204</td>
<td>7.8</td>
<td>630K</td>
<td>1</td>
<td>20</td>
<td>0.98</td>
<td>Agglomerated particles and strings with a few nanoparticles</td>
</tr>
<tr>
<td>04080201</td>
<td>7.8</td>
<td>1300K</td>
<td>1</td>
<td>20</td>
<td>0.98</td>
<td>Nanoparticles with polygon shape</td>
</tr>
</tbody>
</table>

Figure 4-9 shows the TEM images of Ni nanoparticles synthesized with PVP of different molecular weights by adding the same amount of DDA (1 mg). With PVP molecular weight of 10k, synthesized Ni nanoparticles have larger particle size of about 133 nm on average (shown in Figure 4-9 a). With PVP molecular weight of 630K, Ni strings and a small amount of Ni nanoparticles were obtained (Figure 4-9 b). By increasing the PVP molecular weight (1300K), dispersed Ni nanoparticles of smaller particle size were obtained. Their particle size is about 55 ± 4 nm (Figure 4-9 c).
Figure 4-9: TEM images of Ni nanoparticles synthesized with PVP of different molecular weights (a, 10K; b, 630K; c, 1300K) by adding 1mg DDA. (a, sample 04080307; b, sample 04080204; c, sample 04080201)
To form well-separated Ni nanoparticles, the amount of DDA can be decreased with increasing molecular weight of PVP because PVP of higher molecular weight provides stronger steric hindrance due to the larger size. With low PVP molecular weight, such as 40K, the steric barrier formed at the surface of Ni particles is not as strong as that formed with high PVP molecular weight. Therefore, larger amount of DDA is needed to form well-dispersed Ni nanoparticles compared with using PVP of higher molecular weight. Table 4-6 lists the optimum amounts of DDA needed for the formation of well-dispersed Ni nanoparticles with PVP of different molecular weights. Figure 4-10 presents the approximate linear relationship of PVP molecular weight and the optimum amount of DDA added in the reaction solutions.

Table 4-6: Optimum amount of DDA needed for the formation of well-dispersed Ni nanoparticles with PVP of different molecular weight and particle size of synthesized Ni nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Metal precursors (mg)</th>
<th>Weight of PVP (mg)</th>
<th>Weight of DDA (mg)</th>
<th>Volume of ethylene glycol (ml)</th>
<th>Amount of H$_2$PtCl$_6$ (mg)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni(CH$_3$CO$_2$)$_2$•4H$_2$O MW 40K MW 630K MW 1300K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>04080901</td>
<td>7.8</td>
<td>120</td>
<td>---</td>
<td>10</td>
<td>20</td>
<td>0.98</td>
</tr>
<tr>
<td>04072804</td>
<td>7.8</td>
<td>---</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
</tr>
<tr>
<td>04080201</td>
<td>7.8</td>
<td>---</td>
<td>---</td>
<td>1</td>
<td>20</td>
<td>0.98</td>
</tr>
</tbody>
</table>
By manipulating the amount of DDA and the molecular weight of PVP, not only the morphology but also the particle size can be controlled. Figure 4-11 shows TEM images and size distributions of Ni nanoparticles synthesized with different molecular weights of PVP and the optimum amount of DDA. With the PVP molecular weight of 40K and 10 mg DDA, particles size of synthesized Ni nanoparticle is $68 \pm 4$ nm (shown in Figure 4-11 a). With PVP molecular weight of 630K and 5 mg DDA, particle size is $63 \pm 2$ nm (Figure 4-11 b). With PVP molecular weight of 1300K and 1 mg DDA, particle size is $51 \pm 2$ nm (shown in Figure 4-11 c).
Figure 4-11: TEM images of Ni nanoparticles synthesized with PVP of different molecular weights by adding the optimum amount of DDA. (a, sample 04080901 with PVP of MW 40K and 10 mg DDA; b, sample 04072804 with PVP of 630K and 5 mg DDA; c, sample 04080201 with PVP of 1300K and 1 mg DDA.)
By increasing the molecular weight of PVP, particle size decreased. This is because the higher the PVP molecular weight the stronger is it’s steric hindrance, which contributes to preventing the growth of Ni nanoparticles. Figure 4-12 shows the approximate linear relationship between PVP molecular weight and average particle size.

![Graph showing relationship between PVP molecular weight and average particle size.](image)

**Figure 4-12**: Relationship of PVP molecular weight and average particle size of Ni nanoparticles synthesized with optimum amount of DDA.

### 4.4.3 Optical properties of Ni nanoparticles

UV-Vis absorbance spectra of Ni nanoparticles were obtained in ethanol. Ni\(^{2+}\) and PVP mixture and Ni\(^{2+}\), PVP, and DDA mixture were dissolved in ethanol and their UV-Vis spectra were also collected. The reaction mixture of synthesized Ni nanoparticles in ethylene glycol was diluted with ethanol prior to UV-Vis experiments. Based on
theoretical calculation, Ni nanoparticles exhibit surface plasmon resonance (SPR) absorption between 300 nm and 400 nm\textsuperscript{16}. It has been reported that Ni-implanted silica glass exhibited absorptions at 354 nm\textsuperscript{17}.

Figure 4-13 presents the calculated UV-Vis spectrum of Ni nanoparticles according to the Equation 3-1, showing the SPR absorption of Ni nanoparticles is at about 330 nm. The optical constants as a function of wavelength for the bulk metal (Ni) were taken from the article of Johnson (1974)\textsuperscript{18} for the calculation of UV-Vis spectrum of Ni nanoparticles. The index of refraction of ethanol is 1.36.

![Image of graph](image_url)

Figure 4-13: Calculated UV-Vis spectrum of Ni nanoparticles of less than 20 nm.

Figure 4-14 shows the UV-Vis absorbance spectra from Ni\textsuperscript{2+}—PVP, Ni\textsuperscript{2+}—PVP—DDA, and Ni nanoparticles stabilized with PVP and DDA in ethanol. Ni ions in solution exhibit two absorption bands assigned to crystal field transition of octahedral Ni\textsuperscript{2+}: one strong band at around 400 nm and one weak band at about 600 to
800 nm. The two absorption bands of Ni\(^{2+}\)-DDA-PVP solution are slightly shifted towards shorter wavelengths compared to that of Ni\(^{2+}\) - PVP only, indicating that DDA has stronger binding with Ni ions. The UV-Vis absorption of reaction solution of Ni nanoparticles stabilized with PVP and DDA shows one peak at around 300 to 350 nm attributed to SPR absorption of Ni nanoparticles, which proves the formation of Ni nanoparticles.

Figure 4-14: UV-Vis absorbance spectra from ethanol solution of Ni\(^{2+}\)–PVP, Ni\(^{2+}\)–PVP—DDA, and synthesized Ni nanoparticles stabilized with PVP and DDA (sample 05013108).

Figures 4-15 and 4-16 show the UV-Vis spectra of Ni nanoparticles synthesized with PVP of different molecular weights (630K and 1300K). Compared with the UV-Vis absorption of Ni nanoparticles synthesized with PVP molecular weight of 630K, SPR absorptions band of Ni nanoparticles produced with PVP molecular weight of 1300K are
broad and weak. This is probably because the effect of PVP surrounding Ni nanoparticles on the SPR absorption. The interaction between PVP and Ni ions broadens the SPR absorption band. PVPs with higher molecular weight have more N or O atoms to bind with Ni nanoparticles, thus broaden the SPR absorption band.
Figure 4-15: UV-Vis absorbance spectra from ethanol solution of synthesized Ni nanoparticles stabilized with DDA and PVP with molecular weight of 630K (sample 04072804 and 05013109).

Figure 4-16: UV-Vis absorbance spectra from ethanol solution of synthesized Ni nanoparticles stabilized with DDA and PVP with molecular weight of 1300K (sample 04080201 and 04072801).
4.4.4 Comparison of microwave-assisted technique with conventional method

Ni nanoparticles were synthesized by conventional polyol (C-P) method and compared with those of M-P method. The reduction reactions were carried out at 195 °C for 2 h, 5 h, and 17 h in an oven by the former method. Table 4-7 lists the reaction time and the quantities of chemicals of reaction solutions.

Table 4-7: List of reaction time and quantities of chemicals of reaction solutions carried out at 195°C and the formation and morphology and Ni nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Metal precursor (mg)</th>
<th>Weight of PVP (mg)</th>
<th>Weight of DDA (mg)</th>
<th>Volume of ethylene glycol (mL)</th>
<th>Amount of H$_2$PtCl$_6$ (mg)</th>
<th>Reaction time (h)</th>
<th>Formation of Ni nanoparticles</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>04121606</td>
<td>Nickel acetate tetrahydrate 7.8</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
<td>2</td>
<td>No</td>
<td>Agglomerated nanoparticles</td>
</tr>
<tr>
<td>05011701</td>
<td>Nickel acetate tetrahydrate 7.8</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
<td>5</td>
<td>Yes</td>
<td>Agglomerated nanoparticles</td>
</tr>
<tr>
<td>04120101</td>
<td>Nickel acetate tetrahydrate 7.8</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>0.98</td>
<td>17</td>
<td>Yes</td>
<td>Agglomerated nanoparticles</td>
</tr>
</tbody>
</table>

Ni nanoparticles did not form with a reaction time of 2 h. By increasing reaction time up to 5 h and 17 h, Ni particles were synthesized. Figure 4-17 shows the TEM images of synthesized Ni nanoparticles. With conventional method, larger and agglomerated Ni particles were synthesized. This is probably because with conventional heating, the reaction solution cannot quickly reach the high temperature needed for the reaction. Large number of nuclei did not form for the growth of Ni nanoparticles. Therefore, the particle size was large due to agglomeration. These results clearly show
that the formation of Ni nanoparticles by M-P process is faster than that with C-P process.

Figure 4-17: TEM images of Ni nanoparticles synthesized with conventional method. (Reaction solutions were carried out in an oven at 195 °C, a, sample 05011701, for 5 h, and b, sample 04120101, 17 hours)

4.5 Conclusion

Well-dispersed Ni nanoparticles of about 37 to 107 nm were synthesized in a binary protecting agent system of PVP and DDA with or without Pt seeding. With small amount of DDA added in the reaction solution, Ni nanoparticles were obtained by adding H$_2$PtCl$_6$ in the reaction solution to form Pt nanoparticles as seeds for the nucleation and growth of Ni nanoparticles. The morphology and size of Ni nanoparticles were dependent on the amount of DDA added in these systems. Without DDA or with a small amount of DDA added, Ni metal particles mainly interact with PVP. PVP alone can not prevent the growth and agglomeration of Ni particles well, therefore, larger Ni particles with
agglomeration were obtained. DDA helps to prevent the growth and agglomeration of Ni particles. With a small increase of the amount of DDA, well-dispersed Ni nanoparticles were produced. When the amount of DDA increased, extra DDA reacted with $\text{H}^+$ resulting from the reduction reaction and thus increased the reaction rate. Therefore, the particle size increased. By further increasing the amount of DDA, excessive DDA surrounded the Ni nanoparticles forming a barrier, which prevented the growth of Ni nanoparticles and hence particle size decreased. The particle size of synthesized Ni nanoparticles was also affected by the molecular weight of PVP. PVP with higher molecular weight formed a thicker barrier surrounding Ni nanoparticles. Therefore, the optimum amount of DDA for the formation of well-dispersed Ni nanoparticles can be decreased by using higher molecular weight of PVP.

Adding large amounts of DDA is also helpful for the formation of Ni nanoparticles without the use of Pt metal source to form seeds in reaction solutions. The particles size and size distributions were controlled by changing the amount of DDA added in the reaction solution. With a proper amount of DDA, monodispersed Ni nanoparticles were obtained. With highly excessive amount of DDA Ni nanoparticles with bimodal size distribution were obtained.

UV-Vis spectra show that synthesized Ni nanoparticles have absorption band around 300 to 350 nm. When higher molecular weight PVP coordinated with Ni nanoparticles, broad and weak absorption peaks resulted.

Compared with conventional method, microwave-assisted method produced well-dispersed Ni nanoarticles and microwave-assisted polyol process is faster than conventional-polyol process in the synthesis of Ni nanoparticles.
4.6 References


Chapter 5

Synthesis of Pd nanoparticles by using methanol and ethanol as reducing agents

5.1 Introduction

Palladium is one of the most important catalytic materials that is used in various reactions in both industry and fundamental chemistry\(^1\), hence its physical and chemical properties have been extensively investigated\(^2-4\). Palladium nanoparticles can also be used in fuel cells and gas sensors\(^2,3\). The size of dispersed metallic clusters affects not only their chemical activity but also their application in technology of fuel cells, gas sensors and heterogeneous catalysis\(^4\). Different approaches have been developed to synthesize Pd nanoparticles, including electrochemical deposition\(^5,6\), sonochemical decomposition\(^7,8\), interfacial synthesis\(^9\), and chemical methods by using a variety of reducing agents\(^10,11\).

In order to get monodispersed nanoscale particles, polymers, surfactants, and ligands, are often used as stabilizing matrices\(^10,12-14\). It was reported that during synthesis the size of Pd nanoparticles can be manipulated by changing the type of protecting agents and the amount of protecting agents and metal precursors\(^10,12\). Palladium nanoparticles were synthesized with the mean diameter ranging from 1.7 to 3.0 nm by changing the amount of protective polymer, poly(N-vinyl-2-pyrrolidone) (PVP) and the kind and/or the concentration of alcohol (methanol, ethanol, or 1-propanol) in the solvent\(^10\). Palladium nanoparticles ranging from 6.2 to 18.5 nm of diameter were obtained by using various surfactants at predetermined concentrations of surfactants and the metal precursor\(^12\).
Methanol and ethanol have been used as reducing agents in many syntheses of metal nanoparticles\textsuperscript{10,15}. In this study, the synthesis of Pd nanoparticles with microwave-assisted method has been investigated using methanol and ethanol as reducing agents. PVP was used as protecting surfactant. Particle size was controlled in the range of 2 to 10 nm by manipulating the concentration of PVP and the metal precursor in this study.

5.2 Experimental

The materials used in the synthesis of Pd nanoparticles are listed in Table 5-1. Polyvinylpyrrolidone with an average molecular weight of 40K was first dissolved in methanol or ethanol. Methanol and ethanol act as both reducing agents and solvents in the synthesis procedure. Table 5-2 lists the quantities of chemicals and volumes of methanol and ethanol used in the synthesis. Palladium (II) 2,4-pentanedionate was used as metal precursor. This metal cation was added to the methanol-PVP and ethanol-PVP solutions. The reactants were heated at 90\textdegree C and 120\textdegree C for 60 min by using a microwave digestion system. The particle size, shape, size distribution, and state of aggregation were determined by Philips 420 or JEOL 2010F transmission electron microscope operated at 120KeV and 200KeV, respectively. The TEM sample was prepared by placing several drops of the reaction solution onto a carbon-coated copper grid (300 mesh), followed by evaporating the ethanol in air at room temperature. The particle size distribution was calculated with Image J\textsuperscript{TM} software by collecting about 100 nanoparticles and particle size was calculated based on 95\% confidence interval.
Table 5-1: List of materials used in the synthesis of Pd nanoparticles.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Company</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal precusor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palladium (II) 2,4-pentanedionate</td>
<td>Alfa Aesar A Johnson Matthey Company</td>
<td>Pd 34.7% (assay)</td>
</tr>
<tr>
<td>Protecting agent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVP) (M W 40K)</td>
<td>Aldrich Chemical Company, Inc</td>
<td></td>
</tr>
<tr>
<td>Reducing agents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>Aldrich Chemical Company</td>
<td>99.8%</td>
</tr>
<tr>
<td>Ethanol 200 proof anhydrous</td>
<td>Aldrich Chemical Company</td>
<td>99.5%</td>
</tr>
</tbody>
</table>

Table 5-2: The Concentrations of chemicals and volumes of methanol and ethanol used in the synthesis under different reaction temperatures for 60 min.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>C_{Metal precursor}, mM</th>
<th>C_{PVP}, mM</th>
<th>R</th>
<th>V_{methanol}, ml</th>
<th>V_{ethanol}, ml</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd(C_5H_7O_2)_2 MW 40K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>04081710</td>
<td>9</td>
<td>0.4</td>
<td>18</td>
<td>10</td>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td>04081712</td>
<td>9</td>
<td>0.4</td>
<td>18</td>
<td>10</td>
<td></td>
<td>120°C</td>
</tr>
<tr>
<td>04082016</td>
<td>9</td>
<td>0.04</td>
<td>1.8</td>
<td>10</td>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td>04082028</td>
<td>9</td>
<td>0.04</td>
<td>1.8</td>
<td>10</td>
<td></td>
<td>120°C</td>
</tr>
<tr>
<td>04082019</td>
<td>0.9</td>
<td>0.04</td>
<td>18</td>
<td>10</td>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td>04082029</td>
<td>0.9</td>
<td>0.04</td>
<td>18</td>
<td>10</td>
<td></td>
<td>120°C</td>
</tr>
<tr>
<td>04081406</td>
<td>9</td>
<td>0.4</td>
<td>18</td>
<td>10</td>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td>04081908</td>
<td>9</td>
<td>0.04</td>
<td>1.8</td>
<td>10</td>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td>04081928</td>
<td>9</td>
<td>0.04</td>
<td>1.8</td>
<td>10</td>
<td></td>
<td>120°C</td>
</tr>
<tr>
<td>04081909</td>
<td>0.9</td>
<td>0.04</td>
<td>18</td>
<td>10</td>
<td></td>
<td>90°C</td>
</tr>
<tr>
<td>04081929</td>
<td>0.9</td>
<td>0.04</td>
<td>18</td>
<td>10</td>
<td></td>
<td>120°C</td>
</tr>
</tbody>
</table>

T: temperature; C: concentration; V: volume; R: molar ratio of PVP repeating unit to metal precursor.
5.3 Results and discussion

Pd nanoparticles were synthesized with methanol and ethanol as reducing agents under microwave-assisted solvothermal conditions. Tables 5-3 and 5-4 list the morphologies and particle size of Pd nanoparticles synthesized under different reaction conditions for 60 min with methanol and ethanol as reducing agents, respectively.

Table 5-3: List of particle sizes of Pd nanoparticles synthesized by using methanol as a reducing under different reaction conditions for 60 min.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Temperature (°C)</th>
<th>Concentration of metal precursor (mM)</th>
<th>Ratio*</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>04081406</td>
<td>90</td>
<td>9</td>
<td>18</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>04081908</td>
<td>90</td>
<td>9</td>
<td>1.8</td>
<td>7.0 ± 0.4</td>
</tr>
<tr>
<td>04081909</td>
<td>90</td>
<td>0.9</td>
<td>18</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>04081928</td>
<td>120</td>
<td>9</td>
<td>1.8</td>
<td>8.2 ± 0.5</td>
</tr>
<tr>
<td>04081929</td>
<td>120</td>
<td>0.9</td>
<td>18</td>
<td>5.2 ± 0.3</td>
</tr>
<tr>
<td>04090709</td>
<td>120</td>
<td>45</td>
<td>3.6</td>
<td>10.1 ± 0.2</td>
</tr>
</tbody>
</table>

Ratio*: molar ratio of PVP repeating unit to Pd$^{2+}$

Table 5-4: List of particle sizes of Pd nanoparticles synthesized by using ethanol as a reducing agent under different reaction conditions for 60 min.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Temperature (°C)</th>
<th>Concentration of metal precursor (mM)</th>
<th>Ratio*</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>04081710</td>
<td>90</td>
<td>9</td>
<td>18</td>
<td>6.5 ± 0.3</td>
</tr>
<tr>
<td>04082016</td>
<td>90</td>
<td>9</td>
<td>1.8</td>
<td>6.0 ± 0.1</td>
</tr>
<tr>
<td>04082019</td>
<td>90</td>
<td>0.9</td>
<td>18</td>
<td>6.5 ± 0.2</td>
</tr>
<tr>
<td>04081712</td>
<td>120</td>
<td>9</td>
<td>18</td>
<td>9.1 ± 0.2</td>
</tr>
<tr>
<td>04082028</td>
<td>120</td>
<td>9</td>
<td>1.8</td>
<td>8.3 ± 0.1</td>
</tr>
<tr>
<td>04082029</td>
<td>120</td>
<td>0.9</td>
<td>18</td>
<td>8.8 ± 0.2</td>
</tr>
</tbody>
</table>

Ratio*: molar ratio of PVP repeating unit to Pd$^{2+}$
5.3.1 Effects of molar ratio of PVP repeating unit to metal source (Pd$^{2+}$)

5.3.1.1 Effect on morphology

When methanol was used as a reducing agent, uniform Pd nanoparticles with some degree of agglomeration were obtained with a low PVP repeating unit to Pd$^{2+}$ molar ratio (hereafter denoted as ‘PVP to Pd$^{2+}$ ratio’) of 1.8 at 90°C and 120°C (Table 5-3). Figure 5-1 shows the TEM image of nanoparticles (sample 04081908) synthesized with PVP to Pd$^{2+}$ ratio of 1.8 and 9mM concentration of Pd$^{2+}$ at 90°C.

![TEM image of Pd nanoparticles (sample 04081908)](image)

**Figure 5-1**: TEM image of Pd nanoparticles (sample 04081908) synthesized at the concentration of Pd$^{2+}$ at 9mM and PVP to Pd$^{2+}$ ratio of 1.8 at 90°C for 60 min (Table 5-3).

SAED pattern of the sample proves that these nanoparticles are Pd nanocrystallites with FCC structure as shown in Figure 5-2. The following d values were
calculated: d1 = 2.28 Å {111}, d2 = 1.91 Å {200}, d3 = 1.38 Å {220}, and d4 = 1.18 Å {311}. EDS spectrum (Figure 5-3) confirms the formation of Pd metal nanoparticles (sample 04081908 in Figure 5-2). Peaks corresponding to Cu and C in the EDS spectrum result from the copper grid and carbon film.
Figure 5-2: Selected Area Electron Diffraction (SAED) pattern of synthesized Pd nanoparticles (sample 04081908). SAED pattern shows the FCC structure of crystallized Pd nanoparticles. (The following d values were calculated. d1 = 2.28 Å {111}, d2 = 1.91 Å {200}, d3 = 1.38 Å {220}, and d4 = 1.18 Å {311})

Figure 5-3: Energy dispersive spectrometry of Pd nanoparticles (sample 04081908) shown in Figure 5-1. EDS spectrometry further proves the formation of Pd nanoparticles.
When methanol was used as a reducing agent (Table 5-3), high PVP to Pd$^{2+}$ ratio of 18 led to the formation of nonuniform, irregular shaped Pd nanoparticles, or agglomerated Pd nanorods. Figure 5-4 shows the TEM images of Pd nanoparticles synthesized with high PVP to Pd$^{2+}$ ratio of 18 (Table 5-3) and Pd$^{2+}$ concentration of 0.9mM at 120°C (sample 04081929), 9mM at 90°C (sample 04081406), and 0.9mM at 90°C (sample 04081909) for 60min. This is probably because of the higher PVP to Pd$^{2+}$ ratio, which might have prevented the growth of Pd nanoparticles; therefore the Pd nanoparticles formed under these conditions did not grow well into well-shaped nanoparticles, which is consistent with the smaller average particle sizes of 5.2 nm (sample 04081929), 4.3 nm (sample 04081406), and 2.0 nm (sample 04081909) (Table 5-3). UV-Vis spectra also show that Pd metal precursor was not reduced completely, which will be discussed in detail in the section 5.3.5 on optical properties of Pd nanoparticles.
Figure 5-4: TEM images of Pd nanoparticles synthesized with PVP to Pd$^{2+}$ ratio of 18 and Pd$^{2+}$ concentration of (a) sample 04081929, 0.9mM at 120°C; (b) sample 04081406, 9mM at 90°C; and (c) sample 04081909, 0.9mM at 90°C for 60min.
With ethanol as the reducing agent and solvent, PVP to Pd$^{2+}$ ratio did not affect the morphology much when compared with methanol as the reducing agent and solvent. Even with higher PVP to Pd$^{2+}$ molar ratio of 18, well-dispersed Pd nanoparticles with polygon shape can be produced at higher temperature of 120$^\circ$C.

5.3.1.2 Effect on particle size

When methanol was used as the reducing agent and solvent, the higher PVP to Pd$^{2+}$ ratio led to the formation of smaller Pd nanoparticles (Table 5-3). With Pd$^{2+}$ concentration of 9 mM, average particle size decreased from 7.0 to 4.3 nm (at 90$^\circ$C) with the increase of PVP to Pd$^{2+}$ ratio from 1.8 to 18. The decrease of particle size is due to the thicker barrier surrounding the surface of Pd nanoparticles, which was formed by PVP in the reaction solution with higher PVP to Pd$^{2+}$ ratio.

From Table 5-4, it can be seen that PVP to Pd ratio of 1.8 and 18 led to the formation of Pd nanoparticles with similar particle size when ethanol was used as a reducing agent. At low temperature of 90$^\circ$C, average particle sizes are 6.0 nm (sample 04082016) and about 6.5 nm (sample 04081710) with PVP to Pd$^{2+}$ ratio of 1.8 and 18 respectively. At high temperature of 120$^\circ$C, particle sizes are around 8.3 nm (sample 04082028) and about 9.1 nm (sample 04081712) on the average with PVP to Pd$^{2+}$ ratio of 1.8 and 18, respectively.
5.3.2 Effect of concentration of Pd metal source on particle size of synthesized Pd nanoparticles

The concentration of Pd metal source (Pd$^{2+}$) affected the particle size of obtained Pd nanoparticles. It can be seen from Table 5-3, at 90°C with methanol as a reducing agent, particle size decreased from about 4.3 nm (sample 04081406) to 2.0 nm (sample 04081909) as the concentration of Pd$^{2+}$ decreased from 9 to 0.9 mM. This is because higher metal precursor concentration provides more metal source for the growth of metal nanoparticles. Therefore, particle size decreased with the decrease of Pd$^{2+}$ concentration. However, when ethanol was used as a reducing agent, particle sizes were not affected by the Pd$^{2+}$ concentration (Table 5-4). The reason for this is not understood at present.

5.3.3 Effects of reaction temperature on morphology and particle size of synthesized Pd nanoparticles

5.3.3.1 Effect on morphology

When ethanol was used as a reducing agent (Table 5-4), the higher temperature of 120°C favored the formation of well-dispersed Pd nanoparticles regardless of PVP to Pd$^{2+}$ ratio or the concentration of Pd$^{2+}$. At the low temperature of 90°C, Pd nanoparticles with some degree of agglomeration were obtained with high Pd$^{2+}$ concentration of 9mM and high PVP to Pd$^{2+}$ ratio of 18. The Pd nanoparticles obtained at 90°C had smaller sizes (6.5 nm, sample 04081710) than those synthesized at 120°C (9.1 nm, sample 04081712). Due to the larger surface energy of the smaller nanoparticles, the Pd nanoparticles produced at 90°C tended to agglomerate. Figure 5-5 a and b show TEM
image of synthesized Pd nanoparticles with the PVP to Pd$^{2+}$ ratio of 18 and Pd$^{2+}$ concentration of 9 mM at 90°C and 120°C, respectively. The Pd nanoparticles synthesized at 120°C have definite geometric shapes, including triangular, rhombohedral or square, pentagonal, and hexagonal as shown in Figure 5-5 b.

Figure 5-5: TEM image of synthesized Pd nanoparticles with the PVP to Pd$^{2+}$ ratio of 18 and Pd$^{2+}$ concentration of 9 mM at (a) 90°C/60 min. (sample 04081710) and (b) 120°C for 60 min (sample 04081712).
Figure 5-6 shows a size distribution histogram of well-crystallized Pd nanoparticles, which are shown in Figure 5-5 b. The particles are more or less monodispersed and the average size is around 10 nm. Figure 5-7 shows the SAED pattern of the synthesized Pd nanoparticles, proving the FCC structure of Pd nanoparticles. Figure 5-8 shows the EDS spectrum of Pd nanoparticles, which are shown in Figure 5-5 b. EDS spectrum shows the formation of Pd metal nanoparticles. The peak corresponding to oxygen could be due to the surface oxidation of Pd nanoparticles or the residue of surfactant around the nanoparticles.

![Size distribution histogram of Pd nanoparticles](image)

**Figure 5-6**: Size distribution histogram of Pd nanoparticles (sample 04081712 in Figure 5-5 b) synthesized at 120 ºC with PVP to Pd$^{2+}$ ratio of 18 and Pd$^{2+}$ concentration of 9 mM. (The histogram was made from 150 nanoparticles.)
Figure 5-7: Selected Area Electron Diffraction (SAED) pattern of synthesized Pd nanoparticles (sample 04081712). SAED pattern shows the FCC structure of crystallized Pd nanoparticles.

Figure 5-8: Energy dispersive spectrum of Pd nanoparticles shown in Figure 5-5 b. EDS shows the formation of Pd nanoparticles.
5.3.3.2 Effect on particle size

It is well known that increase in temperature increases the reaction rate and thus increases the growth rate of nanoparticles. Higher temperature resulted in the formation of larger Pd nanoparticles. For example, when ethanol was used as a reducing agent, at the higher temperature of 120°C, the average size of synthesized Pd nanoparticles is about 8-9 nm (Table 5-4). When the temperature was decreased to 90°C, spherical Pd nanoparticles formed and the average particle size is about 6 nm.

5.3.4 Effects of the reducing agent on the morphology and particle size of synthesized Pd nanoparticles

5.3.4.1 Effect on particle size

When methanol was used as the reducing agent and solvent, higher PVP to Pd$^{2+}$ ratio of 18 and low concentration of Pd$^{2+}$ led to smaller Pd nanoparticles. With ethanol as a reducing agent and solvent, synthesized Pd nanoparticles had similar particle size regardless of the PVP to Pd$^{2+}$ ratio or the concentration of Pd$^{2+}$.

With high PVP to Pd$^{2+}$ ratio of 18, particle size of obtained Pd nanoparticles with ethanol as the reducing was larger than those synthesized with methanol as a reducing agent. From Tables 5-3 and 5-4, it can be seen that with high PVP to Pd ratio of 18, average particle sizes of Pd nanoparticles produced at 90°C were 2.0 nm (sample 04081909) and 4.3 nm (sample 04081406) with methanol as a reducing agent, while particle sizes were about 6.5 nm (samples 04082019 and 04081710) with ethanol as a
reducing agent. At 120°C, average particle size was 5.2 nm (sample 04081929) with methanol as a reducing agent. However, with ethanol as a reducing agent, particle size was 8.8 nm (sample 04082029).

With low PVP to Pd\(^{2+}\) ratio of 1.8, synthesized Pd nanoparticles had similar particle sizes with methanol and ethanol as reducing agents. From Tables 5-3 and 5-4, it can be seen that at 90°C average particle sizes were 7.0 and 6.0 nm with methanol and ethanol as reducing agents, respectively. At 120°C, average particle sizes were 8.2 and 8.3 nm with methanol and ethanol as reducing agents, respectively. The larger particle size at higher temperature can be explained by the increased growth of the metal particles.

**5.3.4.2 Effect on morphology**

As discussed before, the experimental results have shown that for the synthesis of Pd nanoparticles using methanol as a reducing agent, the shape of nanoparticles was affected by the ratio of PVP to Pd\(^{2+}\). A high PVP to Pd\(^{2+}\) ratio of 18 gave rise to the formation of Pd nanoparticles with irregular shapes.

When ethanol was used as a reducing agent, the synthesis of Pd nanoparticles was less affected by the PVP to Pd\(^{2+}\) ratio. The high temperature of 120°C or low Pd\(^{2+}\) concentration of 0.9 mM favored the formation of well-dispersed Pd nanoparticles regardless of the PVP to Pd\(^{2+}\) ratio. The PVP to Pd\(^{2+}\) ratio appeared to affect the morphology of Pd nanoparticles only at a low temperature of 90°C and a high Pd\(^{2+}\) concentration of 9 mM, which led to some extent of agglomeration. Low temperature
gave rise to the formation of smaller Pd nanoparticles regardless of the Pd$^{2+}$ concentration. High concentration led to high concentration of obtained Pd nanoparticles. Therefore, under these reaction conditions synthesized Pd nanoparticles tended to agglomerate.

The differences between the results of using methanol and ethanol as reducing agents are not fully understood at this time.

In addition, methanol was found to have stronger reducing ability than ethanol at the same temperature, which will be further discussed in the following section.

### 5.3.5 Optical properties of synthesized Pd nanoparticles

Ho et al., (2004)$^{12}$ reported that Pd(fod)$_2$, where fod is 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate, has absorption peak at 342 nm. Creighton and Eadon have reported that the surface plasmon resonance (SPR) absorption of palladium nanoparticles should appear between 200 and 300 nm on the basis of theoretical calculation$^{16}$. Figure 5-9 shows the calculated UV-Vis spectrum of Pd nanoparticles according to the Equation 3-1. The optical constants data for the bulk metal (Pd) were from the article of Johnson$^{17}$ for the calculation of UV-Vis spectrum. The index of refraction of ethanol is 1.36. The color of the reaction solution turned from pale yellow to dark brown after reaction.
UV-Vis spectra results exhibited an absorption peak at around 325 nm due to Pd(C₅H₇O₂)₂—PVP shown in Figure 5-10. The Pd nanoparticles synthesized at 90°C for 60 min exhibited weak absorptions at around 285 nm and 325 nm (for sample 04081710 and 04082019). The former can be attributed to the surface plasmon resonance of Pd nanoparticles (Figure 5-10). The absorption at 325 nm indicates that the metal source of Pd²⁺ was not reduced completely at 90°C for 60 min, which is corroborated by the weak metal absorption at 285 nm. As pointed out above, the absorptions at around 285 nm indicate the formation of Pd nanoparticles. In the case of sample 04082016, the absence of absorption at 285 nm may be due to the very low concentration of obtained Pd nanoparticles.
Figure 5-10: UV-Vis absorbance spectra of Pd$^{2+}$—PVP in ethanol and reaction mixtures of Pd nanoparticles (sample 04081710, 04082016, and 04082019) synthesized in ethanol at 90°C for 60 min. Legend in the Figure gives the sample codes and corresponding particle sizes.

Figure 5-11 presents the UV-Vis spectra of synthesized Pd nanoparticles at 120°C for 60 min. The strong absorptions at around 270 nm and weak absorption at around 325 nm (or absence of the absorption at 325 nm) indicate that most of the Pd metal source was reduced to Pd metal at 120°C for 60 min. The peak position shifts a little from 285 nm to 270 nm. This might be because of the surrounding environment of metal nanoparticles, which affects the absorption. For the synthesized Pd nanoparticles at 90°C, since there was a large amount of Pd$^{2+}$ left after the reaction there were more molecules
surrounding the obtained Pd nanoparticles. Therefore, the absorption red shifts and this is another factor, which caused the intensity of the absorption to be low.

Figure 5-11: UV-Vis absorbance spectra reaction mixtures of Pd nanoparticles (sample 04081712, 04082028, and 04082029) synthesized in ethanol at 120ºC for 60 min. Legend in the Figure gives the sample codes and corresponding particle sizes.
Figure 5-12 shows UV-Vis absorbance spectra of reaction solutions of Pd nanoparticles (samples 04081406, 04081908, and 04081909) synthesized in methanol at 90°C for 60 min. Strong peak appeared around 290 nm attributed to SPR absorbance of Pd nanoparticles (sample 04081908) synthesized with low PVP to Pd$^{2+}$ ratio of 1.8. Compared with the UV-Vis spectrum of sample 04082016 (no peak attributed to SPR absorbance of Pd nanoparticles appeared as shown in Figure 5-10) synthesized under the same reaction condition except using ethanol as a reducing agent, the absorbance peak at 290 nm indicates that methanol has stronger reducing ability than ethanol. For samples 04081406 and 04081909 synthesized with higher PVP to Pd$^{2+}$ ratio of 18 in methanol, the UV-Vis spectra show the peaks around 325 nm instead of exhibiting the peaks around 290 nm, indicating that large amount of Pd ions were not reduced at 90°C for 60 min. These results are consistent with TEM observations, which showed smaller particle sizes for sample 04081406 (~4.3 nm) and 04081909 (~2.0 nm) compared with sample 04081908 (~7.0 nm).
Figure 5-12: UV-Vis absorbance spectra reaction mixtures of Pd nanoparticles (sample 04081406, 04080908, and 04081909) synthesized in methanol at 90ºC for 60 min. Legend in the Figure gives the sample codes and corresponding particle sizes.

Figure 5-13 presents the UV-Vis absorbance spectra of reaction solutions of Pd nanoparticles (sample 04081928 and 04081929) synthesized in methanol at 120ºC for 60 min. Strong peaks appear around 280 nm (for sample 04081929) and 290 nm (for sample 04081928), which are attributed to the SPR absorption of Pd nanoparticles. The absorptions at around 325 nm disappear, indicating most Pd metal source was reduced to Pd metal at 120ºC for 60 min. The absorption peaks shifted from 290 to 280 nm due to particle size decrease from 8.2 to 5.2 nm. The broadened peak of smaller particles (sample 04081929) is due to the higher PVP to Pd$^{2+}$ ratio of 18. With higher PVP to Pd$^{2+}$ ratio, more PVP molecules surround the Pd nanoparticles and thus broadened the peak of SPR absorption.
Figure 5-13: UV-Vis absorbance spectra reaction mixtures of Pd nanoparticles (04081928 and 04081929) synthesized in methanol at 120ºC for 60 min. Legend in the Figure gives the sample codes and corresponding particle sizes.

5.3.6 Comparison of microwave-assisted technique with conventional method

For comparison of the microwave-assisted technique with conventional method, Pd nanoparticles were synthesized with ethanol as a reducing agent in an oven at 90ºC and 120ºC for 2 and 4 hours. Table 5-5 lists the concentrations of chemicals, ratio of PVP repeating unit to metal ions, volumes of ethanol used in the reduction reaction, and particle sizes of resulting Pd nanoparticles.
Table 5-5: List of the concentrations of chemicals, ratio of PVP repeating unit to metal ions, volumes of ethanol used in the reduction reaction, and particle sizes of resulting Pd nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>metal precursor (mM)</th>
<th>PVP (mM)</th>
<th>R</th>
<th>T</th>
<th>Time (h)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
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<td>90°C</td>
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<td>5.1 ± 0.2</td>
</tr>
<tr>
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<td>90°C</td>
<td>4</td>
<td>6.7 ± 0.2</td>
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<td>04121403</td>
<td>9</td>
<td>0.04</td>
<td>18</td>
<td>120°C</td>
<td>2</td>
<td>6.9 ± 0.2</td>
</tr>
<tr>
<td>0412006</td>
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<td>0.04</td>
<td>18</td>
<td>120°C</td>
<td>4</td>
<td>11.3 ± 0.3</td>
</tr>
</tbody>
</table>

C: Concentration;  
V: Volume;  
R: Ratio of PVP repeating unit to metal ions;  
T: Temperature.

Through conventional synthesis method, Pd nanoparticles of approximately 5 nm and 7 nm were obtained for 2 h and 4 h treatments, respectively at 90°C. At 120°C, average particle sizes were about 7 nm for 2 h and 11 nm for 4 h. The particle sizes of Pd nanoparticles synthesized at both temperatures with 2 h treatment time are slightly smaller than those synthesized by microwave-assisted method at 90°C (6 nm) and 120°C (9 nm) for 1 h. Synthesized Pd nanoparticles by conventional method; however, have similar morphology as those produced by microwave-assisted method. Figures 5-14, 5-15, 5-16, and 5-17 show the TEM images of Pd nanoparticles synthesized by conventional method at 90°C and 120°C for 1 and 2 h. Both microwave-assisted and conventional methods yielded Pd nanoparticles of similar shape and these results are similar to the syntheses of Ag nanoparticles. However, longer time was needed for conventional method compared to microwave-assisted method to achieve similar size. These results show that microwave-assisted method saves time and thus energy compared to the conventional method.
Figure 5-14: TEM image of Pd nanoparticles (sample 04121402) synthesized by the conventional method at 90°C for 2 h (particle size = 5.1 ± 0.2 nm)

Figure 5-15: TEM image of Pd nanoparticles (sample 04121003) synthesized by the conventional method at 90°C for 4 h (particle size = 6.7 ± 0.2 nm)
Figure 5-16: TEM image of Pd nanoparticles (sample 04121403) synthesized by the conventional method at 120°C for 2h (particle size = 6.9 ± 0.2 nm)

Figure 5-17: TEM image of Pd nanoparticles (sample 04121006) synthesized by the conventional method at 120°C for 4h (particle size = 11.3 ± 0.3 nm)
5.4 Conclusion

Pd nanoparticles of about 2 to 10 nm were synthesized with methanol and ethanol as reducing agents. The particle size is dependent on the reaction temperature. Higher reaction temperature resulted in Pd nanoparticles with larger particle size, as expected. When methanol was used as a reducing agent, the morphology of Pd nanoparticles was affected by the PVP to Pd$^{2+}$ ratio. The higher ratio of 18 led to the formation of Pd nanoparticles with irregular shapes. Particle size was also controlled by varying the concentration of Pd$^{2+}$ and the PVP to Pd$^{2+}$ ratio. Higher PVP to Pd$^{2+}$ ratio or lower concentration of Pd$^{2+}$ led to the formation of smaller particles. When ethanol was used as a reducing agent, particle shape of Pd nanoparticles was less affected by the PVP to Pd$^{2+}$ ratio. Particle size was also not affected by the PVP to Pd$^{2+}$ ratio or the concentration of Pd$^{2+}$. Pd nanoparticles synthesized by conventional method have similar shape as those of the microwave-assisted method. However, it takes longer time by conventional method to produce particles with similar size by the conventional method i. e., slower kinetics compared to microwave-assisted method. UV-Vis spectra show that synthesized Pd nanoparticles stabilized with PVP have absorption bands at around 280 to 290 nm and also indicated that methanol had stronger reducing ability than ethanol.
5.5 References


Chapter 6

Synthesis of Pt nanoparticles by using methanol and ethanol as reducing agents

6.1 Introduction

Platinum nanoparticles currently are of intense interest due to their unique catalytic properties. A range of organic chemical reactions can be catalyzed by Pt nanoparticles such as hydrosilylation, oxidation, and hydrogenation reactions\(^1\). Furthermore, Pt nanoparticles are catalytically active in room temperature electro-oxidation reactions for fuel cell applications\(^2\). Pt nanoparticles have been deposited in multilayer films and used as electrocatalyst for dioxygen reduction\(^3\). Therefore, the synthesis of Pt nanoparticles has developed into an increasingly important research area. It is well-known that the catalytic activity of the metal is strongly dependent on the particle shape, size, and size distribution\(^4\). Many methods have been developed for the synthesis of Pt nanoparticles and controlling the particle size and shape\(^5\)-\(^14\). A phase-transfer method has been developed for synthesis of Pt nanoparticles. The efficiency of this method was nearly 100\(^\%\)\(^14\). Lately, dendrimers have been used as templates to produce Pt nanoparticles and the catalytic properties of the encapsulated Pt nanoparticles have been studied\(^13,15,16\). Pt nanoparticles with well-controlled shape (cubic and tetrahedral shapes) have been synthesized by changing the ratio of the capping polymer material (sodium polyacrylate) to the concentration of the platinum cations\(^4\). In this work,
Pt nanoparticles have been prepared with methanol and ethanol as reducing agents by microwave-assisted solvothermal technique.

6.2 Experimental

PVP with an average molecular weight of 40K was used in all the experiments. PVP polymer was dissolved in methanol or ethanol. Dihydrogen hexachloroplatinate(IV), was used as metal precursor. Table 6-1 lists the chemicals used in the synthesis. The metal cation was added to the methanol-PVP, and ethanol-PVP solutions. Distilled water was added in the case of methanol to investigate the effect of water on the morphology.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Company</th>
<th>Purity</th>
</tr>
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<td>Metal precusor</td>
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<tr>
<td>Dihydrogen hexachloroplatinate(IV)</td>
<td>Alfa Aesar A</td>
<td>99% (metal basis)</td>
</tr>
<tr>
<td></td>
<td>Johnson Matthey Company</td>
<td></td>
</tr>
<tr>
<td>Protecting agent</td>
<td>Polyvinyl pyrrolidone (PVP) (M W 40K)</td>
<td>Aldrich Chemical Company, Inc</td>
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<td>Reducing agents</td>
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</tr>
<tr>
<td></td>
<td>Ethanol 200 proof anhydrous</td>
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Tables 6-2 and 6-3 list the concentrations of chemicals and volumes of methanol and ethanol used in the synthesis under different reaction temperatures. The reactants were heated at 90°C and 120°C for 60 min. All the powders were characterized by Philips 420 or JEOL 2010F transmission electron microscope operated at 120KV or 200KV, respectively. For TEM measurements a drop of the nanoparticle solution was
placed on a copper grid covered with a continuous carbon film. Excess solution was imbibed with an adsorbent paper. The average particle size and particle size distribution were obtained from approximately 100 to 200 nanoparticles randomly chosen from a few areas in the TEM image.

Table 6-2: List of the concentrations of chemicals, volumes of methanol and ethanol, molar ratio of PVP repeating unit to Pt$^{4+}$, and the reaction temperature of solutions for 60 min.

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<tr>
<th>Sample code</th>
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<th>$C_{\text{PVP}, \text{mM}}$</th>
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<th>$V_{\text{methanol,ml}}$</th>
<th>$V_{\text{ethanol,ml}}$</th>
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Table 6-3: List of the concentrations of chemicals, volumes of methanol and distilled water, molar ratio of PVP repeating unit to Pt$^{4+}$, and the reaction temperature of solutions for 60 min.

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<th>$C_{\text{PVP}, \text{mM}}$</th>
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6.3 Results and discussion

6.3.1 Synthesis of Pt nanoparticles with methanol and ethanol

When methanol was used as a reducing agent, with concentrations of Pt⁴⁺ and PVP at 9 mM and 0.04 mM, respectively, well crystallized and monodispersed Pt nanoparticles were obtained at 120 °C for 60 min. Figure 6-1 gives the TEM image and particle size distribution histogram of synthesized Pt nanoparticles. Size distribution histogram shows Pt nanoparticles are more or less monodispersed and the size of nanoparticles is approximately 3 nm on the average.

Figure 6-1: TEM image (a) and size distribution histogram (b) of Pt nanoparticles (sample 04081921) formed with the concentrations of PVP at 0.04 mM and Pt⁴⁺ at 9 mM at 120 °C without distilled water but with methanol as a reducing agent. (150 nanoparticles were collected in the calculation of size distribution.)
Figure 6-2 presents the SEAD pattern, showing the FCC structure of synthesized Pt nanoparticles. Debye rings are very dim due to the smallness of Pt nanoparticles (~3 nm). Figure 6-3 shows the EDS spectrum of Pt nanoparticles given in Figure 6-1 a. EDS spectrum proves the formation of Pt metal nanoparticles. High intensity peaks corresponding to Cu and C in the EDS spectrum result from the copper grid with carbon film. The EDS peaks corresponding to Pt are very small because only small amount of Pt nanoparticles were collected.
Figure 6-2: Selected area electron diffraction (SAED) pattern of Pt nanoparticles in Figure 6-1 a. This pattern verifies formation of crystallized Pt nanoparticles with FCC structure.

Figure 6-3: Energy dispersive spectrum (EDS) of Pt nanoparticles in Figure 6-1 a. EDS proves the formation of Pt nanoparticles.
The morphology of Pt particles was affected by the reaction temperature. Agglomerated Pt nanoparticles formed when the sample was heated for 60 min at 90°C, as shown in Figure 6-4. This result agrees with the result of synthesis of Pd nanoparticles. The lower temperature of 90°C led to smaller nanoparticles than those synthesized at 120°C. Therefore, the higher surface energy due to smaller particles resulted in the agglomeration of Pt nanoparticles.

Figure 6-4: TEM image of agglomerated Pt nanoparticles (sample 04081901) formed with the concentrations of PVP at 0.04 mM and of Pt⁴⁺ at 9 mM at 90 °C for 60 min with methanol as a reducing agent.

When ethanol was used as a reducing agent Pt nanoparticles did not form at 90°C after treatment for 1 h. However, at 120°C agglomerated Pt nanoparticles were obtained (Figure 6-5).
6.3.2 Synthesis of Pt nanoparticles with distilled water in methanol

6.3.2.1 Effect of concentration of metal source of Pt$^{4+}$ on morphology of Pt nanoparticles

With distilled water in the reaction system, Pt nanorods appear to have formed. When the reactants were prepared with a low concentration of Pt$^{4+}$ (around 0.90mM) and PVP concentration of 0.04 mM, agglomerated Pt nanorods formed in the presence of distilled water at 90 ºC for 60 min. The morphology of Pt nanoparticles is dependent on the concentrations of Pt$^{4+}$ and PVP. Figure 6-6 presents the TEM images and major and minor axis size distribution of Pt nanorods synthesized with different concentrations of Pt$^{4+}$.
Figure 6-6: TEM images and major axis size distribution of Pt nanorods synthesized with PVP concentration of 0.04mM but with different Pt$^{4+}$ concentration of, (a) 0.75mM (sample 04061606); (b) 0.9mM (sample 04061607); and (c) 2.4mM (sample 04070206) at 90°C for 60min. Inset of Figure b (TEM image) shows the high resolution TEM image of a single nanorod.
At concentration of 0.9 mM, more Pt nanorods were obtained. At lower or higher concentration of 0.75 mM or 2.4 mM, less Pt nanorods were produced. Size distributions show that the minor axis length of nanospheres is in the range of about 2 to 5 nm and the length of nanorods is approximately 5 to 10 nm. Particle size of Pt nanospheres synthesized at low Pt$^{4+}$ concentration of 0.75 mM ranges from 2 to 4 nm and the major axis length of Pt nanorods varies from about 5 to 8 nm. With even higher Pt$^{4+}$ concentrations of 0.9 mM and 2.4 mM, particle size of Pt nanospheres is larger ranging from 3 to 5 nm and the major axis length of Pt nanorods ranges from 6 to 10 nm. The major axis lengths of nanorods were approximately twice to four times the minor axis lengths. With higher Pt$^{4+}$ concentrations, particle size increases, while only Pt$^{4+}$ concentration of about 0.9 mM produces more nanorods. The possible mechanism of the growth of nanorods is that nanospheres formed first. Then two or more nanospheres gathered together and grew as nanorods. Another possible mechanism is that nanorods grew from the nanospheres along some direction. Both mechanisms assume that resulting nanospheres were not fully covered by the protecting agent (PVP) and the PVP molecules probably bonded to certain planes while others were not coordinated by them and this may have led to the preferential growth of nanorods. The former mechanism seems more likely because it can be seen from the TEM pictures (Figure 6-6) that there were some nanospheres, which agglomerated. That the major axis lengths were two or four times the minor axis length further indicates the former mechanism. For either of the mechanisms, the low Pt$^{4+}$ concentration led to the low concentration of formed nanospheres. Therefore, the possibility for the nanospheres gathering together is low (for the former mechanism) or there are not enough Pt$^{4+}$ ions for the growth of nanorods (for the latter mechanism).
The higher concentration of Pt\textsuperscript{4+} led to lower PVP to Pd\textsuperscript{4+} ratio, which gave rise to even less protecting agent (PVP) surrounding the Pt nanospheres. This probably resulted in larger particle size instead of nanorods (shown in inset of minor axis size distribution in Figure 6-6).

6.3.2.2 Effect of PVP concentration on the morphology of Pt nanoparticles

Figure 6-7 gives the TEM images of Pt nanoparticles synthesized with different PVP concentrations at 90\degree C/60 min in methanol. At higher concentration of PVP (0.16 mM), less amount of nanorods formed as shown in Figure 6-7 a. On other hand, lower concentration (0.01mM) of PVP led to the formation of agglomerated nanorods as shown in Figure 6-7 b. As discussed before, this is probably because at low concentration of PVP, the growing Pt nanoparticles during the reaction cannot be fully covered by PVP molecules, which may have led to the preferential growth of nanorods.
6.3.2.3 Effects of temperature and distilled water on the morphology of Pt nanoparticles.

The temperature and the presence of distilled water affect the morphology of Pt nanoparticles. High temperature (120 °C) and the presence of distilled water favor the...
formation of agglomerated Pt nanorods. Agglomerated Pt nanorods formed at 120 °C in the presence of distilled water. The reaction rate was increased by the higher temperature of 120°C. Therefore, more nanorods formed. Figure 6-8 shows the TEM image of agglomerated Pt nanorods formed with the concentration of Pt⁴⁺ at 0.9 mM and PVP concentration at 0.04 mM at 120 °C. At low temperature (90 °C), the obtained Pt nanoparticles contain both nanorods and nanoshpere (shown in Figure 6-6 b). Without distilled water, well-dispersed Pt nanospheres were obtained at 90 °C (Figure 6-9). The reason why distilled water in the reaction system favored the formation of nanorods is not understood.

Figure 6-8: TEM Image of Pt nanorods formed (sample 04072904) with PVP concentration of 0.04 mM and the concentration of Pt⁴⁺ at 0.9 mM at 120°C with the presence of distilled water.
Figure 6-9: TEM Image of Pt nanorods formed (sample 04072907) with PVP concentration of 0.04 mM and the concentration of Pt$^{4+}$ at 0.9 mM at 90°C without the presence of distilled water.

### 6.3.3 Optical properties

Figure 6-10 gives the calculated UV-Vis spectrum of Pt nanoparticles according to Equation 3-1. The optical constants as a function of wavelength for the bulk metal (Pt) were obtained from the book of Weaver et al.$^{17}$ used here for the calculation of UV-Vis spectrum of Pt nanoparticles. The index of refraction of ethanol is 1.36. According to the theoretical calculation, Pt nanoparticles have SPR absorption at about 220 nm, which is beyond the detected wavelength range (260 nm to 1100 nm) of the UV-Vis instrument used here. Therefore, the UV-Vis spectra of synthesized Pt nanoparticles are not given.
Figure 6-10: Calculated UV-Vis spectrum of Pt nanoparticles of less than 20 nm in ethanol

6.3.4 Comparison of microwave-assisted technique with conventional method

Platinum nanoparticles were also synthesized by conventional method in an oven at 120°C for 2 and 4 h. Table 6-4 lists the reaction conditions of the concentrations of chemicals, volumes of methanol, molar ratio of PVP repeating unit to Pt⁴⁺, reaction time and temperature at 120°C.
Table 6-4: List of the reaction conditions of the concentrations of chemicals, volumes of methanol, molar ratio of PVP repeating unit to Pt$^{4+}$, reaction time at 120°C, and particle size of synthesized Pt nanoparticles.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>C_{Metal precursor} (mM)</th>
<th>C_{PVP} (mM)</th>
<th>R</th>
<th>V_{methanol} (ml)</th>
<th>Time (h)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>05022405</td>
<td>H$_2$PtCl$_6$ 9</td>
<td>0.04</td>
<td>1.8</td>
<td>10</td>
<td>2</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>05022406</td>
<td>H$_2$PtCl$_6$ 9</td>
<td>0.04</td>
<td>1.8</td>
<td>10</td>
<td>4</td>
<td>----</td>
</tr>
</tbody>
</table>

The particle size of sample 05022406 is not given due to particle agglomeration.

Particle size of synthesized Pt nanoparticles with 2 hours is 3.9 ± 0.1 nm and TEM image is shown in Figure 6-11. With the reaction time of 4 h, obtained Pt nanoparticles agglomerated (Figure 6-12). Compared with Pt nanoparticles synthesized by microwave-assisted method (sample 04081921 shown in Figure 6-1 a, which were synthesized under the same reaction conditions), produced Pt nanoparticles (sample 05022405) by conventional method for 2 h have similar morphology. This result is consistent with those for Ag and Pd nanoparticles because these metal ions are easily reduced. The average particle size (3.9 nm) of Pt nanoparticles (sample 05022405) obtained in an oven for 2 h is slightly larger than that (2.8 nm) of Pt nanoparticles (sample 04081921) produced by microwave heating for 1 h.
Figure 6-11: TEM image of Pt nanoparticles (sample 05022405) synthesized by conventional method in an oven at 120°C for 2 h.

Figure 6-12: TEM image of Pt nanoparticles (sample 05022406) synthesized by conventional method in an oven at 120°C for 4 h.
6.4 Conclusion

In conclusion, well-dispersed Pt nanoparticles were obtained using methanol as a reducing agent. The morphology of Pt nanoparticles is dependent on the temperature, concentrations of PVP and Pt$^{4+}$, and the presence or absence of distilled water. Without distilled water in the reaction system, Pt nanospheres were obtained. Particle size is approximately 2 to 3 nm at 120°C for 60 min. With the distilled water in the system, Pt nanorods can be obtained. The higher temperature, lower concentration of PVP, and proper concentration of Pt$^{4+}$ favor the formation Pt nanorods. In addition, Pt nanoparticles were also synthesized using ethanol as a reducing agent at 120°C. However, obtained Pt nanoparticles were not dispersed. At 90°C for 1 h, Pt nanoparticles cannot form.

Both microwave-assisted and conventional methods produced Pt nanoparticles with similar morphology and particle size i.e., no difference could be detected between the two methods. This is because Pt metal ions are easy to be reduced under both conditions.
6.5 References


Chapter 7
Summary and Future Work

7.1 Summary of research

Metal nanoparticles of Ag, Ni, Pd, and Pt have been synthesized by microwave-assisted method with ethylene glycol, methanol or ethanol as reducing agents. Particle size and shape have been controlled to some extent. Optical properties of metal nanoparticles have been studied.

7.1.1 Synthesis of Ag nanoparticles

Silver nanoparticles of about 10 nm to 1 µm have been synthesized with ethylene glycol as a reducing agent. The morphology and particle size of Ag nanoparticle are controlled by varying the concentration of Ag metal source (AgNO₃), PVP molecular weight, and ligands.

By varying Ag metal precursor concentration, particle size was controlled in the range of 10 to 30 nm. Particle size increased initially with an increase of AgNO₃ concentration due to the availability of more Ag ions for the growth of Ag particles. However, further increase of AgNO₃ concentration led to the decrease of Ag nanoparticle size because large number of nuclei formed with excess Ag metal source but their growth was limited. The particle size of synthesized Ag nanoparticle was also dependent on the PVP molecular weight. When PVP of low molecular weight (8K, 10K, 40K, and 1300K)
was used in the synthesis, particle sizes of obtained Ag nanoparticles are around 27 nm. When PVP molecular weight of 630K was used as a protecting agent, particle size decreased to about 10 nm. The growth of Ag nanoparticles was controlled by adding ligands in the reaction solutions. By binding Ag\(^+\) ions with ligands, Ag nanoparticles with larger particle size can be obtained by a slow supply of silver ions during growth period. Adding ligands was also found to control the morphology of synthesized Ag nanoparticles. Furthermore, the growth rate can be increased by adding NaOH in the system.

### 7.1.2 Synthesis of Ni nanoparticles

Well-dispersed Ni nanoparticles are difficult to synthesize due to the large forces between particles. These forces are due to the high electron affinity and the high surface tension arising from the partially filled d--orbital, from the van der Waals forces between polarizable metal particles, and from magnetic dipole interactions. In this research work, well-dispersed Ni nanoparticles were obtained in a binary protecting agent system of PVP and DDA with or without Pt seeding. By adding DDA to the reaction system, particle size and shape was controlled. Moreover, DDA also increased the reduction reaction rate, thus helping the formation of Ni nanoparticles even without Pt seeding. With small amount of DDA added in the reaction solution, Ni nanoparticles were obtained with Pt as seeds. With initial increase of the amount of DDA, particle size increased. Further increase of the amount of DDA led to the decrease of particle size. The particle size of synthesized Ni nanoparticles was also affected by the molecular weight of PVP. PVPs
with higher molecular weight led to smaller particles and less amount of DDA was needed for the formation of well-dispersed Ni nanoparticles. With large amounts of DDA added, Ni nanoparticles were synthesized without Pt seeds. The particles size and size distributions were controlled by changing the amount of DDA added in the reaction solution. With a proper amount of DDA, monodispersed Ni nanoparticles were obtained. Further increasing the amount of DDA led to the formation of Ni nanoparticles with bimodal size distribution.

7.1.3 Synthesis of Pd nanoparticles

Pd nanoparticles of about 5 to 10 nm were synthesized with methanol and ethanol as reducing agents. The particle size was found to be dependent on the concentration of Pd metal source and the reaction temperature. High concentration of Pd$^{2+}$ and high reaction temperature resulted in Pd nanoparticles with larger particle size. When methanol was used as a reducing agent, the morphology of Pd nanoparticles was affected by the molar ratio of PVP to Pd$^{2+}$. A high PVP to Pd$^{2+}$ ratio of 18 led to the formation of Pd nanoparticles with irregular shapes. When ethanol was used as a reducing agent, particle shape of Pd nanoparticles was less affected by the ratio of PVP to Pd$^{2+}$. The reason for this is not clear and further studies are needed. Pd nanoparticles synthesized by conventional method gave similar shape, but it took longer time to produce particles with similar size. UV-Vis spectra showed that Pd nanoparticles stabilized with PVP have absorption bands at around 280 to 290 nm and the spectra also indicated that methanol has stronger reducing ability than ethanol.
7.1.4 Synthesis of Pt nanoparticles

Well-dispersed Pt nanoparticles were obtained using methanol as a reducing agent. The morphology of Pt nanoparticles was found to be dependent on the temperature, concentrations of PVP and Pt$^{4+}$, and the presence or absence of distilled water. Without distilled water in the reaction system, Pt nanospheres were obtained. Particle size was approximately 2 to 3 nm at 120°C after treatment for 60 min. With the distilled water in the system, Pt nanorods can be obtained. Higher temperature, lower concentration of PVP, and proper concentration of Pt$^{4+}$ favored the formation of Pt nanorods. Pt nanoparticles were also synthesized using ethanol as a reducing agent at 120°C. Pt nanoparticles, however, did not form by a lower temperature treatment at 90°C.

7.1.5 Optical properties

Metal nanoparticles exhibit unusual optical properties due to the surface plasmon resonance (SPR) absorption. Creighton and Eadon (1991) have reported the calculated optical spectrum of various metal nanoparticles in water and in vacuum. They reported that the SPR absorption of Ag, Pd, Pt, and Ni nanoparticles are at around 350 to 400 nm, 200 nm to 300 nm, 200 nm to 300 nm, and 300 nm to 400 nm, respectively. From the UV-Vis experiments reported here, the Ag, Pd, and Ni nanoparticles showed the SPR absorption at about 410 nm to 420 nm, 280 nm to 290 nm, and 300 nm to 350 nm, respectively, and these results are in close agreement with those of Creighton and Eadon (1991). The UV-Vis spectra of Pt nanoparticles could not be obtained with the UV-Vis instrument used in this study.
7.1.6 Comparison of microwave-assisted technique with conventional method

Metal nanoparticles of Ag, Ni, Pd, and Pt have also been synthesized by conventional method. In general, longer times were needed to obtain these metal nanoparticles with similar size by the conventional method compared to the microwave-assisted process, confirming that the microwave-assisted method is time and perhaps, energy efficient. For the synthesis of Ag, Pt, and Pd metals, well-dispersed nanoparticles with similar shapes were obtained by both the microwave-assisted and conventional methods. However, microwave-assisted method was found to be faster than conventional method for producing well-dispersed Ni nanoparticles. Because Ag, Pt and Pd ions can be easily reduced; their metal nanoparticles were obtained by conventional heating also. On the other hand, Ni ions are difficult to be reduced compared with noble metal ions (Ag, Pt, and Pd) and hence conventional heating did not produce Ni nanoparticles. Conventional heating, however, led to the formation of larger particles and this can be explained as follows. Conventional heating unlike microwave heating did not provide enough energy in a short time, which is required to produce large number of nuclei for the formation of nanoparticles. Since less number of nuclei were formed with conventional heating, larger particles resulted by growth.
7.2 Future work

7.2.1 Study on synthesis

Magnetic nanoparticles have been produced by using organometallic precursors because organometallic compounds are easy to be pyrolyzed and thus to form metal nanoparticles. Well-dispersed magnetic nanoparticles are difficult to be obtained with inorganic metal salts as precursors. With the success of synthesis of well-dispersed Ni nanoparticles with PVP and DDA as protecting agents, it may also be possible to produce Fe and Co nanoparticles with future studies.

For the synthesis of Ag nanoparticles, using ligands can control the growth of particles. Resulting complexes reduce the free metal ions in the reaction solution for the nucleation and growth of nanoparticles and also can release metal ions gradually during the reduction. The stability constants of complexes determined the rate of release of metal ions. Therefore, it is possible to control the particle size by changing the ratio of ligand to Ag ions or by using different ligands. The structures of ligands may also affect the morphology of resulting Ag nanoparticles. Further study can be carried out on the synthesis of Ag nanoparticles to control particle size and shape to a high degree.

7.2.2 Study on mechanisms

The mechanism of DDA controlling particle size and shape can be further studied in detail. For example, an increase of the amount of DDA beyond the optimum amount
led to changes in morphology and in some cases led to a bimodal size distribution. The reasons for this may be explored.

During the synthesis of Pt nanoparticles, adding distilled water favored the formation of Pt nanorods. The reason for this is not fully understood and can be explored further.
7.3 References


VITA

Dongsheng Li

Dongsheng Li was born on December 12th, 1975 in Changchun, The People’s Republic of China. She graduated from Jilin Experimental High School in 1994. She then entered Jilin University and obtained a B. S. from chemistry department (major, applied chemistry) four years later. She stayed in Jilin University for another three years and received a M. S from the same department in 2001. She continued her education at The Pennsylvania State University in Fall 2001, where she began her Ph. D studies in Intercollege Graduate Program in Materials with Dr. Sridhar Komarneni.