

**EPOXIDIZED NATURAL RUBBER (ENR-50) STABILIZED  
GOLD AND PLATINUM ORGANOSOLS**

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GOLD AND PLATINUM ORGANOSOLS**

**by**

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## LIST OF ABBREVIATIONS

$2\theta$	Bragg angle
ABS	Absorbance
AgI	Silver iodide
AgNO <sub>3</sub>	Silver nitrate
AgSO <sub>4</sub>	Silver sulphate
AOT	Diethyl sulfosuccinate sodium
Au <sup>0</sup>	Gold metal
ca.	Carcinoma (in approximately, about)
DDAC	Dimethyldioctadecylammonium chloride
EC	Ethylene carbonate
ENR	Epoxidized natural rubber
fcc	Face-center cubic
FTIR	Fourier transform infrared
GPC	Gas permeation chromatography
H <sub>2</sub> PtCl <sub>6</sub>	Hexachloroplatinic acid
HAuCl <sub>4</sub>	Hydrogentetrachloroauric acid
hCG	Human chorionic gonadotropin
IgG	Immunoglobulin G
K	Kelvin
KBH <sub>4</sub>	Potassium borohydride
M <sub>n</sub> <sup>+</sup>	Charge metal clusters
M <sub>n</sub> <sup>0</sup>	Metal clusters
MTP	Multiply twinned particle
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	Sodium citrate
NaBH <sub>4</sub>	Sodium borohydride
ABR	Acrylonitrile butadiene rubber
PAA	Polyacrylic acid
PC	Propylene carbonate
PE	Poly(ethylene)
PEG	Poly(ethylene glycol)

PI	Polyimide
PMMA	Polymethylmethacrylate
PVA	Poly(vinyl alcohol)
PVC	Polyvinyl chloride
PVP	Polyvinylpyrrolidone
SBR	Styrene butadiene rubber
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
SET	Single electron tunneling
TEM	Transmission electron microscope
$T_g$	Glass transition temperature
$TiO_2$	Titanium dioxide
TOAB	Tetraoctylammonium bromide
UV-Vis	Ultraviolet-visible spectrophotometer
XRD	X-ray diffractometer
ZnSe	Zinc selenide
$\lambda_{max}$	Wavelength at maximum absorbance

# AURUM DAN PLATINUM ORGANOSOL DISTABILKAN DENGAN GETAH ASLI TEREPOKSIDA (ENR-50)

## ABSTRAK

Organosol logam aurum dan platinum telah disintesis secara *in-situ* dengan kehadiran ENR-50 melalui kaedah penurunan kimia menggunakan 2-propanol sebagai agen penurun. Organosol yang setara juga telah disediakan melalui teknik pemindahan fasa dari air ke toluena bagi partikel yang telah terbentuk dalam pelarut akueus melalui penurunan ion logam oleh natrium borohidrida ( $\text{NaBH}_4$ ). Bagi penyediaan *in-situ*, nanopartikel aurum dan platinum yang terbaik dari segi saiz, taburan dan kestabilan boleh diperolehi dengan mengubah kepekatan ion logam dan suhu tindak balas. Saiz nanozarah aurum berkurang dengan pengurangan kepekatan ion aurum dan pada suhu tinggi (refluks) menghasilkan partikel sekecil 9.6 nm manakala saiz nanozarah platinum berkurang dengan peningkatan kepekatan ion platinum dan suhu sederhana (ca.  $80^\circ\text{C}$ ) dengan penghasilan saiz partikel sekecil 1.7 nm. Perubahan suhu tindak balas akan mempengaruhi kadar penurunan ion logam serta isipadu hidrodinamik ENR, menghasilkan partikel aurum dalam lingkungan 9.6 hingga 45.6 nm dan bagi platinum pula dalam lingkungan 1.7 hingga 173.6 nm. Namun, bagi platinum dengan kepekatan berbeza, zarah terkecil hanya mungkin apabila rantai ENR mengalami pembukaan separa gelang epoksida yang terjadi pada kepekatan ion platinum tinggi dan membuka ruang bagi logam kepada tapak C=C pada rantai ENR. Walau bagaimanapun, afiniti aurum dan platinum yang berbeza terhadap C=C menyumbang kepada tren saiz yang diperolehi bagi logam-logam ini dalam penyediaan *in-situ*. Nanopartikel aurum dan platinum yang lebih kecil bersaiz 4.0 hingga 7.2 nm dengan taburan saiz yang kecil boleh didapati dari kaedah pemindahan fasa cecair-cecair. Pemindahan nanopartikel logam dari fasa akueus ke organik adalah sangat cekap dan mempunyai perubahan saiz nanopartikel yang sangat kecil sebelum dan selepas

pemindahan. Nanopartikel logam yang berpindah distabilkan oleh nano-lubang yang wujud dalam rangkaian ENR dan kestabilan itu diperkukuhkan melalui kompleks logam dengan C=C dan gelang epoksida ENR. Terdapat bukti bahawa logam partikel dilucutkan dari penstabil awal, sitrat, semasa pemindahan dari fasa akueus ke fasa organik disebabkan oleh keupayaan ENR sebagai penstabil yang lebih baik dalam fasa organik. Pelbagai morfologi nanozarah aurum dan platinum yang terbentuk melalui dua kaedah ini boleh dinilai dari model yang telah diketahui. Daripada penyelidikan ini, didapati bahawa ENR adalah penstabil serba boleh bagi nanozarah aurum dan platinum yang diperolehi dari kedua-dua kaedah penyediaan ini iaitu secara *in-situ* dan teknik pemindahan fasa tanpa mengambil kira terhadap perubahan struktur ENR.



# EPOXIDIZED NATURAL RUBBER (ENR-50) STABILIZED GOLD AND PLATINUM ORGANOSOLS

## ABSTRACT

Gold and platinum metal organosols were synthesized *in-situ* in the presence of ENR-50 via chemical reduction method by employing 2-propanol as the reducing agent. A similar organosols was also prepared via water to toluene phase transfer technique of the preformed particles in aqueous solution by sodium borohydride ( $\text{NaBH}_4$ ) reduction of metal ions. For the *in-situ* preparation, the finest gold and platinum nanoparticles in terms of size, dispersability and stability can be obtained by varying the metal ions concentrations and reaction temperatures. The size of gold nanoparticles decreased with decreasing gold ions concentrations and at higher (reflux) temperature affording the smallest particles of 9.6 nm while the size of platinum nanoparticles decreases with increasing platinum ions concentration and moderate temperature (*ca.* 80°C) with 1.7 nm particle size obtained. Changes in the reaction temperatures will influence the rate of reduction of metal ions and the hydrodynamic volume of ENR, forming gold particles in the size range of 9.6 to 45.6 nm and for platinum ranging from 1.7 to 173.6 nm. However, for platinum at different concentrations, the smallest particles is only possible when the ENR chain experience partial opening of epoxide ring which occurs at high platinum metal ion concentration thus creating accessibility for the metal to the C=C sites in the ENR chain. Nonetheless, the different affinity of gold and platinum towards C=C contributes to the different size trends obtained for these metals in the *in-situ* preparation. Smaller gold and platinum nanoparticles in the size range of 4.0 to 7.2 nm with very narrow size distribution can be prepared through the liquid-liquid phase transfer technique. The transfer of the metal nanoparticles from aqueous to organic phase was highly efficient and with very little variation on the size of the nanoparticles before and after transfer.

The metals transferred were stabilized by the nano-void exist in the ENR interchains and the stability was further enhanced by the metal complexation to the C=C and epoxide ring of ENR. There is evidence that the metal particles are stripped of the initial stabilizer, citrate, during transfer from aqueous to organic phase due to the better stabilizing capability of ENR compared to citrate in the organic phase. Various morphologies of gold and platinum nanoparticles formed via both methods can be evaluated in terms of the known models. From this research, ENR was a capable stabilizer for gold or platinum nanoparticles obtained from both the *in-situ* and phase transfer method regardless of the changed in the structure of ENR.

# CHAPTER 1

## INTRODUCTION

Metals and polymer are two very useful and undeniably indispensable materials to humankind. However, upon blending these two materials, a new polymer-metal composite material will be formed. The polymer-metal composite may exhibit its respective individual properties or a new range of properties due to the interaction of metals with polymers. In the era of nanotechnology, research on nanomaterials is growing by the day with rising demand. This is because metals in nanometer size will exhibit special properties and characteristic that differ and are more superior from bulk metals. Therefore, it is utmost important to study the formation of metal nanoparticles within a polymeric matrix. However, the usage of natural polymers especially natural rubbers has been trailing in the production of nanomaterials. This does not however implicate that natural rubber is inferior in properties for the formation of nanomaterials. In contrast, the derivatives of natural rubbers such as epoxidized natural rubber (ENR) had some excellent properties comparable to synthetic polymer. With the easily available source of natural rubbers and its derivatives here in Malaysia, it is vital to utilize our natural resources to its core as part of the competition towards new and enhanced materials. Therefore, this thesis is dedicated to the investigation of nanocomposites formation of noble metal nanoparticles and epoxidized natural rubber.

### 1.1 Nanostructured Metals

Nanostructured metals are becoming more important in applications of catalysis<sup>1</sup>, sensors<sup>2</sup>, electronics<sup>3</sup>, biotechnology<sup>4</sup> and biomedicine<sup>5</sup>. Shrinking of bulk metals into subatomic metal particles resulted in new physical properties such as optical and magnetic properties and chemical reactivity such as catalytic activity. This phenomenon is associated with the quantum size effect<sup>6</sup>. The valence and conduction band of a metal nanoparticles are well separated into two discrete bands<sup>7</sup> as compared to bulk

metals that have a continuous band. As the diameter of the particle decreases towards de Broglie wavelength <sup>7</sup>, the electrons will be accumulated around the surface of the nanoparticles. Therefore, the physical properties and chemical reactivity of nanoparticles are expected to differ from its respective bulk metals.

Among the metals that were employed in the study of nanostructured materials are those of the noble or precious metal such as gold, platinum, palladium, copper and silver. Since the Middle Ages, colloidal gold was termed by the alchemists as 'drinkable gold'. Many philosophers, medical practitioners and chemists had attributed colloidal gold with curatives properties for treatment of various diseases such as venereal diseases, dysentery, epilepsy and tumors <sup>8</sup>. In the later years, platinum was discovered. Michael Faraday once termed platinum as a "beautiful, magnificent and valuable metal". Platinum was later revered for its uses in heterogeneous catalysis, making of alloy steels, preparation of optical glasses and also in electrochemical applications <sup>9</sup>. With the evolution of nanomaterials and nanotechnology, gold nanoparticles have now been widely used in catalysis <sup>10</sup>, sensors <sup>11</sup>, electronic devices <sup>12</sup>, super paramagnetic devices <sup>13</sup>, and in drug delivery <sup>14</sup>. Platinum nanoparticles have also been employed in various applications such as in the catalytic hydrogenation of ethylene <sup>15</sup>, magnetic devices <sup>16</sup> and superconductors <sup>17</sup>. Gold and platinum nanoparticles were also known for its diverse morphology. Chiang and Turkevich <sup>18</sup> had observed the formation of plate-like, rods and spherical gold nanoparticles. Then again, platinum nanoparticles can exist in cube, tetrahedron, trigonal and they can even generate several truncated derivatives <sup>19</sup>.

The reactivity of the nanoparticles is affected by their size, shape and dispersity. The shape and size of the nanoparticles may vary according to its preparation methods. Reducing agents and matrices and/or stabilizers used such as polymers or surfactants will thus affect the overall morphology. It is therefore very important that a protocol can be derived in the manipulation of particle morphology, size and also the organization of nanoparticles. One of the purposes of preparing gold nanoparticles in

colloidal form is to be able to control the size, dispersion, stability and morphology of the nanoparticles. Chemical <sup>20</sup>, electrochemical <sup>21</sup>, electromagnetic <sup>22</sup> and sonochemical reduction methods <sup>23</sup> have been widely applied for the synthesis of colloidal metal nanoparticles. Among some of the chemical reducing agents commonly used are the borohydrides <sup>24</sup>, hydrazine <sup>25</sup>, citrates <sup>26</sup> and alcohols such as methanol, ethanol and 2-propanol <sup>27</sup>. The reaction that takes place using chemical reducing agent is the reduction of metal ions to form metal atoms that subsequently coalesces to nanoparticles. Different reducing agents have different reducing abilities that influence the rate of reductions. Therefore, one of the advantages of employing chemical reducing agent is that varying the preparation condition can control the formation of the nanoparticles <sup>28</sup>. Apart from this, only a small amount is needed to complete a reaction. However, most of the chemical reducing agents are more easily dissolved in aqueous solution compared to organic solvents, making it harder to prepare nanoparticles in organic solution (organosol). Impurities such as boron <sup>24</sup>, phosphorous <sup>29</sup> and oxides <sup>30</sup> also tend to form after reduction using chemical reductants which further complicates the scenario.

## 1.2 Matrices/Stabilizers for Metal Nanoparticles

Even during the middle ages, there had been observation of materials that act as metal stabilizers. It was found that boiled starch will enhanced the stability of colloidal gold <sup>8</sup>. Stabilizers such as ligands <sup>31</sup>, surfactants <sup>32</sup> and polymers <sup>33</sup> were usually used to prevent the growth of the nanoparticles after nucleation. Under normal circumstances, small nanoparticles will aggregate to form larger particles. This is also known as Ostwald Ripening <sup>34</sup>. Both the synthetic and natural polymers have been used to stabilize metal nanoparticles. The former is widely employed. The most common synthetic polymer used is polyvinylpyrrolidone {PVP} <sup>35</sup>. Other examples are poly(vinyl alcohol) {PVA} <sup>36</sup>, poly(ethylene glycol) {PEG} <sup>37</sup> and polymethylmethacrylate {PMMA} <sup>38</sup>. Compared to the numerous synthetic polymers, few natural polymers have

been employed as a stabilizer for the synthesis of metal nanoparticles. Among some of the natural polymers that have been used are chitosan <sup>39</sup>, gelatin <sup>40</sup>, cellulose <sup>41</sup> and tripsin <sup>42</sup>.

### **1.3 Natural Polymers**

One of the problems facing today's environment is disposing synthetic polymeric materials. Even though there are new synthetic polymers that are biodegradable, most synthesized polymers available are not biodegradable. Therefore, use of natural polymers has an added advantage. Natural polymers are the self-occurring polymers that can be found in living things like bacteria, plants and animals. One of the most important polymers in life is the deoxyribonucleic acid or most commonly known as DNA, which can be found in the nuclei of all animals and plants <sup>43</sup>. Among the polymers that originated from plants are cellulose, lignin, and natural rubbers. Natural rubber and its derivatives have never been reported as matrix and/or stabilizer in the production of metals nanoparticles.

### **1.4 Epoxidation of Natural Rubber**

The most common natural rubber originated from the plant *Hevea brasillensis*. The main natural rubber producers in the world are Malaysia, Thailand and Indonesia<sup>44</sup>. The major uses of a natural rubber are for making tires, molded goods and mechanical parts while the lesser uses are the chemical derivatives of rubber <sup>45</sup>. Improved properties of natural rubber for certain applications can be made via chemical modifications. This is possible because of the presence of double bonds (C=C) in the natural rubber polymer chain that act as simple olefin <sup>44</sup>. One of the important products of chemical modification of natural rubber is the epoxidized natural rubber, ENR. Reacting natural rubber with peroxy formic acid can produce ENR <sup>46</sup> (Figure 1.1). It was stated that 1-90% epoxidation of the natural rubber is possible <sup>47</sup>, however only 3 types of ENR were considered as commercial standard <sup>48</sup>. These are ENR-10, ENR-25

and ENR-50 where the integers designate 10, 25 and 50-mole % of epoxide incorporated into the natural rubber chain respectively. Through chemical modification, natural rubber properties would be enhanced. Thus ENR also display properties that are the same as a specialty elastomer such as decrement in air permeability, which is comparable to a butyl rubber and increment in oil resistance, which is comparable to acrylonitrile butadiene rubber (ABR)<sup>49</sup>.

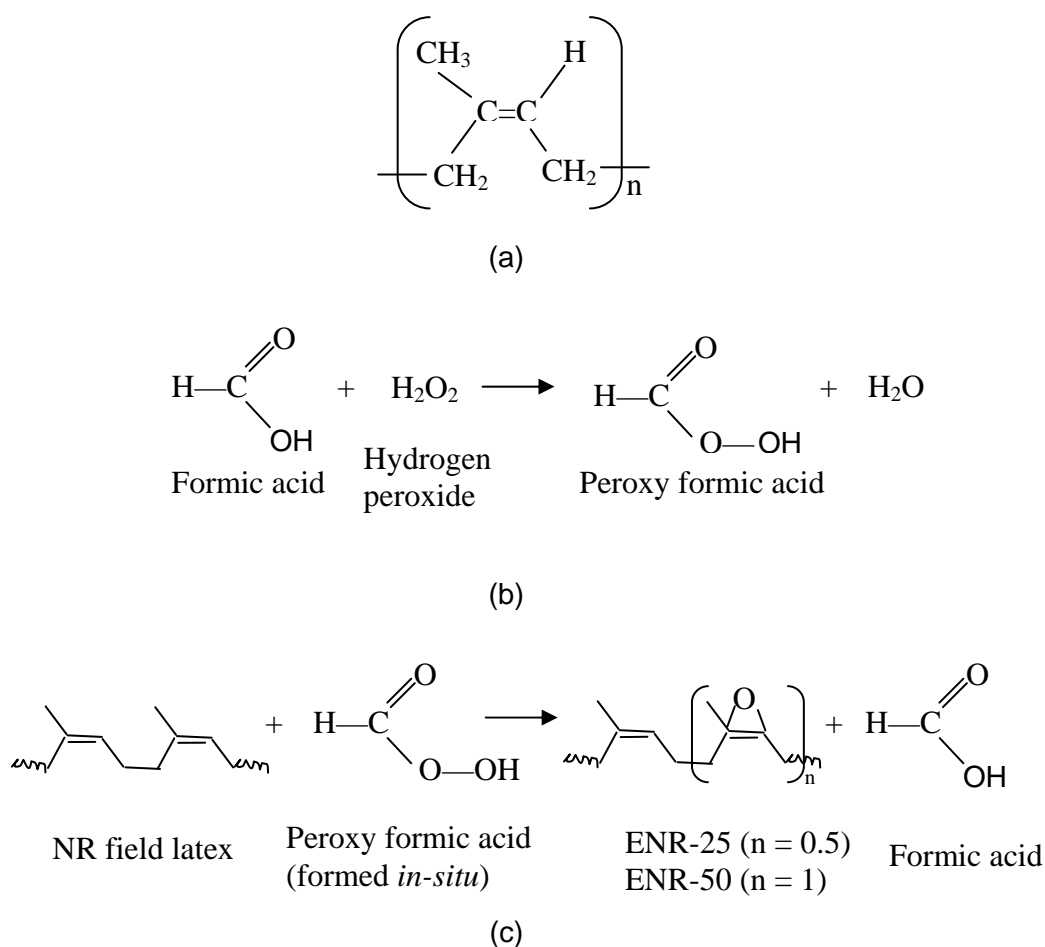


Figure 1.1. (a) Structure of natural rubber, cis-1, 4-polyisoprene, (b) formation of peroxy formic acid and (c) the production of ENR<sup>46</sup>.

Apart from being renewable, the choice of ENR-50 is based on its structural composition of 50 mole % of C=C and epoxide groups respectively, which are randomly distributed in its polymer chain providing sites for physical or chemical interaction. The C=C functional group of ENR can bind with metal ions,  $M_n^+$  and metal particles,  $M_n^0$  respectively<sup>50</sup>. The  $\text{COC}$  groups can also bind to metals through the O

atom but it was reported that binding of oxygen to metals are rather weak <sup>51</sup>. As the mole % epoxidation increases, the rubber becomes much more polar. This means that it will be harder to dissolve in non-polar solvents. Organic solvents such as chloroform, dichloromethane, toluene, xylene, benzene, tetrahydrofuran, dimethylformamide, 1, 2-dimethoxyethane and methylethyl ketone are solvents that ENR can dissolve in <sup>52</sup>. The ENR-50 chains in the organic solution would assume random coil configuration with constant hydrodynamic volume only at equilibrium and dilute solution conditions. According to Flory-Huggins theory <sup>53</sup>, at these conditions, the consequent polymer-solvents and polymer-polymer interactions due to the hydrodynamic volume can be expressed as equation [1.1].

$$\chi_1 = \frac{\Delta H_M}{kTN_1v_2} \quad [1.1]$$

Where  $\chi_1$  is the interaction parameter (unitless),  $\Delta H_M$  represents the enthalpy of mixing,  $k$  is the Boltzmann's constant,  $T$  is temperature,  $N_1$  represents the number of molecules and  $v_2$  is the volume fraction of polymer. Equation [1.1] relates the interaction parameter  $\chi$  to temperature  $T$ , which qualitatively indicates an increase in solubility with temperature where the value of  $\chi$  decreases corresponding to enhanced solubility. Increase in solubility is accompanied by the increase in the hydrodynamic volume due to the extended chain configuration of the random coil. The influence of hydrodynamic volume of chain coil in providing accessible sites in a polymeric chain is crucial for adsorption or interaction with the said metal ions or its metal on nanoscale size.

#### 1.4.1 Utilization of ENR

ENR, exhibits both rubber and special elastomer characteristics that can be tailored for various usages. Some of the potential commercial uses of ENR with respect



to its special characteristics are shown in Table 1.1 <sup>49</sup>. Besides the proposed commercial uses shown, ENR has the potential to be further exploited for its usage as advanced materials such as in blends, additives and fuel cells applications.

Table 1.1. Potential commercial uses of ENR <sup>49</sup>.

	Characteristics	Applications
1	Wet grip, low rolling resistance	Tires, non-slip flooring, sports shoe soles
2	Oil resistance, high strength	Hoses, seals, blow-out preventors, milking inflation, connector and tubing
3	Glass transition temperature, $T_g$ , variable with degrees of epoxidation to that of ambient temperature	Coatings and paints
4	Silica and pigments reinforcements	Cosmetics, color coding
5	Damping	Anti-vibration mountings and other engineering applications
6	Adhesion	Adhesives, cover for PVC conveyor belt
7	Low gas permeability	Bladders, inner tubes, and tire liners

#### a) Polymer blends

Blending of two or more of different polymers can provide a combination of properties which cannot be attained by a single polymer component <sup>54</sup>. ENR had been blended with various polymers such as natural rubber <sup>55</sup>, styrene butadiene rubber (SBR) <sup>56</sup> and polyvinyl chloride (PVC) <sup>57</sup>. One of the polymer blends is exemplified with the blending of ENR with styrene butadiene rubber. It was reported that its processability, stiffness, resilience had been improved while the damping property had been reduced <sup>58</sup>. Blending of ENR with different types of polymers will also exhibit different properties of the blends with respect to the concentration of each polymers, concentration and types of additives added and content of stabilizer <sup>59</sup>.

#### b) Additives <sup>60</sup>

Catalyst such as  $TiO_2$  was used in the photocatalytic detoxification of water and wastewater treatments. The catalyst can either be deposited on a substrate or in a

suspension mode for it to be usable. It was found that ENR as an additive would improve the adhesiveness on the deposition of  $\text{TiO}_2$  to its substrate while different amount of ENR added will influence the adhesiveness of the catalyst and its photocatalytic activity.

### **c) Fuel cell applications**

ENR can perform as polymer electrolytes just like polyethylene oxide, which can be used in rechargeable lithium batteries <sup>61</sup>. With an addition of ethylene carbonate (EC) and propylene carbonate (PC), the ionic conductivities of the polymer can be enhanced at ambient temperature <sup>62</sup>. The ability of ENR to form films and also behave as electrolytes can be further utilized for fuel cell and solar cell applications.

## **1.5 Problem Statements**

ENR possessed enhance properties comparable to several commercially popular synthetic polymers. ENR have found applications in advanced materials preparation such as in polymer blends <sup>56,57</sup>, adhesives <sup>49</sup> and fuel cell applications <sup>61,62</sup> but have not been used as a stabilizer and/or matrix for the preparation of metal nanoparticles, which are currently the many precursors to numerous other advanced materials. Since ENR is insoluble in aqueous solution but soluble in limited organic solvents, indigenous methods have to be developed in order to be able to utilize ENR to the described potentials. The synthesis of metal nanoparticles in organic phase (organosol) produces larger particles with little control on the morphology as compared to synthesis in the aqueous phase. In addition, aqueous phase syntheses have several advantages such as numerous reducing agents available, provision of protoxic environments and solubility of metal salts among others. Controlling the size and morphology of nanoparticles in organosol is proving to be a challenge. It is important to be able to control the size and morphology of the said nanoparticles by simply varying the conditions and the environments during preparation. This is because noble metals especially gold and platinum nanoparticles can have different applications according to

size and shape. Another interesting point is the dispersion of the nanoparticles. Aggregation tends to occur in these small particles due to its clusters that are metastable while it is known that finely dispersed metal nanoparticles have a much higher surface area compared to aggregated metals. Therefore, suitable stabilizers are needed to stabilize the nanoparticles against aggregation. One of the added advantages of using ENR is that metal colloidal composites can be casted into a thin film. Therefore, thin film comprising of gold or platinum nanoparticles embedded in the matrix of ENR can also be formed upon drying of the colloids. It is reported that by using polymer, the nanoparticles can be redispersed without forming aggregates<sup>63</sup>.

### **1.6 Aims and Scope of This Work**

The aim in the present study is to use ENR as a stabilizer for gold and platinum nanoparticles synthesized as organosols such that a disperse nanometer size metal particles that is stable (against precipitation and aggregation) when in colloidal form and well dispersed when in the form of thin film.

As ENR is only soluble in limited organic solvent, the ENR-metal composite can only be prepared as organosols. The organic solvent chosen is toluene. Two methods will be employed in the preparation of organosols. The first method will be dedicated to the *in situ* formation of gold and platinum organosols and will be synthesized by alcohol reduction, namely isopropanol. Preparation conditions such as concentration of metal precursors used and reaction temperatures are the parameters to be investigated. This is then related to the size, dispersability and morphology of the metal nanoparticles formed. The second method will be dedicated to the synthesis of the respective metal organosols via the transfer of pre-synthesized gold and platinum nanoparticles in aqueous solution to the organic ENR-toluene solution. The pre-synthesized hydrosol will be formed via the chemical reduction using sodium borohydride as the reducing agent. Size control capability and the morphological outcome resulting from the above organosols prepared will be compared.

## 1.7 Objectives of Thesis

The work described in this thesis has the following objectives:

1. To synthesize gold and platinum metal organosols in the presence of epoxidized natural rubber (ENR-50) via chemical reductions by employing 2-propanol as reducing agents (*in-situ* preparation).
2. To synthesize gold and platinum metal organosols stabilized by epoxidized natural rubber (ENR-50) via water to toluene phase transfer technique with  $\text{NaBH}_4$  as the reducing agent.
3. To study the effect of various experimental parameters such as concentration of metal ions used and reaction temperatures of the *in-situ* preparation (1) for the formation of finest colloidal nanoparticles in term of size, dispersability and stability.
4. To evaluate the extent and capability of ENR as stabilizer for the respective organosols.
5. To evaluate the morphology outcome of the colloidal nanoparticles in the organosols in terms of known models.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Nanotechnology**

Nanotechnology is often described as the future of technology. It is not just about downsizing the existing devices from micron scale to the nanometer scale but is also concern in creating a completely new technology based on nanomaterials with undreamt-of sensitivity and efficiency <sup>64</sup>. The three most important commercial nanomaterials are nanoclays, nanoscale metals and metal oxides and the carbon nanotubes <sup>65</sup>. By manipulating matter at the atomic level, the nanomaterials employed in nanotechnology is widely viewed as a potential source of advances in various fields such as in electronics, fuel cells, computers, telecommunications, sensors and development of new disease-fighting drugs <sup>66</sup>.

It was reported that between 1997 and 2003, the worldwide investment for research and development in nanotechnology has increased six fold (with most lavish investments by the Western Europe, Japan and USA) and at least 35 countries have begun national activities in this field <sup>67</sup>. The top 10 countries with the largest number of nanotechnology patents are the United States, Japan, France, the United Kingdom, Taiwan, Korea, the Netherlands, Switzerland, Italy and Australia <sup>68</sup>. These tremendous leaps in nanotechnology development are due to the necessity to improve some of the technologies that are already in use while others are due to the needs and future applications as listed in Table 2.1 <sup>69, 70</sup>.

Table 2.1. Current and future applications of nanotechnology.

Area	Application
Medicine	Medical nanodevices that could locate and disable unwanted and dangerous bacteria, viruses, parasites and also cancer cells.
Cosmetics	Creams packed with nanomachines can be more effective to remove dead skin, excess oils, restore missing oils, control the right amount of moisturizer needed and achieve better deep pore cleansing.
Sensors	Improvement in medical sensors means more precise and accurate diagnostic while improvement in chemical sensing will be an added advantage for development in research.
Instrumentations	Nanostructured metals can be made to produce different cutting tools.
Colloids science	Nanoparticles can be used in paints and colorants to enhance and modify its physical characteristics and also to increase its lifetime longevity.
Catalysts	Catalyst depends on its surface area for maximum reactivity. Reduction in size of catalysts will increase its surface area. Thus, the rate of reactivity will also increase.
Electronic devices	Based on single electron tunneling (SET) devices that can be produce from self-assembly of metallic or nanoparticles network linked by organic molecules such as alkyl-thiol.

## 2.2 Nanoparticles

What is nanoparticle? When is a particle a “nanoparticle”? The prefix nano is a billionth of a meter or the measurement of  $10^{-9}$  m, which is roughly five times the diameter of one hydrogen atom <sup>71</sup>. A nanoparticle is also term as any solid material falling within the classical colloidal size range <sup>72</sup>. There is not a definite agreement on the range of the nanometer size particle. Henglein terms nanoparticle as ‘small-particle’, which meant clusters of atoms such as molecules of metals and semiconductors, ranging in size from 1 nm to 10 nm, or having agglomeration numbers from less than ten up to a few hundreds <sup>73</sup>. Other researchers define it from 1 nm to 100 nm <sup>74</sup>. Rotstein and Tannenbaum <sup>75</sup> described that metal nanoclusters are in the range of 1 nm to 1000 nm between the regime of metal atoms in the molecular scale and bulk metal at mesoscale, as shown in Figure 2.1.

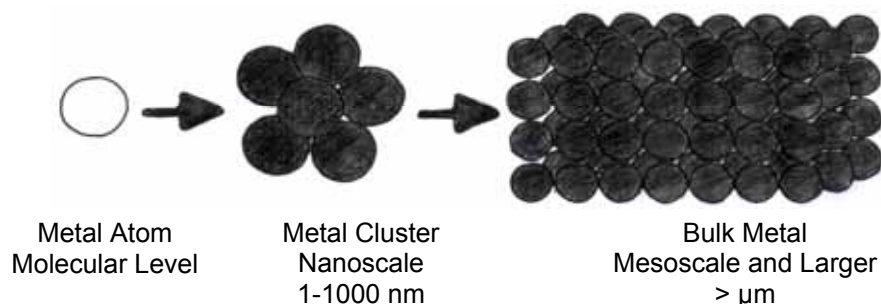


Figure 2.1. Schematic description of the relationship of the transition nanocluster regime between the discrete atom state and the solid bulk state as depicted by Rotstein and Tannenbaum <sup>75</sup>.

Johnson <sup>76</sup> gives a more specific division for small metal particles, as depicted in Figure 2.2., where the smallest structure is made up of a single metal ion followed by transition metal clusters in the nanometer range. The difference in the classification between that of Johnson’s and Rotstein and Tannenbaum <sup>75</sup> is in the subdivision of colloidal metals in the range of  $10^{-7}$  m and  $10^{-8}$  m. However, both transition metal clusters and colloidal metals are all within the range of 1 to 1000 nm.

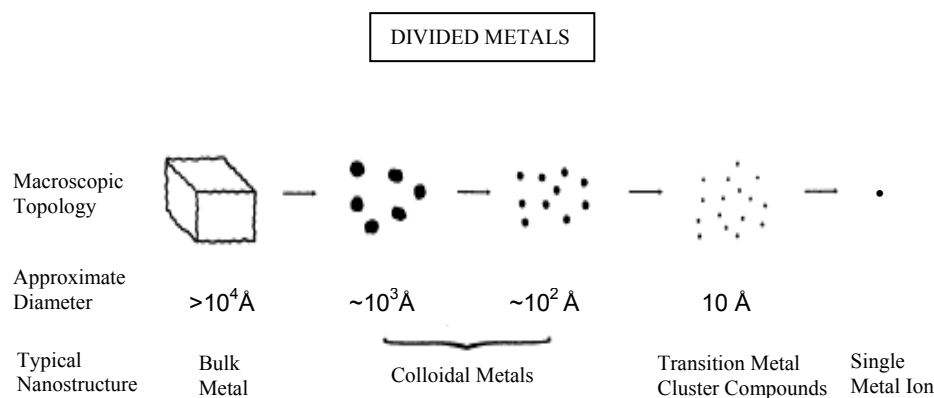


Figure 2.2. Division of metals as depicted by Johnson and co-workers <sup>76</sup>.

In general, clusters or aggregates of small particles can be divided into 6 types <sup>77</sup>, as shown in Table 2.2. Metal clusters or particles are one out of the six divisions together with semiconductor clusters, ionic clusters, rare gas clusters, molecular clusters and cluster molecules. Metal nanoparticles can be synthesized with or without a support. Unsupported nanoparticles are sometimes known as bare or naked nanoparticles. Most of the commonly used supports are surfactants, ligands and polymers. Supported nanoparticles usually exist in the form of nanocomposites.

Table 2.2. Types of clusters.

Type of Clusters	Description
Metal clusters	Metallic elements from across the periodic table such as the alkali and alkaline earth metal and the transition metals.
Semiconductor clusters	Clusters made up of elements such as carbon, silicon and germanium.
Ionic clusters	Bonding in the clusters is ionic or electrostatic in nature caused by the electronegativity difference between two elements.
Rare gas clusters	Forms at low temperatures bound by van der Waals bonding.
Molecular clusters	Formed by supersonic expansion of molecular vapor.
Cluster molecules	Inorganic and organometallic clusters which are thermodynamically and/or kinetically stable.



## **2.3 Nanocomposites**

Nanocomposites can be identified as a combination of two or more phases containing different compositions or structures where at least one of the constituent phases are in the dimension of nanometer scale <sup>74, 78</sup>. The dimension could either be its length, width or even thickness. The phases of a conventional nanocomposite are in the dimension of microns. Therefore, nanocomposite has a more enormous surface area and larger interfaces compared with the conventional phases. Nanocomposite can be classify into two types according to its existing form. They can either be in colloidal form or in the form of film.

### **2.3.1 Colloidal Metal Nanoparticles**

Colloids was firstly defined by a Scottish's' chemist named Thomas Graham in the year 1861 <sup>79</sup>. He defined it as "a substance, such as starch or gelatin, which will not diffuse through a membrane". Later on, colloids were differentiated from true solutions by the presence of particles that were too small to be seen under normal microscope yet much larger than normal molecules. Colloids are now termed as a heterogeneous system in which the particles, droplets or bubbles are dispersed in another phase (continuous phase) where the dispersed phases are in the dimensions of 1 nm to 1000 nm <sup>72, 80</sup>. Therefore, colloids can be classified into different systems according to its dispersed and continuous phase. Colloidal metal can then be synthesized via supported metal nanoparticles method and is in the solid- liquid colloidal form. The types of colloids available are shown in Table 2.3.

Table 2.3. Types of colloids <sup>72, 81</sup>.

<b>Dispersed Phase</b>	<b>Continuous Phase</b>	<b>System Name</b>	<b>Examples</b>
Liquid	Gas	Aerosol of liquid droplets	Fog, mist
Gas	Liquid	Foam	Soapsuds
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Solid suspension	AgI, ink gels, bacteria in water
Liquid	Solid	Solid emulsion	Opal
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Solid	Solid foam	Expanded polystyrene
Solid	Solid	Solid suspension	Ruby-stained glass, pearl

### 2.3.2 Film

In general, there are four phases in the formation of films. Examples of the thin film formation can be seen through the drying of polymer latex dispersion in water <sup>82</sup> as shown in Figure 2.3. Polymer-metal thin film (Ag, Au, Pt and Cu) had been synthesized by various methods such as vacuum evaporation <sup>83</sup>, solvent evaporation <sup>84</sup>, spin coating <sup>85</sup> and sputtering <sup>86</sup>.

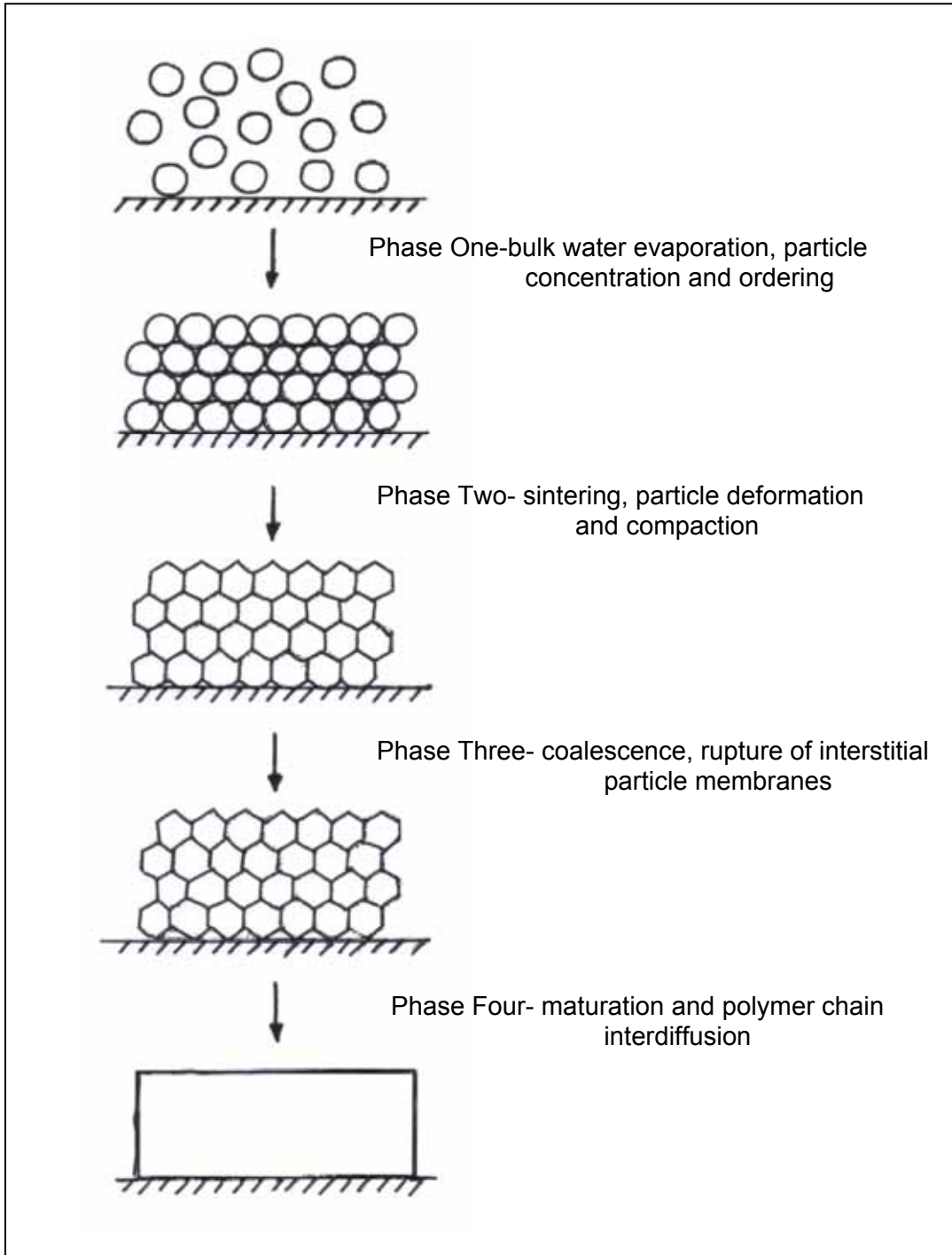


Figure 2.3. Idealized film formation process from latex dispersions <sup>82</sup>.

## 2.4 Synthesis of Metal Nanoparticles

According to Warner and Hutchison <sup>87</sup>, the “ideal” nanoparticle samples for investigative and application purposes are highly influenced by the following five fundamental characteristics:

- Metal core size, which will manipulate its optical and electronic properties
- Core size dispersity, which will influence the distribution of its properties
- Surface functionalization, which will stabilize and control its reactivity
- Stability, for ease of isolation, purification and storage
- Ease of synthesis

Generally, particles are generated through nucleation and growth. The growth of the particles could either be the primary growth or the secondary growth <sup>88</sup>. The primary growth refers to the growth of the particle size by molecular diffusion on the seed of the nuclei. On the other hand, the secondary growth refers to the collision and joining of two or more particles to form a new particle. The final state of the particles through the secondary growth may be in the form of agglomerate or aggregate. The difference between agglomerate and aggregate is in the binding of the nanoparticles. It was described that agglomerate is a collection of two or more particles held together by a strong interparticle force. In contrast, aggregate is described as particles that are held together by a weak cohesive force. The schematic diagram of the particle formation can be seen in Figure 2.4 <sup>88</sup>. Therefore, supporting agents can be employed to achieve well-dispersed small metal nanoparticles against agglomeration or aggregation. Figure 2.5 depicts the simplified way for the synthesis of unsupported and supported metal nanoparticles.

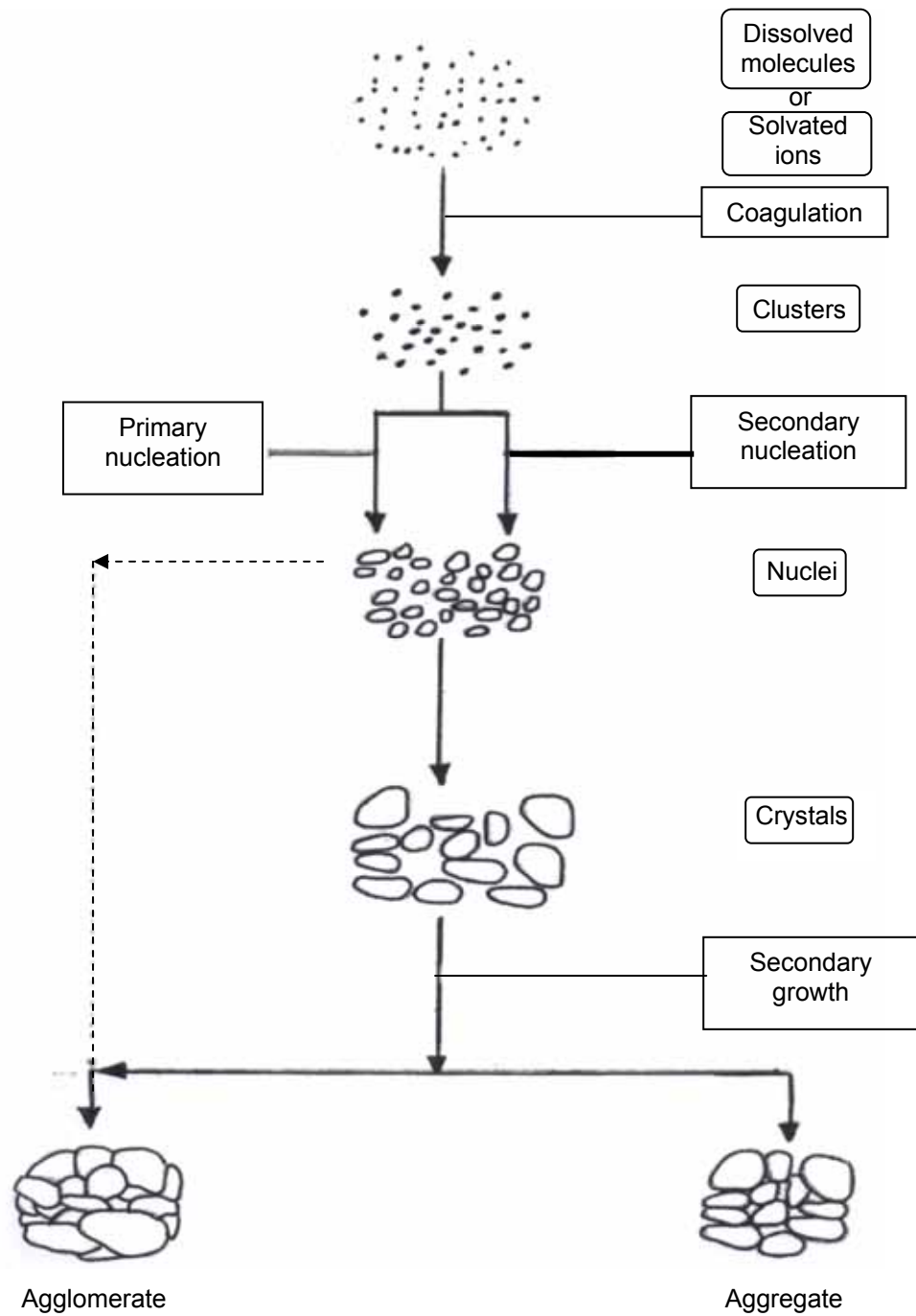


Figure 2.4. The schematic diagram of the particle formation in solution <sup>88</sup>.

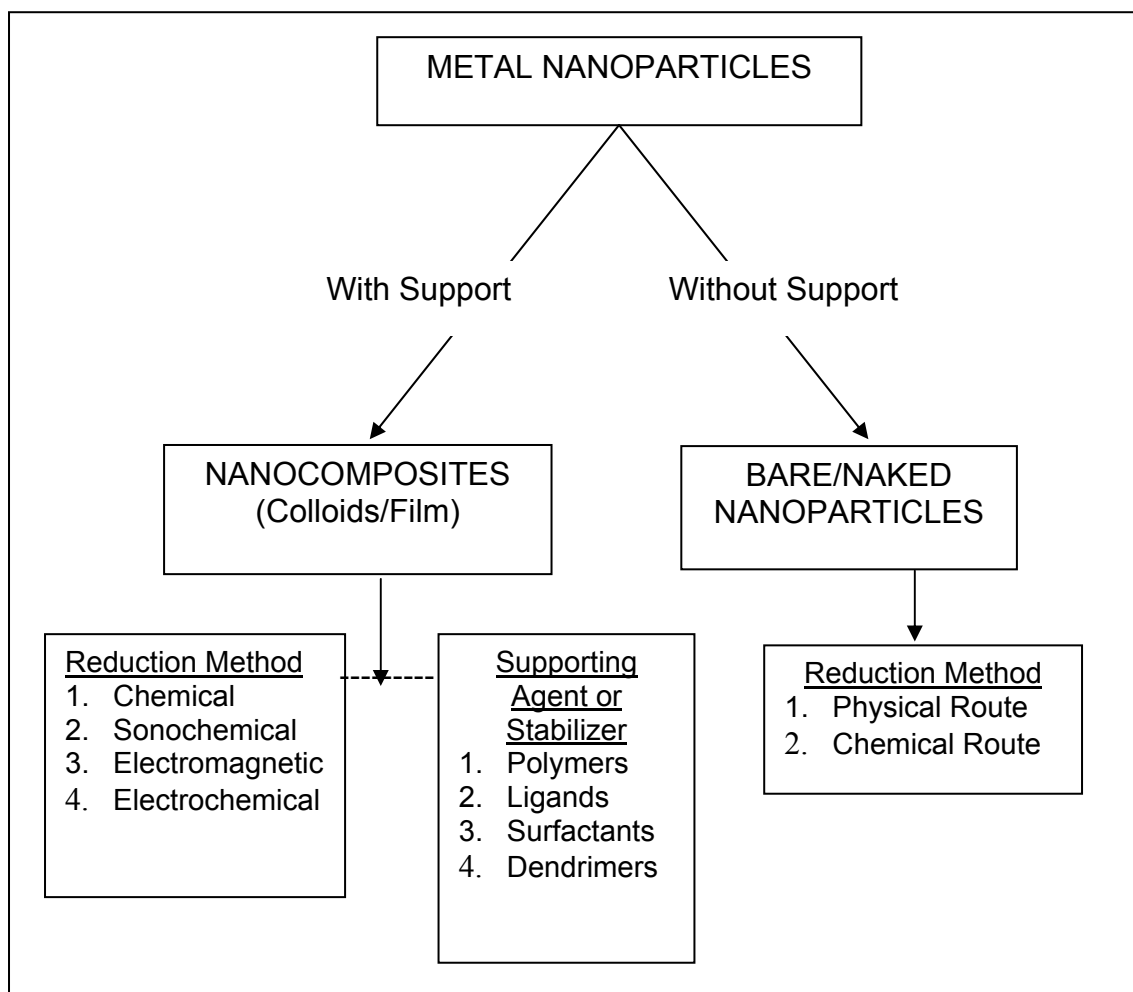


Figure 2.5. Route to synthesis of unsupported and supported metal nanoparticles.

### 2.4.1 Unsupported Metal Nanoparticles

Metal nanoparticles are easily driven together upon collision caused by the attraction forces between the particles namely the van der Waals forces<sup>89</sup>. Without a support or barrier between each particle, the metal particles do not have enough repulsion energy to overcome the attraction forces.

In general, there are two synthetic routes to unsupported nanoparticles. They can be synthesized either by the chemical route or the physical route. For chemical route<sup>90</sup> or also known as the wet method, the particles are nucleated or formed from its respective metal precursor by reduction using a suitable reducing agent/technique. This is sometimes label as the “bottom–up” processes. For physical route though, mechanical devices were used to reduce the size of bulk metals to nanosize particles.

#### **2.4.1.1 Chemical Route to Bare/Naked Metal Nanoparticles**

One of the most common routes to bare/naked metal nanoparticles is by chemical reduction using a compatible reducing agent without any supporting agent. Among some of the well-known reducing agents are sodium borohydride ( $\text{NaBH}_4$ )<sup>91</sup>, alcohols such as isopropanol or methanol<sup>92</sup>, sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ )<sup>93</sup>, hydrazine ( $\text{N}_2\text{H}_4$ )<sup>94</sup> and electromagnetic irradiation such as microwave and ultra-violet<sup>95</sup>. Bonet et al.<sup>96</sup> have synthesized metal nanoparticles of Au, Pt, Pd, Ru and Ir by reduction using only ethylene glycol. The sizes of the metal nanoparticles produced are small and in the range of 10 nm. However, apart from Ir, all the other metal nanoparticles are aggregated.

#### **2.4.1.2 Physical Route to Bare/Naked Metal Nanoparticle**

##### **a) Mechanical attrition**

A simple way to describe the physical method is grinding of bulk metals into smaller particles, which is also known as mechanical attrition. However, to achieve it in nano size, mechanical devices have to be applied together with energy. In general, this method is called the milling process. According to Castro and Mitchell<sup>90</sup>, three steps are involved in the milling process. The first step is the rearrangement and restacking of particles, which will form at first, irregular shape particles. The second compaction step involves the elastic and plastic deformation of particles while the third compaction step involves deformation and fragmentation leading to small particles. One of the limiting factors in the milling process is that, with the increment of cohesion between particles during milling, agglomeration tends to occur following the decrement of the particle size.

## **b) Evaporation-condensation method**

Evaporation-condensation method is also known as the gas-phase technique or inert gas-aggregation technique. The metal nanoparticle was evaporated from a metal source with the assistance of a high-energy beam, with all of this carried out in an inert atmosphere either in vacuum or filled with inert gas such as helium or argon. Tohno et al.<sup>97</sup> had produced bare Ag, Bi, Cu and Te nanoparticles. The nanoparticles were evaporated from a granular or powdered form of each of the corresponding metals by heating, which was held in a tungsten basket, coated with alumina. The experiment was also conducted in a vacuum chamber to produce contact free nanoparticles. It was found that the evaporated metal clusters were also coagulated.

For the study of size-dependant surface plasmon resonances of bare silver nanoparticles, Heath<sup>98</sup> uses an excimer laser to generate bare silver nanoparticles from a silver rod. It is found that large clusters are in favor at low pressure or when helium gas is use. On the other hand, Vitulli et al.<sup>99</sup> employed a different metal vaporization method to prepare unsupported Rh nanoaggregates by heating a tungsten wire coated with electrodeposited Rh that will generate the Rh vapor. An organic solvent called mesitylene was then used as stabilizer to produce small Rh particles. To obtain the bare Rh aggregates; the solution was allowed to decompose at room temperature under argon or hydrogen atmosphere.

### **2.4.2 Reduction Techniques to Metal Nanoparticles**

There are many types of reducing techniques applicable to reduce metal ions from its metal salts. Some of the most common reducing techniques are the chemical, photochemical, electrochemical and sonochemical reduction. Each of these techniques was elaborated as follow;

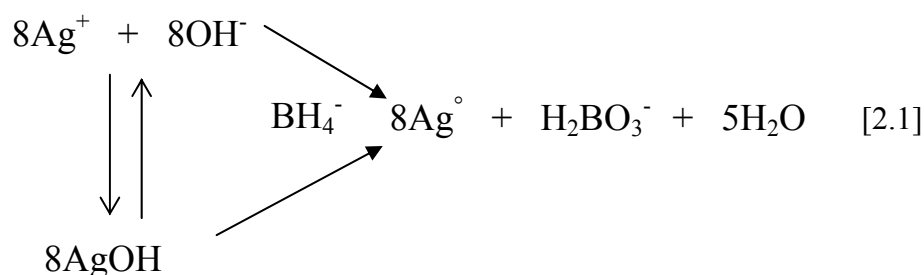


### 2.4.2.1 Chemical Reduction

Different chemical agents have different reducing ability. Among some of the most widely employed reducing agents in nanometals productions are hydroborates, hydrazine and alcohols. Other types of reducing agents such as citrates and glycols can act as both reducing and protective agents.

#### a) Hydroborates

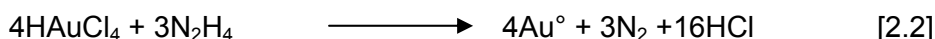
Fairly monodispersed small particles were produced by hydroborates such as the sodium borohydrides ( $\text{NaBH}_4$ ) and potassium borohydrides ( $\text{KBH}_4$ )<sup>100, 101</sup>. The adsorption of  $\text{BH}_4^-$  nucleophile on to the surface of metal nanoparticles will increase its Fermi potential, thus reducing its reduction potential<sup>102</sup>. Hydroborates have been widely used to produce metal sols such as gold, silver and platinum<sup>40</sup>. Below are some of the reactions that could take place for the reduction of  $\text{AgNO}_3$  in the presence of  $\text{NaOH}$  as was done by Shirtcliffe, Nickel and Schneider<sup>20</sup>.



#### b) Hydrazines

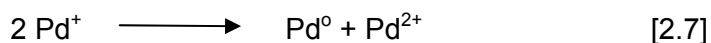
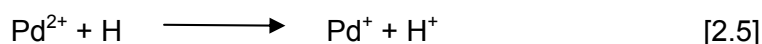
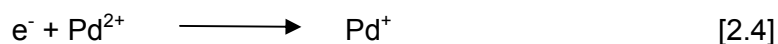
Hydrazine is relatively slower in the reduction rate compared to hydroborates. Tan, Li and Zhu attributed the slower action of hydrazine as the reason for the hexagon shaped silver nanocrystals obtained<sup>103</sup>. They have found that  $\text{AgSO}_4$  reduced by hydrazine in the presence of aniline stabilizer will produced hexagonal shaped nanocrystals in comparison to those obtain by  $\text{NaBH}_4$ , which were mainly spherical. The slower rate of reduction allowed ample time for the silver particles to agglomerate and grew into more regular shapes. Hydrazines have been used in the reduction of

silver <sup>103</sup>, gold <sup>25</sup>, copper <sup>104</sup> and iron <sup>105</sup>. Examples of the reactions involving hydrazine in the reduction of gold ions is shown in equation 2.2 <sup>25</sup>:



### c) Alcohols

Alcohols such as methanol, ethanol and isopropanol had been used as reducing agents due to its ability to form reactive radicals. When energy was introduced in the form of heat <sup>106</sup>, ultrasonic waves <sup>107</sup> or electromagnetic irradiation such as ultra violet <sup>106</sup>, the dissociation of water molecules will produce the hydroxyl radicals ( $\cdot\text{OH}$ ), hydrated electrons ( $e^-$ ) and hydrogen atoms ( $\text{H}\cdot$ ). The hydroxyl radicals and hydrogen atom will react with isopropanol to form 1-hydroxyl ethyl methyl radicals. After that, the hydrated electrons, hydrogen atoms and organic radicals previously formed will act as the reducing agent. The reactions are as follows:



Wang et al. had successfully employed this method in the production of palladium nanorods and nanofractals <sup>108</sup>.

### d) Citrate ligands

The usage of citrate to produce gold sols dated back to 1951 by Turkevich, Stevenson and Hillier <sup>26</sup>. Addition of the aqueous solution of sodium citrate to a boiling chloroauric acid solution will produce the gold sols. The color of the sol would vary from