PREPARATION OF NANOPARTICLES OF PLATINUM, NICKEL, AND COPPER AND STUDIES OF FILM FORMATION, OXIDATION, AND CARBURIZATION

by

Jie Ren

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ABSTRACT

The diffusive motion of atoms can lead to a variety of changes in the physical and chemical properties of solid materials over time. Though solid-state diffusion (SSD) and new phase formation (NPF) in bulk systems have been studied for more than 100 years, high quality 2-D diffusion couples and 0-D and 1-D diffusion couples have been much less extensively studied. This work focuses on the synthesis of samples for the study of diffusion: highly uniform films for two specific 0-D nanomaterial systems: platinum and nickel containing nanoparticles systems, including large-area uniform Pt nanoparticles film synthesis and film assembly mechanism study, and different structure Ni (fcc and hcp-Ni₃C), Cu/Ni core/shell nano-structural material study.

Large area, uniform films of 5-6 nm diameter Pt nanoparticles self-assembled into 30-40 nm diameter aggregates have been prepared at the interface of two immiscible liquid phases: an aqueous Pt colloidal solution and hexane. A possible film formation mechanism was proposed wherein three key aspects related to the film formation: the appropriate surface charges on the nanoparticle surface (ζ -potential of the colloidal Pt must be adjusted to about -30 mV), the driving-force for particles moving from water to water/hexane interface (addition of ethanol minimizes the interfacial energy), and the ability to assemble the film (creation of the gradient of the surface tension makes NPs migrate toward the area of higher tension with formation of a dense monolayer).

In addition, XRD showed an unusual lattice parameter evolution of the Pt nanoparticles, which was not dependent on the inverse grain size with the monolayer film formation. Because the Pt NP surface was slowly oxidized overtime, which was shown by XPS, a reasonable explanation was proposed that the partially oxidation of the surface of Pt film reduced the compressive surface stress and lead to the lattice expansion (still small than the bulk value).

In a separate study, different composition of nanoparticles of Cu_xNi_y (Cu, Cu_1Ni_1 , Cu_1Ni_2 , Cu_1Ni_3 , Cu_2Ni_1 and Ni) with a core/shell structure were synthesized by two reducing agents: sodium hypophosphite (NaH₂PO₂) and hydrazine (N₂H₄), via reduction of copper acetate tetrahydrate and nickel acetate tetrahydrate, respectively, in ethylene glycol. NaH₂PO₂ reduced Cu²⁺ at 100 °C and reduced Ni²⁺ at 175 °C, while N₂H₄ with NaOH, which have a higher reducing power, can reduce Cu²⁺ at room temperature and reduce Ni²⁺ at 100 °C. Both of these two processes form Cu/Ni core/shell structures. The Cu/Ni core/shell nanoparticles were successfully assembled into uniform films and this set of core/shell structure can be used as Cu/Ni diffusion couple.

Chapter 1

INTRODUCTION

1.1 Solid State Diffusion (SSD) on the Nanoscale

Nano-structured materials have attracted considerable attention due to their wide range of applications in many fields: biomedical, [1] energy storage, [2] heterogeneous catalysis [3] and more. [4, 5] Unlike the properties of bulk matter which can generally be characterized as either intensive (i.e. size independent) or extensive, the very large surface-to-volume ratios [6] found in nanostructured materials result in extensive properties that do not scale with the volume and intensive properties that are size dependent. The special size-dependent properties make nanoparticles exhibit remarkably different properties compared to the bulk, such as quantum confinement in semiconductor particles, [7] and super-para-magnetism in magnetic materials. [8] Also, it provides diffusion a tremendous faster speed than that of larger particles, and it allows sintering to take place at lower temperatures and over shorter time scales than for larger particles. As a result, the study of nanostructured materials can lead to new insights into fundamental physical and chemical processes. [9-11]

Diffusion is an old and classic problem in many fields, especially in physics. Historically, solid-state diffusion (SSD) and new phase formation (NPF) in multicomponent bulk system have been studied for more than 100 years. [12, 13] However, SSD and NPF in high quality 2-D diffusion couples have only been systematically studied since the late 1960's [14-16] and SSD and NPF in 0-D and 1-D diffusion couples have been much less extensively studied. [17, 18] These studies reveal that the SSD and NPF in bulk systems and 2-D films are different and sometimes these differences lead to interesting results. For example, 2-D thin films exhibit interdiffusion at relatively lower temperatures compared to the bulk couples. This is due to the cleanliness of the interface between thin films and highly defective microstructures. The low diffusion temperature and the film thickness limitation on diffusion distance impose a kinetic constraint on thin film interdiffusion. [15] As a result, new phenomena in thin film interdiffusion studies.

Furthermore, most investigations of the diffusion processes were done by "traditional" methods, with measurement time scales from seconds to months. More specifically, with long excitation time followed by long measurement time, the time resolution of the collected data is low. Therefore, "modern" ultra-fast time resolved measurements with the typical time scale of sub-nanoseconds is a good choice for studying the diffusion processes.

The "ultra-fast time resolved hybrid pump-probe" technique is this: study photoinduced phase transition which is a succession of out-of-equilibrium states triggered by a laser pulse and then probed after a chosen time delay by a light pulse, X-ray, which can be generated by a synchrotron source. [19] The time resolution scale, which is determined by the longer of the pump and probe pulses, is pico-second. For each pump– probe time delay, the pump-probe process has to be repeated several times in order to generate enough statistics to get a comprehensive scattering pattern, and this process is a "destructive" process, and irreversible. Therefore, the sample needed for pump-probe measurement is required to be the large surface area with enough equivalent testing spots. As a result, the motivation of this thesis is focused on making the large surface area substrate-supported 0-D metallic or bimetallic core/shell nano-structured (nanoparticle or core/shell nanoparticle) uniform films to provide hybrid pump-probe sample to study the solid-state diffusion (SSD) and new phase formation (NPF).

1.2 Nano-structured Material Synthesis

The formation of the nano-structured materials (metal-based nanoparticles and metal-based core/shell nanoparticles) is the first step in creating the thin films of 0-D nanoparticles. The nanomaterials can be synthesized by various methods that are categorized into bottom-up or top-down methods. A simplified representation of the process is presented in Figure 1.1. [20] The top-down approach includes slicing of bulk materials into reduced size. The bottom-up approach, on the other hand, exploits the chemical properties of molecules, involving assembly of a defined structure by joining atom by atom, molecule by molecule, cluster by cluster, i.e., self-assembly of single molecules to build up complex structures on the nanoscale. [21, 22] The bottom up mode is more widely used, since it is more inclined toward synthesis of nanoparticles of different chemical composition, sizes, morphologies and mono-dispersity. [23] For example, some common bottom-up approaches that have been reported to synthesize nanoscale structures are sol-gel process, [24] and chemical reduction to create colloidal suspensions of NPs [25] etc. Among them, chemical reduction to create colloidal suspensions of NPs is one of the most efficient and quickest ways to create metallic NPs. One of the disadvantages of this method is that the synthesized NPs have high surface energies and will tend to agglomerate. To prevent this and maintain a stable colloidal solution, a "capping agent" (e.g. an organic surfactant) is often needed.



Figure 1.1 Synthesis of nanomaterials (NPs) via top-down and bottom-up approaches. Adapted from Reference. [20] Copyright @ 2019 Elsevier B.V.

Moreover, appropriate metallic precursor, reducing reagents or even using a two-step reaction instead of a one-step can be considered. After completion of the reaction, the NPs are treated with simple downstream processing such as high-speed centrifugation for recovery from colloids. [26] Different form synthesize of nanoparticles, the synthesize metallic cores or shells of the core/shell nanoparticles is that the synthesis of core and shell should be separate, so the choice of the reducing agent is important for controlling the reaction rates of the formation of cores and shells. In general, metallic NPs (either core or shell) are synthesized via reduction of their corresponding metal-



Figure 1.2 (a) Redox transmetalation processes for core/shell nanoparticle synthesis. During the reaction, the Pt^{2+} of $Pt(hfac)_2$ is reduced to Pt, while the surface Co atom of the Co nanoparticles is oxidized via hfac ligand migration to form Co(hfac)₂ as a reaction byproduct. Repeating cycles of this reaction result in core/shell bimetallic nanoparticles. (b) HRTEM images of 6.4 nm Co/Pt core/shell nanoparticles. Adapted from Reference. [28] Copyright @ 2004 American Chemical Society.

-salts, either using external reducing agents (such as NaBH₄, hydrazine, etc.) or via using different intrinsic redox properties of the metal precursors, which is using an electroless redox-trans-metalation process where a metal-ligand complex in a positive oxidation state can be reduced through the oxidation of the second surface atoms; repeating this process results in the complete coverage of shell layers on the core metals (such as Ni/Au [27] and Co/Pt [28] (Figure 1.2)). The reaction medium, temperature and type of reducing agent influence the reaction kinetics, and any manipulation of these parameters may lead to significant differences in particle growth, size, shape, and thereby different chemical, physical, optical and biological properties. [29]

1.3 0-D Nanostructure Film Fabrication

Following the formation of the desired nano-structured materials, a second key step is assembling them into a homogeneous film. Numerous studies have been performed in the past decades on film fabrication to produce uniform structures with fine-tuned dimensions, but most of them, for example, chemical vapor deposition (CVD) [30-32] and atomic layer deposition (ALD), [33-35] require a high quality of the substrates and specialized reaction equipment, and therefore are associated with high operating costs. [36] For example, atomic layer deposition instruments can range anywhere from \$200,000 to \$800,000 based on the quality and efficiency of the instrument. Compared with the above methods, the solution-based self-assembly strategy provides a low-cost and effective route for the fabrication of films of nanoparticles. [37-39]

Self-assembly is a process to make disordered small building blocks spontaneously assemble into nanostructures. Two of the most frequently used approaches of traditional solution-based methods for assembly of nanomaterials to films are Langmuir-Blodgett (LB) deposition [40, 41] and layer-by-layer (LbL) sequential adsorption. [42, 43] LB films are formed when amphiphilic (surfactant) molecules or nanoparticles are collected at an air-water interface. The LB technique involves transfer of the assembled LB film to a solid substrate. Although the LB technique is an efficient way to build single and multilayer films, it suffers from the requirement for amphiphilic surfaces of nanomaterials and expensive instruments. [44] Different from LB deposition, LbL is simpler and low-cost beakers and tweezers are the only apparatus required. The LbL method was first proposed by Iler in 1966, who created multilayers of inorganic "colloidal particles" without the use of any organic molecules. [45] LbL assembly is conducted through electrostatic interaction and films are formed by depositing alternating layers of oppositely charged materials with wash steps in between (Figure 1.3). Specifically, the high concentrations of the substances in solution lead to excess adsorption of the substances, and the alternation of the surface charge results in a continuous assembly between positively and negatively charged materials of layers. [44] However, this method has difficulties to fabricate monolayers because the number of deposition cycles usually does not represent a true monolayer, in which a single adsorbate is attached to a single binding site of the substrate. As a result, simple and more flexible approaches to the fabrication of uniform monolayer films of nanomaterials are highly required.

In recent decades, the formation of nanofilms from self-assembled colloidal nanoparticles at an aqueous-organic interface has attracted intense attention. [46-52] Different from the air-water interface (which is used to form LB films), the organic-aqueous interface acts as an ideal template for self-assembly of particles since the liquid-liquid interface is a nonhomogeneous region having a thickness on the order of a few nanometers, which gives a medium to generate nanofilms. [46] The first study of the



Figure 1.3 Outline of LbL assembly through electrostatic interaction. Adapted from Reference. [44] **Copyright @2007 Royal Society of Chemistry**.

absorption of micrometer-sized colloidal particles (e.g. colloidal silica) at the interfaces between two liquids appeared in 1907 by Pickering. Accordingly, an emulsion that is stabilized by colloidal particles is named a Pickering emulsion. [53] Though the particle aggregation at an interface has a century-long history, the controlled interfacial selfassembly of NPs has been realized only recently. In 2004, Vanmaekelbergh and coworkers first observed that ethanol can induce hydrophilic citrate-stabilized Au nanoparticles to spontaneously self-assemble into a monolayer film at a water/hexane interface. [48] Meanwhile, Russell and co-workers assembled hydrophobic CdSe nanoparticles at the water/toluene interface. [54] These two observations present a promising way to assemble both hydrophilic and hydrophobic nanoparticles at water/organic interfaces. Recently, Yeung and co-workers reported a facile method to fabricate large-area (more than 200 cm²) nanoparticle films at the water/toluene interface by simply pouring a quantity of water into the hydrophilic NPs/ethanol/toluene system. [55] As a result, fabrication of large area 0-D nano-structured (nanoparticle or core/shell nanoparticle) uniform films at the organic/aqueous interface is a promising way to prepare samples for hybrid pump-probe experiments.

1.4 Thesis Overview

This thesis describes the synthesis of highly uniform films of two specific nanomaterial systems: platinum-containing and nickel-containing (Cu/Ni, Ni/Pt) nanoparticles. Platinum containing nanoparticles are of interest due to their potential use as catalysts in energy storage fields [56-58]. In this thesis, Pt nanoparticles are synthesized via a "grain-growth" technique [59] and then self-assembled into uniform monolayer films. In addition, the general film formation mechanism has been studied and its details are described in Chapter 3. Synthesis of Pt-containing core-shell metal nanoparticles, Au/Pt and Ni/Pt, as well as the film formation with the same film making strategy of Pt are described.

The abnormal evolution of the lattice parameter of Pt nanoparticles at the surface of film after Pt film is formed is discussed and the origin is further explored in Chapter 4.

The Ni-containing nanoparticle diffusion couples are also of great interest, based on two considerations. First, nickel nanoparticles are widely studied due to their important magnetic and catalytic properties. [60-63] For example, Ni-Pt NPs are well known catalysts for oxidation-reduction reactions in fuel cells. [64-66] Second, Ni containing binary alloy systems have a variety of different phase behaviors. For example, the Cu-Ni system forms solid solutions at all compositions, while the Ni-Pt system forms intermetallic compounds. Study of these specific materials is broadly applicable to other materials with similar phase behaviors. In Chapter 5, the phase transformation between fcc-Ni and presumed hcp-Ni (or more appropriately hcp-Ni₃C) is studied and the formation of the Ni₃C phase is proved by several techniques. Chapter 5 describes synthesis processes for fcc Ni and hcp Ni₃C nanoparticles by the "polyol method", which is a versatile liquid-phase method utilizing high boiling and multivalent alcohols to produce NPs. The detailed process of phase transformation, including the specific reaction temperature and other conditions are presented. At the end of this chapter, whether the hexagonal Ni phase is hcp Ni or Ni₃C is discussed. In Chapter 6, different composition of Cu/Ni core shell nanoparticles are made by two reducing reagents and the resulting Cu_xNi_y structures are discussed in detail.

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Chapter 2

CHARACTERIZATION TECHNIQUES

2.1 X-Ray Diffraction

X-ray diffraction (XRD) analysis is a technique that can be used for characterizing of ordered crystalline materials. It provides important information on phases, structures, and other structural parameters, such as average grain size, crystallinity, strain, and lattice parameter.

2.1.1 Lattice structure

Crystals are regular arrays of atoms, and X-ray diffraction is the elastic scattering of X-ray photons by atoms in a lattice of crystals. According to Bragg's law:

$$n\lambda = 2d\sin\theta \tag{1}$$

where n is an integer referring to the order of reflection, λ is the wavelength of X-rays, d is the characteristic spacing between the crystal planes of a specific material and θ is the angle between the incident beam and the lattice plane. By measuring the angles, θ , under which the constructively interfering X-rays leave the crystal, the inter-planar spacing, d, of every single crystallographic phase can be determined. Diffraction of Xrays by crystal planes allows one to derive lattice spacings. Every material has its own characteristic X-ray diffraction pattern and in order to identify an unknown material, a list of d-values and the relative intensities of the diffraction lines is prepared from XRD. Then compared with the standard line patterns in the Powder Diffraction File (PDF) database, the crystalline structure and the phase of the unknown sample can be determined.

2.1.2 Crystal size and lattice parameter

The observed XRD pattern of a sample can vary in three ways: change the peak position (moving to higher angle or moving to lower angle), change the shape of the peak (broadening the peak or narrowing the peak) or change the intensity of the peak. Usually, peak position changing is affected by both the temperature and lattice parameter. High temperatures lead to increasing the kinetic energy on atomic level of the material and usually cause an increase of the lattice parameter. This lattice parameter increase will be reflected in a shift of the diffraction peaks to smaller angles in the XRD pattern. This process is normally called the thermal expansion. If the surface stress is positive, i.e. in tension stress, then the lattice parameters contract and the diffraction peaks are shifted to higher angles (and to lower angles when in compression). Based on the above relation, the diffraction angle changes can be used to determine the surface stress. The lattice parameters can be calculated. Use FCC structure as an example (in this work, fcc phase is the major phase studied), and the equation is as follows:

$$d_{hkl} = \frac{u}{\sqrt{h^2 + k^2 + l^2}}$$
(2)

where d is the lattice plane distance, h k l are miller indices, a is the lattice parameter.

Except peak position change, peak shape change is another effect. From Scherrer equation:

$$D_{hkl} = \frac{K\lambda}{B_{hkl}\cos\theta} \tag{3}$$

where D_{hkl} is the crystallite size in the direction perpendicular to the lattice planes, hkl are the Miller indices of the planes being analysed, K is a crystallite-shape factor (K =

0.9 for spherical particle), λ is the wavelength of the X-rays, B_{hkl} is the width (fullwidth at half-maximum) of the X-ray diffraction peak in radians, and θ is the Bragg angle. Normally if K λ , and θ are constants, the larger the particle sizes, the narrower the peak is, and vice versa.

2.2 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS), sometimes called Quasi Elastic Light Scattering (QELS), is a technique that can measure molecules or particles size and size distribution, typically in the submicron region, and with the latest technology, lower than 1 nm. It can be used for emulsions, micelles, polymers, proteins, nanoparticles or colloids. The Brownian motion of particles or molecules in suspension causes laser light to be scattered at different intensities. Analysis of these intensity fluctuations yields the velocity of the Brownian motion. The particle size can be gotten from the Stokes-Einstein relationship (Here particle size refers to hydrodynamic size).

Stokes-Einstein Equation:

$$R_H = \frac{k_B T}{6\pi\eta D_\tau} \tag{4}$$

where R_H is the hydrodynamic size of particles, k_B is the Boltzmann's constant, T is the absolute temperature, η is the dynamic viscosity and D_{τ} is the translational diffusion coefficient (m^2/s), the speed of the particles (or velocity of the Brownian motion).

In Chapter 4, DLS is used to measure Pt nanoparticle hydrodynamic size and to be compared with TEM particle size and its corresponding size distributions.

2.3 ζ-potential

Surface charges on nanoparticles play a key role on the nanoparticle aggregate to film process since the electro-static repulsion provided by charges around particle
surfaces can prevent nanoparticles from aggregation or precipitation. ζ -potential analysis, which is in abbreviation of electro-kinetic potential analysis, is a technique for determining the surface charges on nanoparticles in colloids. Nanoparticles with surface charges can attract a thin layer of ions of opposite charge to the nanoparticle surface. This double layer of ions travels with the nanoparticle as it diffuses throughout the solution. The electric potential at the boundary of the double layer is called the ζ - potential of the particles. The magnitude of the ζ -potential is a prediction of the colloidal stability. Dispersions with a low ζ -potential value will aggregate due to Van Der Waal inter-particle attractions.

Nanoparticle ζ -potential is routinely obtained from electrophoretic light scattering. The excitation laser beam with a known wavelength passes through the sample while an electric field E is applied to induce particle electrophoresis and also scattered by the particle. Upon recombination of the scattered and reference beams, a frequency difference is produced, which can be measured by the ELS detector to provide the particle electrophoretic drift velocity v.

$$v = \mu E$$
 (5)
 $\zeta = \eta \mu / (\varepsilon \varepsilon_0)$ (Smoluchowski's formula) (6)

For equation (5), μ is the electrophoretic mobility and ν is the particle electrophoretic drift velocity, E is the electric field that is applied. And from equation (5), electrophoretic mobility can be computed. The Zeta potential ζ is calculated using an approximation such as the Smoluchowski formula (equation (6)) where η is the solvent viscosity ($\approx 8.9 \times 10^{-4}$ Pas for water at 25 °C), ε is the solvent dielectric constant (≈ 80 for water at 25 °C) and ε_0 ($\approx 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1}\text{m}^{-2}$) is the vacuum permittivity.

In this work, all ζ -potentials were measured by the "PALS" (Phase Analysis Light Scattering), which is a more precise and faster method than ELS. PALS method determines the phase difference of the sample interfering beam with the reference beam instead of frequency difference in ELS. And this phase difference can be detected and quantified several hundred times faster than the frequency shift, this means it is much more precise than traditional ELS method.

2.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), which is also called electron spectroscopy for chemical analysis, is a surface-sensitive analytical technique that is used to determine quantitative surface composition and the valence state of the elements that are present on the surface. XPS spectra are obtained by irradiating a solid sample surface with a beam of X-rays while simultaneously measuring the kinetic energy of the electrons that are emitted from the top 1-10 nm of the material. A photoelectron spectrum is recorded by counting ejected electrons over a range of electron kinetic energies. The energies and intensities of the photoelectron peaks enable identification and quantification of all surface elements (except hydrogen). The balance between the X-ray energy, hv (in vacuum), and the kinetic energy of photoelectron, E_K , is expressed as:

$$h\nu = E_K + E_B + \phi \tag{7}$$

where E_B is the binding energy of the electron relative to the Fermi level and ϕ is the work function of the solid sample. The value of E_B and the chemical shift are utilized for identification of an element and estimation of its chemical bonding state (or oxidation state). Electrons from oxidized species typically show a shift to a higher

binding energy. XPS can also be used quantitatively to determine relative surface species concentrations by comparing the intensities or areas of the peaks after taking into account the atomic sensitivity factor for each component, which is a known value related to the detection efficiency of each element and can vary greatly depending on the X-ray source. In this thesis, the X-ray photoelectron spectroscopy was collected on a Thermo Scientific (East Grinstead, UK) K-Alpha+ XPS (hv = 1486.6 eV). The measurements were performed in a vacuum chamber with a base pressure of 1.3×10^{-7} Pa. The X-ray spot size was 400 μ m, and a low-energy electron flood gun was used to stabilize sample charging. High-resolution spectra were collected with a pass energy of 20 eV, and an energy step size of 0.1 eV. The binding energies from XPS were calibrated values with respect to C 1s at 284.7 eV. In all cases, XPSPEAK41 software was used for data processing and peak fitting.

Chapter 3

FORMATION AND CHARACTERIZATION OF THE LARGE AREA MONOLAYER FILMS FROM COLLOIDAL SOLUTIONS OF Pt, Au/Pt AND Pt/Ni CORE/SHELL NANOPARTICLES AND STUDY OF THE FILM FORMATION MECHANISM

3.1 Introduction

In recent decades, numerous researchers have studied the nanoparticle film fabrication and have developed various methods to prepare such films. Two main methods [1] are: (i) evaporation of solvent from a colloidal solution of nanoparticles spread on a solid substrate [2–4] to form a close-packed nanoparticle film; (ii) spreading surfactant-stabilized nanoparticles on the water-air interface to form organized films by the Langmuir–Blodgett technique. [5, 6] Due to the non-uniform evaporation rates of a colloidal suspension of NPs placed on a surface, capillary flow often leads to a "coffeering" structure, with most of the NPs aggregating at the perimeter of the colloidal suspension droplet. [7-9] Therefore, it is very difficult to obtain uniform nanoparticle films by method (i). Although method (ii) can fabricate uniform nanoparticle films, the instruments needed are relatively expensive. An immiscible aqueous/organic interface can act as a template for self-assembly of nanoparticles into uniform films. However, common procedures to assemble particles into uniform films typically involve large organic stabilizer groups to stabilize nanoparticle colloidal dispersions. Without those capping agents, nanoparticles are much more difficult to be assembled into uniform thin films because of irreversible aggregation. [10] Therefore, nanoparticles capped with organic molecules have been widely explored. For example, Russell and coworkers observed that with the help of the capping agent tri-n-octylphosphine oxide (TOPO), CdSe NPs can self-assemble at the water/toluene interface. [11] Möhwald and coworkers further developed this general protocol by adding capping ligands to make the NPs interface active, i.e. with capping ligand to NPs renders the contact angle of water/NPs close to 90°, thus pushing them to the water/toluene interface. They capped aqueous Au-and Ag-NPs with 2,2'-dithiobis[1-(2-bromo-2-methylpropionyloxy)ethane] (DTBE) and 11,11'-dithiobis[1-(2-bromo-2-methylpropionyloxy)undecane] (DTBU) and nonaqueous γ -Fe₂O₃ nanoparticles with 2-bromo-2-methylpropionic acid (BMPA) and drove the NPs to the water/toluene interface to self-assemble into closely packed films. [12] Besides hydrophobic ligand (usually non-polar organic molecules) capped NPs, Sun and co-workers created an ordered 2D monolayer film of hydrophilic nanoparticles (citrate-stabilized Au, polyvinylpyrrolidone (PVP)-stabilized Pt, and SiO₂ microspheres) at a toluene-water interface. [13] Yeung and co-workers modified Sun's method by rapidly pouring a large quantity of distilled water into the alcohol (NPs dispersed in alcohol) and toluene system. In less than 10 s, NPs (citrate-stabilized Au, polyvinylpyrrolidone (PVP)-stabilized Pt or Ag, and SiO₂ microspheres) in the dispersion self-assembled to a close-packed, large-area (> 200 cm^2) monolayer film at the water/toluene interface. [1] Though capping large organic ligands onto NPs prevented the nonuniform clumps of NPs and lead to homogeneous films, removing the capping ligands later after film formation can be a problem. Therefore, assembly of uncapped, charged nanocrystals into arrays needs more considerations. In 2004, Vanmaekelbergh and co-workers first observed that the addition of ethanol to the citrate-stabilized Au colloids gradually decreased the surface charge density of Au NPs, very likely because of the competitive adsorption of ethanol molecules to negative

citrate ions, thus pushing citrate-stabilized Au nanoparticles to assemble into films at a water/hexane interface. [14] Nevertheless, no studies on the self-assembly of charged Pt or Pt-containing nanoparticles without organic stabilizers into a uniform monolayer at a liquid-liquid interface have been reported. In addition, there is another important question that should be addressed here: why do these capped or uncapped nanoparticles self-assemble at the water/organic interface to form a densely packed film? In two-phase systems, the driving forces for the formation of nanoparticle films at the interface have been studied intensively. [7, 11, 12, 15-23] For example, several research groups proposed that the driving force is the reduction in the total interfacial energy, [11, 15-18] and some groups believed the contact angle of the particle with water/organic interface plays a pivotal role for film formation, [7, 12, 14, 18-23] respectively. Given that there are relatively few reports for clarifying the links among these mechanisms or discussing limitations of each mechanism, it is necessary to develop new approaches for evaluating the above mechanisms (e.g. measure the contact angles or interfacial tension) and discussing them in detail.

Chapter 3 describes a simple way of self-assembly of $30 \sim 40 nm$ diameter charged Pt NP aggregates into highly uniform monolayer films with relatively large areas ($\sim 20 \text{ cm}^2$) at the water/hexane interface. A combination of microscopy and spectroscopy techniques was used to characterize the film. In addition, two other Pt containing metal systems, Au/Pt and Ni/Pt core shell nanostructures, were also screened for film formation. At the end, a detailed discussion about the driving force of formation of nanoparticle films at the water/hexane interface was presented.

3.2 Experimental Section

3.2.1 Preparation of Pt nanoparticles (Pt NPs)

All of the nanostructured Pt samples were prepared by a modification of the seed-mediated growth method described by Bigall et al. [24] The seed solution prepared by this method proved stable for the duration of several months, whereas the larger nanoparticles were prepared fresh for most experiments.

3.2.1.1 Preparation of Pt seed solution

An aqueous solution of 5 nm diameter platinum seeds was made by adding 36 mL of a 0.2 % aqueous solution of chloroplatinic acid hexahydrate (H₂PtCl₆ · 6H₂O) (0.14 mmol, 3.86 mM) to 464 mL of boiling deionized water. After vigorously stirring at boiling temperature for 1 minute, 11 mL of a solution prepared by dissolving 109 mg sodium citrate dihydrate (HOC(COONa)(CH₂COONa)₂·2H₂O) (0.37 mmol, 34.0 mM) and 5.5 mg citric acid (HOC(COOH)(CH₂COOH)₂) (0.03 mmol, 2.60 mM) was added to above Pt⁴⁺ solution. Followed 30 seconds later by a quick injection of 5.5 mL of a solution prepared by dissolving 4.4 mg sodium borohydride (NaBH₄) (0.12 mmol, 21.2 mM), 55 mg sodium citrate dihydrate (HOC(COOH)(CH₂COOH)₂) (0.015 mmol, 34.0 mM) and 2.8 mg citric acid (HOC(COOH)(CH₂COOH)₂) (0.015 mmol, 2.60 mM). After stirring at boiling temperature for 10 minutes, the color turned to light brown. The Pt seed solution was quenched in an ice water bath to room temperature (~ 22 °C) and stored until needed (The prepared Pt seed solution was stable in water at room temperature over months).

3.2.1.2 Preparation of Pt clusters

3.6 mL of the previously synthesized seed solution (0.001 mmol of platinum) was added to 87 mL deionized water at room temperature. Then, 0.135 mL 0.4 M orange chloroplatinic acid solution (10.5 mg, 0.054 mmol of platinum) was added, quickly followed by a 1.5 mL solution prepared by dissolving 15 mg sodium citrate (0.05 mmol, 34.0 mM) and 18.7 mg L-ascorbic acid ($C_6H_8O_7$) (0.10 mmol, 71.0 mM). This solution was heated from room temperature (~ 22 °C) to water's boiling temperature (100 °C) with an oil bath at a rate of ~ 10 °C/min, then kept at the boiling temperature for another 20 minutes until the solution color turned from brown to black, and then quenched in an ice water bath to room temperature. To purify the particles (i.e., to remove unreacted salts and platinum seeds from the platinum particle surface), the solution was placed into a centrifuge and with the spinning rate of 10,000 rpm for 15 minutes, the supernatant was removed and the solid re-dispersed in deionized water. The above cleaning steps were repeated 3 times. After the above purification steps, the particles to be used for synthesis of the large area monolayers were stored in a 90 mL aqueous solution (0.055 mmol of Pt, 0.6 mM); particles to be used for TEM measurements and for XRD measurements were dispersed in ethanol and water, respectively; particles to be used for Pt/Ni nanoparticle synthesis were suspended in oleylamine $(CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2).$

3.2.1.3 Preparation of Pt NPs monolayer film

Before preparing the monolayer film, the above 90 mL washed platinum nanoparticle dispersions were centrifuged at 10,000 rpm for 15 minutes, the supernatant removed and the solid re-dispersed in 30 mL deionized water (0.055 mmol of Pt, 1.8 mM).

A modified method based on a previously reported synthesis of gold nanoparticle films [25] was used to prepare monolayer films of Pt NPs.

10 mL of the platinum nanoparticle aqueous solution (0.018 mmol, 1.8 mM of platinum) was poured over a standard glass microscope slide (size, $7.5 \times 2.5 \times 0.1$ cm, and cleaned with ethanol) in a customized Teflon trough (inner dimension, $8.8 \times 3.8 \times 2.5$ cm). This trough contained a hole and a screw acting as a drain at the bottom to drain off liquids without removing the glass slide. 10 mL of hexanes were poured on top of the colloidal solution to form an immiscible water/hexane interface. Finally, 5 mL of ethanol (99.5%, ACS reagent, absolute, 200 proof) was injected into the aqueous layer (Pt colloids) over 10 minutes (rate, 0.5 mL/min). Upon injection of ethanol, the platinum clusters gradually aggregated at the water/hexanes interface, forming a thin layer film floating at the water/hexane interface. Water, ethanol and hexane were drained out, leaving this film deposit on top of the slide, and residual hexane evaporated spontaneously. A schematic of this film formation process is shown in Figure 3.1. An example of this film in a Teflon trough is shown in Figure 3.2.



Figure 3.1. A schematic of the platinum film formation process. (a) a clean glass slide at the bottom of the Teflon trough, (b) platinum NP colloidal solution was added, (c) hexanes was added to form an immiscible water/hexane interface, (d) ethanol was injected into the water layer and particles accumulated at the interface, (e) a thin layer film floating at the water/hexane interface, and (f) Water and ethanol were drained out and the film deposited on the glass slide.



Figure 3.2. Pt nanoparticles monolayer floating at a water/hexane interface in a Teflon trough.

3.2.2 Preparation of Au/Pt core/shell nanoparticles

3.2.2.1 Preparation of Au seed solution

The preparation of the gold seed solution was carried out according to Zhang et al. [26, 27]

An aqueous solution of ~ 20 nm diameter gold seeds (from TEM image of Au seed, Figure 3.4a.) was made by heating a 100 mL aqueous solution containing 10 mg tetrachloroauric (III) acid trihydrate (HAuCl₄·3H₂O) (0.025 mmol, 0.3 mM) to boiling. 1% Then 3 ml of а solution of sodium citrate dihydrate (HOC(COONa)(CH₂COONa)₂·2H₂O, 30 mg, 0.102 mmol, 34.0 mM) was added to the boiling solution, which turned from yellow to red. After stirring at boiling temperature for 40 minutes, the seed solution was cooled down and stored in a refrigerator (temp. \sim 4 °C).

3.2.2.2 Preparation of Au(core)/Pt (shell) nanoparticles

60 mL of the previously synthesized red gold seed solution (0.015 mmol of Au) was added to 165 mL 0.1 mM orange chloroplatinic acid (0.015 mmol of Pt) solution. The mixture was heated to boiling in an oil bath before adding a 1.8 mL 0.1 M citric acid (HOC(COOH)(CH₂COOH)₂) (34.6 mg, 0.18 mmol) solution. After holding at reflux for another 30 minutes, whereupon its color turned from orange red to black, the solution was quenched with an ice water bath to room temperature. The cleaning method was the same as in the case of Pt. After all these cleaning steps, the Au/Pt nanoparticles were re-dispersed in 10 ml deionized water (0.015 mmol, 1.5 mM).

3.2.3 Preparation of Pt(core)/Ni(shell) nanoparticles

The preparation of the Pt/Ni core/shell nanoparticles was based on a modification of the method described in [28].

167 mL previously synthesized (see 3.2.1.2) Pt colloidal solution (0.6 mM Pt) was spun at 10,000 rpm in a centrifuge for 15 minutes, the supernatant removed, and the solid re-suspended in 10 mL oleylamine (CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂) (0.1 mmol, 10 mM of Pt). 51.4 mg green powder of Nickel (II) acetylacetonate (Ni(C₅H₇O₂)₂) (0.2 mmol of Ni) was dissolved into the above mixture (Ni: 0.2 mmol, 20 mM). 2 mL 1-octadecene (CH₃(CH₂)₁₅CH=CH₂) was added to the above mixture, which was then heated to 260 °C in a sand bath with a ramping rate of approximately 15 °C/min. At 260 °C, 52.4 mg triphenylphosphine (0.2 mmol) was quickly added to the above mixture, which immediately brings about the reduction, forming a black colloidal solution. The temperature was maintained at 260 °C for 20 min to complete the reduction and finally the solution was cooled to room temperature with an ice water bath. The Pt/Ni particles were stored in the organic solution.

3.3 Results and discussion

3.3.1 Characterization of large area monolayer films of Pt and Au/Pt core/shell nanoparticles

As-prepared Pt and Au/Pt nanoparticles were characterized by TEM and XRD measurements. Figure 3.3(a) shows TEM images of the Pt clusters (washed, detailed cleaning steps in 3.2.1.2 Preparation of Pt clusters) and the XRD pattern is in 3.3(b). Figure 3.3(c) displays the size distribution of unwashed (Pt clusters sample after quench without further centrifugated cleaning steps) and washed Pt clusters measured by



Figure 3.3. (a)TEM images of washed Pt clusters (Inset shows enlarged image for the sample). (b) X-ray diffraction (XRD) pattern of Pt nanoparticles. (c) Dynamic Light Scattering (DLS) of Pt particle sizes distribution before (blue) and after (red) purification with water.

Dynamic light scattering (DLS). As shown by the TEM images, these Pt clusters had approximately spherical shape and most of them were 35 to 40 nanometers in diameter and were composed of 4 to 5 nm (diameter) Pt grains. The XRD pattern of these asprepared clusters (Figure 3.3(b)) confirmed the fcc crystal structure of elemental Pt, with 2θ values of 39.863°, 46.273°, respectively. [29] The lattice parameter of the Pt nanoparticle was a = 3.915 Å. Scherrer analysis of the XRD pattern of the Pt clusters indicates that the grain sizes of the Pt nanoparticles were 6-7 nm (diameter), consistent with the Pt grain size observed in TEM images (4 ~ 5 nm (diameter)). As revealed by the DLS results (Figure 3.3(c)), the radius of unwashed particles is approximately 20 nm, matching the cluster sizes in TEM images. The washed Pt clusters show a much larger size in DLS and in TEM images (the TEM image shows an agglomerate of ca 200 ~ 250 nm diameter, Figure 3.3(a).) than unwashed Pt clusters because several parts of the Pt clusters were agglomerated into big clumps in solution during the washing procedure.

Similar measurements were performed on the Au/Pt nanoparticles. Figure 3.4(a) shows TEM images of the Au seeds (left) and Au/Pt nanoparticles (right). The XRD and fitted XRD patterns of Au (red), Au/Pt nanostructure (blue) and Pt (black) (Pt clusters prepared before) is shown in 3.4(b). Figure 3.4(c) displays the size distribution





Figure 3.4. (a) TEM images of unwashed Au and washed Au/Pt nanoparticles. (b) XRD and fitted XRD patterns (2θ range: (34° , 42°)) of Au (red), AuPt (blue) and Pt (black) nanoparticles. Black dotted lines mark the measured true Au and Pt peak locations; red dotted lines mark the Au and Pt peak locations in Au/Pt after fitted the Au/Pt peak; (c) DLS of Au/Pt particle sizes distribution before (blue) and after (red) purification with water.

of unwashed and washed Au/Pt particles measured by DLS. Figure 3.4(a) shows Au seeds, which are single crystals and 20 nm in diameter, while Au/Pt nanoparticles were ~ 60 nanometers in diameter and the outer part shows aggregation of Pt grains similar to pure Pt nanoparticles. Figure 3.4(b) shows the XRD pattern of the Au/Pt core/shell nanoparticles (blue curve in the middle of the XRD patterns) contains a doublet peak, which was attributed to Au and Pt peaks. To determine the precise peak position of Au and Pt in Au/Pt XRD pattern and to further checking the existence of the alloy phase (or there is no alloy phase), the strongest peak of the XRD spectrum was fitted (the fitting model is Pearson VII with origin software) [30] and presented in Figure 3.4(b). Here

the fitting model, Pearson VII, was chosen because XRD diffraction peaks are usually a convolution of Gaussian and Lorentzian components and Pearson VII function is basically a Lorentz function raised to a power m: [31]

$$I(2\theta) = I_{max} \frac{w^{2m}}{[w^2 + (2^{1/m} - 1)(2\theta - 2\theta_0)^2]^m}$$

where m is a shape parameter, which is chosen to fit a particular peak shape and determines the relative contributions of Gaussian and Lorentzian type behavior. The above function becomes a Lorentzian as $m \rightarrow 1$ and approaches a Gaussian as $m \rightarrow \infty$ (e.g. m > 10). Pearson VII emphasizes Lorentzian contribution, and the main feature of the Lorentzian function is that it can handle different tail-shapes of a peak by varying the m parameter. w is a parameter related to the peak width, most commonly expressed by the full width at half maximum (FWHM). The fitted peak position of Au (111) is 2θ = 37.735° (lattice parameter a = 4.127 Å) and Pt (111) is $2\theta = 39.151°$ (lattice parameter a = 3.983 Å) of Au/Pt (marked by red dotted line); while the fitted pure Au (111) is located at $2\theta = 37.511^{\circ}$ (lattice parameter a = 4.149 Å) and pure Pt (111) is located at $2\theta = 39.148^{\circ}$ (lattice parameter a = 3.982 Å) (marked by black dotted line), respectively. The XRD pattern of the Au/Pt nanoparticles revealed no evidence of alloying in this system (the Au (111) and Pt (111) peak locations are close to pure Au (111) and pure Pt (111) peak locations), but clearly showed the presence of both fcc Au and Pt phases (Figure 3.4(b)). Scherrer analysis from the XRD pattern of the Au seeds (red) shows the grain sizes of Au are 15~16 nm (diameter), matching what is observed by TEM. Scherrer analysis of the XRD pattern of the Au/Pt nanostructures (black) showed the grain sizes of Pt are 5~6 nm (diameter), matching the grain size of Pt cluster, confirming

the Pt cluster acting as the outer shell. The coexistence of Au and Pt in the TEM and XRD, together with Au/Pt preparation steps (the formation order of Au/Pt is made Au first then Pt), makes it that the Au/Pt product has a core/shell structure. As shown by DLS results (Figure 3.4(c)), the radius of unwashed Au/Pt particles is approximately 30 nm, consistent with TEM sizes (~ 30 nm in radius observed in Figure 3.4(a)). However, the washed Au/Pt particles, by contrast, show a much larger size measured by DLS. There was no cluster of radius > 70 nm shown in the TEM images of the washed particles. The reason for the inconsistency of the particle sizes from TEM and DLS measurements for washed Au/Pt clusters is discussed as follows. First, several parts of the Au/Pt clusters were agglomerated in solution due to the washing procedure that many particles overlapped (refer to Pt clusters). Particle hydrodynamic diameters (measured by DLS) are calculated from intensity-based particle size distributions. The direct intensity size distribution may therefore inherently be weighted to larger sizes than the number distribution, due to the fact that scattered light intensity of particles is strongly size-dependent, increasing with nearly the sixth power of the particle diameter. [32] Larger particles are therefore given more weight, making the "average" size look larger. Under ideal conditions the number distribution transformation of the DLS result should be very close to the TEM size. Due to the washing steps, agglomeration of Au/Pt clusters happens, aggregation of even a small percentage $(1 \sim 2 \text{ vol})$ of larger particles in a particle suspension would dramatically increase the overall particle diameter derived by DLS. [33]

The samples needed for pump-probe measurement must have a large surface area with many equivalent testing spots; therefore, regular films of nanoparticle were supposed to be deposited with a large surface on glass slides. The as-prepared Pt and Au/Pt nanoparticles described in the Experimental section were re-dispersed in deionized water with the Pt source concentration of 1.8 mM. The detailed film making procedure was described in Experimental section. Briefly, 10 mL of the nanoparticle colloidal aqueous solution was added into the Teflon trough with a clean glass slide at the bottom. Then, 10 mL of hexanes were added on top of the water, forming an immiscible two-phase system with a water/hexanes interface. Finally, 5 mL of ethanol was slowly injected into the colloidal solution (i.e., the aqueous phase) over the course of 10 minutes, and at the same time, particles aggregated at the aqueous/hexanes interface and assembled to a film. After draining the water/ethanol mixture and hexanes, the film layer was deposited onto the slide (Figure 3.5(a)). In order to prepare the film sample for TEM measurement, first, a TEM grid (3.05 mm diameter carbon coated copper grid) was put at the top of a clean glass slide, and carefully transferred the glass slide (with the TEM grid on top) into the Teflon trough. The following steps are the same with the film making procedure of preparing the film on the glass slide. When water, ethanol and hexanes were drained, the film was deposited onto the TEM grid.

Figure 3.5(a) shows the film with particles remaining in a thin layer of water in the trough. Figure 3.5 (b) and (c) show examples of dried Pt and Au/Pt uniform films. The particles spread over the entire glass slide ($\sim 20 \text{ cm}^2$) and formed a relatively dense film.

In order to test the uniformity of the Pt nanoparticle film, several methods of characterization have been used. Figure 3.6(a) shows a photograph of Pt nanoparticle



Figure 3.5. Photographs of (a) Pt monolayer deposited on a glass slide in the Teflon trough, while the surface was still wet. The glass slide with film on it was kept in the trough until residue water on the film was evaporated. [34] (b) Pt monolayer deposited on a glass slide. (c) Au/Pt monolayer deposited on a glass slide.

film slide, placed on a white paper with a symbol "Pt" printed on it, showing the absence of any visible cracks in the film. The visibility of the "Pt" indicates that the film is very thin. A TEM image of the Pt film (Figure 3.6(b)) showed that the ~35 nm particles formed a relatively uniform film, with a few voids that had a typical size equivalent to 1~8 nanocrystals. Due to the different sample substrates and the film sample preparation methods of films in glass slide and films in TEM grid, the films deposited on a glass slide (Figure 3.6(a)) is much dense than that deposited on a TEM grid (Figure 3.6(b)).



Figure 3.6 (a) Photograph of Pt film. (b) TEM image of Pt film. (c) XRD pattern of Pt film.

The XRD pattern (Figure 3.6(c)) of the Pt nanoparticle film shows the existence of only pure elemental Pt, the Scherrer size of Pt is $\sim 5\sim 6$ nm, consistent with the as-prepared Pt cluster's grain size.

Atomic force microscopy (AFM) is an ideal technique to investigate the thickness of the nanoparticle film. The AFM results for a Pt film are shown in Figure 3.7. Figure 3.7(a) shows the film sample that was used for AFM measurement. Three rectangle empty spaces, the surfaces of glass slide, were scratched by a razor to provide contrast for measuring film thickness. AFM analysis was done on the sample and the topography is shown in Figure 3.7(b). At each point in the image a measurement of surface height is made, and typically, these heights are displayed as color values, some variant of dark-is-low, bright-is-high. Quantitative analysis of surface coverage shows the thickness distribution of the Pt film (Figure 3.7(c)). Figure 3.7(c) shows two peaks: one of them is sharp, which is the signal of the glass surface; the other one is much broader, which is the Pt signal. The average thickness of the film was approximately 40 nm, which matched the diameter of the Pt nanoparticles.



Figure 3.7 (a) A Pt film sample used for atomic force microscopy (AFM) measurement. The three rectangle clear regions were scratched to provide the glass contrast for film thickness measurements. (b) AFM height image of Pt film. The darker color indicates lower height. Black part is the area with no Pt coverage. (c) AFM of heights distribution of Pt film on a glass slide. The sharp peak refers to the surface of the slide and the broad peak to the Pt film, and the thickness is determined relative to the surface of the glass slide. [34]

This result indicated that majority of the film was a monolayer.

Several factors have effects on film quality, for example the solution pH, ethanol amount, and charges on the surface of the particles. Experiments regarding the effect of changing the ethanol amount have been performed. Specifically, the amount of Pt NPs went to the film was calculated by measuring the concentration of the remaining Pt NPs in water after the film was synthesized. At first, a calibration curve was made by measuring the absorption of aqueous Pt solution at the initial concentration (as-prepared Pt cluster solution: conc. is 1.8mM), 1/4, 1/8, 1/16, 1/32, and 1/64 concentrations using ultraviolet-visible spectroscopy (UV-Vis). The UV-Vis spectrum is graphically represented as absorbance as a function of wavelength, the height of the absorption curves is directly proportional to the concentration of the species, and in this case provides information on the concentration of the species. The UV-Vis spectra of serial dilutions and the aqueous Pt solution calibration curve are shown in Figure 3.8 (a) and (b). With the calibration curve, the percentage of Pt remaining in solution after the film formation could be computed based on the corresponding absorbance. The percentage of Pt in the film can also be computed by subtracting the percentage of Pt remaining in solution. These measurements showed a quantitative relationship of the ethanol addition amount and the amount of Pt in the film (Figure 3.8(c)). Figure 3.8(c) shows that the ethanol addition amount strongly affected the amount of Pt in the film. The more ethanol is added, the more Pt particles appear in the film.



Figure 3.8 (a) UV-Vis spectra for different concentration of Pt colloids. The initial concentration is 1.8mM Pt cluster aqueous solution, measurements were made at the 1/4 (red, 4×diluted), 1/8, 1/16, 1/32 and 1/64 (blue, $64\times$ diluted) concentrations. The dotted line indicates the wavelength used for the analysis, i.e., 550 nm. (b) UV-Vis calibration curve of Pt colloids. With this calibration curve, the remaining Pt concentration after film formation can be computed. Relationship between different amounts of ethanol added and the amount of (c) Pt nanoparticles, and (d) Au/Pt core/shell nanoparticles in the film, respectively. The ethanol addition percentage of the total aqueous solution (if ethanol added volume fraction is 50%, means adding 10 ml ethanol into 10 ml aqueous Pt (or Au/Pt core/shell) colloidal solution.) and the percentage of Pt (or Au/Pt core/shell) present in the film are shown.

Similarly, when adding ethanol into the Au/Pt core/shell aqueous colloidal solution, the amount of ethanol addition has the same effect on the amount of Au/Pt present in the film compared to Pt. Figure 3.8(d) shows the ethanol's effect on the Au/Pt core/shell NPs in film. With more ethanol added, more Au/Pt nanoparticles were in the film.

3.3.2 Mechanism of the monolayer film formation

Self-assembly of colloidal particles at liquid-liquid interfaces has been widely studied. In 1907, Pickering first described a phenomenon in which an emulsion was stabilized by solid particles (e.g. colloidal silica) which adsorb at the interfaces between two liquids. Later, a simple model of adsorption energy, ΔE , of a single particle at the interface of two fluids was introduced by Pieranski. [15] In Pieranski's model, the adsorption energy is obtained by calculating the change in total interfacial energy when a particle moves from one fluid to the lowest-energy position at the interface. The main driving force for the self-assembly of colloidal particles to the liquid/liquid interface is a decrease in total interfacial energy. [23, 35] The decrease of the total interfacial energy depends on the contact angle θ of the particle with water/organic solvent interface, the highest adsorption energy is found when the particle wets both phases equally (i.e. $\theta = 90^{\circ}$). [14, 23] This is because that the energy (- ΔE) required to remove a particle of radius (R) from an organic/water interface with tension ($\gamma_{o/w}$) is given by:

$$-\Delta E = \pi R^2 \gamma_{o/w} (1 - \cos \theta)^2$$

In which θ is the contact angle that the particle was at the organic/water interface. From the equation, $-\Delta E$ has a maximum value when $\cos \theta = 0$, i.e. $\theta = 90^{\circ}$. This equation will be discussing in detail later. Figure 3.9 is a schematic model showing a spherical particle at an organic-water interface. R is the particle radius. $\gamma_{o/w}$ is the interfacial tension of the organic layer-water interface, and $\gamma_{p/w}$ and $\gamma_{p/o}$ are the interfacial tensions of the particle-water and particle-organic layer interfaces, respectively. There are three contributions to the interfacial energy of the particle: [15,36] (1) Energy of the particle-water interface $E_{p/w}$:

$$E_{p/w} = \gamma_{p/w} \cdot 2\pi R^2 \left(1 + \frac{h}{R} \right) \tag{1}$$

(2) Energy of the particle-organic layer interface: $E_{p/o}$:

$$E_{p/o} = \gamma_{p/o} \cdot 2\pi R^2 \left(1 - \frac{h}{R} \right)$$
⁽²⁾

(3) Negative energy of missing organic-water interface: $E_{o/w}$:

$$E_{o/w} = -\gamma_{o/w} \cdot \pi R^2 \left(1 - \left(\frac{h}{R}\right)^2 \right)$$
(3)

The total interfacial energy E:

$$E = E_{p/w} + E_{p/o} + E_{o/w} = \gamma_{o/w} \cdot \pi R^2 \left(\left(\frac{h}{R}\right)^2 + 2(a-b)\left(\frac{h}{R}\right) + 2(a+b) - 1 \right)$$
(4)

Here, $a = \gamma_{p/w} / \gamma_{o/w}$, $b = \gamma_{p/o} / \gamma_{o/w}$, when $h/R = b - a = (\gamma_{p/o} - \gamma_{p/w}) / \gamma_{o/w}$, the total interfacial energy has a minimum value:

$$E_{min} = \gamma_{o/w} \cdot \pi R^2 (2(a+b) - 1 - (a-b)^2)$$
(5)

When the particle is not adsorbed at the organic/water interface (in water h/R > 1, or in organic solvent h/R < -1), the total interfacial energy *E*' is given by:

$$E' = \gamma_{o/w} \cdot \pi R^2 \cdot 4b \text{ or } \gamma_{o/w} \cdot \pi R^2 \cdot 4a$$
(6)

When the particle goes to the interface from water, the binding energy ΔE :

$$\Delta E = E' - E_{min} = -\gamma_{o/w} \cdot \pi R^2 \left[1 - (\gamma_{p/o} - \gamma_{p/w}) / \gamma_{o/w} \right]^2$$
(7)



Figure 3.9 Schematic model of a particle at an organic/water interface with a contact angle less than 90° (left), equal to 90° (middle), and larger than 90° (right). $\gamma_{o/w}$, $\gamma_{p/w}$ and $\gamma_{p/o}$ are the interfacial tensions of organic/water, particle/water and particle/organic interfaces. The parameter h is the vertical distance between the particle's center of mass and the organic/water interface plane.

the three-phase contact angle θ is close to 90°. According to the Young–Dupré equation:

$$\cos\theta = (\gamma_{p/o} - \gamma_{p/w})/\gamma_{o/w} \tag{8}$$

thus $\gamma_{p/o} \cong \gamma_{p/w}$

Adsorption of a particle at the organic/water interface leads to a reduction in the interfacial energy related to the surface tension of roughly $-\gamma_{o/w} \cdot \pi R^2$. In this work, platinum nanocrystals with a diameter of 40 nm and $\gamma_{hexane/water}$ being 50 mN m⁻¹ at T= 298 K, [37] the model predicts the reduction in the interfacial energy $\Delta E \approx -15300$ k_BT (k_BT: thermal energy) per adsorbed particle, where k_BT is the product of Boltzmann's constant and the absolute temperature, T = 298 K. [38] The meaning of using the unit k_BT here is that if a platinum cluster nanoparticle adsorbed at the water/hexane interface, it is possible for this particle to penetrate into the bulk (aqueous

phase), if $|\Delta E|$ is less than k_BT due to the Brownian motion. However, this does not happen, suggesting this platinum cluster is "trapped" at interface in a surface energy well (i.e. $\Delta E \approx -15300 \text{ k}_{\text{B}}\text{T}$) deeper than k_BT.

A reasonable first assumption is that the process of film formation, i.e., Pt NPs moving from the water to the water/hexane interface, is a diffusion-controlled process. This process can be quantitatively described by the Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi\eta r}$$

where D is the diffusion constant, k_B is Boltzmann's constant, T is the absolute temperature, η is the dynamic viscosity of the dispersant (here the dispersant is water/ethanol mixture) and r is the radius of the spherical particle. The diffusion coefficients D can be calculated for the 40 nm (diameter) Pt particles dispersed in water/ethanol (mole fraction of ethanol is 13% when added 5 mL ethanol into 10 mL water) ($\eta = 1.860$ mPa·s [39]) at room temperature (T = 298.15 K), the value of D is 5.87×10^{-12} m²/s. According to Fick's law, the diffusion distance can be calculated by $\sim \sqrt{2Dt}$, where D is the diffusion coefficient and t is the diffusion time. In the Pt NPs film making scenario, 5 mL of ethanol was added into the water layer (Pt colloidal) over 10 minutes, at the hexane/water interface and form a film. If influence of the ethanol addition to the diffusion process is ignored, within 10 minutes, Pt NP diffusion distance is $\sim 8.39 \times 10^{-5}$ m.

In theory, the amount of Pt NPs that are needed to form a monolayer film at the hexane/water interface can be calculated as following:

(1) A slab of area 18.75 cm² (the area of a glass slide: 7.5 cm×2.5 cm) and height 40 nm (= 40×10^{-7} cm, which is the diameter of Pt NPs) has a volume of 7.5×10^{-5} cm³.

(2) A random close packing of spheres has a packing efficiency of ~ 64%; thus, the slab of (1) contains ~ 5.12×10^{-5} cm³ of Pt (assuming NPs are solid spheres of Pt).

(3) The density of Pt is 21.45 g/cm³; i.e. the weight of the Pt NPs in the slab is 1.1×10^{-3} g (= 1.1 mg).

(4) The film formation experiment utilizes 0.018 mmol of Pt in 10 mL aqueous solution; means there are 3.51 mg of Pt in the aqueous solution (the atomic mass of Pt is 195.1 g/mol, the mass of Pt is: 0.018 mmol×195.1 mg/mmol).

(5) 1.1 mg/3.51 mg $\approx 31\%$ Pt NPs are needed to form a monolayer film at the hexane/water interface. The value of the percentage number of Pt (~ 31 %) formed films at the water/hexane interface is consistent with the previous result (Figure 3.8(c)), i.e. the quantitative relationship between the amount of ethanol added and the amount of Pt in the film is: after adding 5 mL ethanol over 10 minutes, ~ 32 % Pt NPs at the water/hexane interface (measured by UV-Vis spectrum).

Within the diffusion distance of 8.39×10^{-5} m, Pt NPs in a volume of $8.8 \times 2.5 \times 8.39 \times 10^{-3} = 0.185$ cm³ will go to the hexane/water interface, and ~ 2.68 % (0.185 cm³/(10 cm³) = 1.85%) Pt NPs in this volume. The number of Pt NPs is definitely not enough to cover the whole area of the hexane/water interface and form a monolayer film (1.85% < 31%). As a result, Pt NPs with diffusion-controlled movement are not enough to cover the hexane/water interface and form a monolayer film; thus, advection motion of solvent needed to be considered.

Although Pt nanoparticles are readily self-assembled at a hexane/water interface due to a large adsorption energy of Pt NPs, the entrapment does not occur with the absence of an inducer (ethanol). The ethanol's role will be discussed in the following paragraphs. Similar to gold nanocrystal aqueous suspensions, Au NP carries a negative surface charge, which is due to the adsorption of citrate and gold-chloride anions, [14, 40] Pt cluster aqueous colloids prepared in this work also have a negative surface charge on Pt surface due to the adsorption of citrate anions. Evidence for citrate molecules adsorbed on Pt NPs is shown in Figure 3.11, using attenuated total reflectance infrared spectroscopy (ATR-IR). Figure 3.11 presents IR spectra of dried Pt NPs and pure trisodium citrate, respectively. Typically, the carboxylate group exhibits an asymmetric ($\nu_{as}(COO^-)$) and a symmetric stretching vibration ($\nu_s(COO^-)$) around 1500~1630 and 1305~1415 cm⁻¹, respectively. [37] The ATR spectra of dried Pt NPs show one distinct peak, the asymmetric COO⁻ stretching vibration at 1611 cm⁻¹, and two symmetric COO⁻ stretching vibrations at 1370 and 1394 cm⁻¹, similar to the COO⁻ peak positions of pure trisodium citrate. This is evidence of adsorption of citrates anion on the Pt NPs surface. Owing to their negatively charged surface, these Pt NPs are highly hydrophilic, making for stable aqueous solutions.

The formation of the Pt nanoparticle film at the hexane/water interface is driven by the reduction in the interfacial energy of the system, while the repulsion between the charged Pt nanocrystals in the monolayer is a destabilizing force. It is possible that the appropriate surface charge on the Pt nanoparticles is a prerequisite for the formation of the 2-D film at the hexane/water interface. It has been reported that hydrophilic Au NPs can be assembled into 2-D films at water/oil interfaces by adding a low-dielectric solvent (e.g. ethanol) to an aqueous colloidal suspension, [13, 14, 19, 22] which was attributed to the possibility of ethanol displacing capping citrate ions on Au NPs. Another explanation for this experimental observation, proposed by Zhang and coworkers, [41] is that adding a low-dielectric solvent enhances ion pairing on the Au NPs, reducing the surface charge density on Au NPs and promoting Au NP aggregation.



Figure 3.10. ATR-IR spectra of washed Pt clusters (purple) and pure trisodium citrate (Na₃Cit) (red). Peaks of the ν_{as} (COO⁻) at 1611 cm⁻¹ and ν_{s} (COO⁻) at 1370 cm⁻¹ and 1394 cm⁻¹.

These authors claimed that the enhanced ion pairing on the Au NPs in the ethanolcontaining solvent is due to the combined effects of stronger electrostatic interaction between cations and anions in ethanol solution than that in water, and the lower solvation energy of ions in ethanol than in water, making the AuNPs easier to be neutralized in nonpolar solvent than in water. [41] Similar to AuNPs, this work also observed that by adding ethanol into a Pt colloidal aqueous solution, Pt NPs spontaneously form a monolayer at the hexane/water. Due to the same reason with that of Au, the addition of ethanol reduces the surface charge density on Pt NPs. The following paragraphs will discuss this in detail and give supporting experimental results.

Surface charges on nanoparticles play a key role in the nanoparticle aggregation into films. ζ -potential analysis is a technique for determining the surface charge of nanoparticles in colloids. High ζ implies highly charged particles, which prevents aggregation of the particles due to electrostatic repulsion. If the ζ is low, attraction may overcome repulsion, and it is likely that the nanoparticles coagulate and form film. [42] A ζ -value more negative than -30 mV is considered optimal for stabilization of a nanodispersion. [43]

To determine ζ – dependence, ζ – potential measurements of Pt colloidal aqueous solution as a function of time were conducted (Figure 3.11(a)). The average ζ of Pt colloidal aqueous solution (Pt NPs dispersed in pure water, without adding ethanol) is approximately – 62 mV, consistent with the observation that the dispersion is stable. Figure 3.11(a) shows that ζ does not systematically vary too much for a long period (~ 60 h), suggesting nanoparticles dispersed well in water. Figure 3.11(b) shows that the aqueous Pt colloid has a ζ of about – 63 (± 2) mV. The addition of successive amounts of ethanol to the Pt colloid gradually increased ζ , which eventually reached ~ -30 mV upon addition of 20 % ethanol (2.5 ml ethanol to 10 ml H₂O), i.e., the threshold for aggregation. In other words, adding more than 20 % ethanol will initiate Pt nanoparticle coagulation to film at the hexane/water interface. At the end, the ζ – potential reached –15 (± 2) mV.

To verify the hypothesis that diminution of the dielectric constant of the medium due to addition of a miscible solvent with a lower dielectric constant lowers ζ of the charged particles, three alcohols with different dielectric constant (methanol, ethanol and isopropanol) were chosen to be added to the colloids. The dielectric constant of isopropanol ($\varepsilon \sim 21.15$), is lower than that of ethanol ($\varepsilon \sim 25.16$), and methanol ($\varepsilon \sim 33.64$) has the lowest dielectric constant of all. All of these alcohols have a significantly lower dielectric constant than water ($\varepsilon \sim 80.20$). [44] Figure 3.12 shows that the addition of alcohols to the water gradually decreases the ζ . Consistent with Figure 3.11(b), the amount of alcohol needed to reach the threshold of nanoparticles aggregation to film ($\zeta \sim -30$ mV) is different, less than 10 % of isopropanol, ~ 18 % of ethanol and 33 % of methanol. These results are in agreement with the expectation that reducing the solvent polarity reduces the ζ -potential of Pt colloidal aqueous solutions.



Figure 3.11 (a) Pt colloid ζ -potential stability test. Washed Pt clusters dispersed in water showed a stable (if noisy) ζ vs. time. (b) Reduced ζ of the Pt colloids on adding ethanol to the aqueous solution consisting of Pt nanoparticles. Initial volume of ethanol is 0ml (volume of water is 10ml), the final volume of ethanol is 10ml (volume of water is 10ml). The ζ results are obtained with a Doppler effect light scattering analyzer.



Figure 3.12. Decrease of ζ -potential of the Pt colloids on adding alcohols with different dielectric constant, isopropanol ($\varepsilon \sim 21.15$) (blue), ethanol ($\varepsilon \sim 25.16$) (red) and methanol ($\varepsilon \sim 33.64$) (black) to the Pt colloidal aqueous solution, respectively.

As described above, in order to assemble nanoparticles into a uniform film, a precondition is the appropriate (i.e., low) surface charge on the Pt NPs (the appropriate ζ -potential of the colloids), giving nanoparticles the ability to agglomerate. Then minimization of the interfacial energy acts as the "driving force", inducing those hydrophilic particles to move from the water phase to the water/hexane interface. The role of ethanol is reducing the surface charges on the Pt NPs, to lower the electrostatic repulsion between particles. The last part left to discuss is how to assemble these particles into a uniform film. Charged NPs can self-assemble into a dense monolayer in response to an interfacial tension gradient. [45]

The interfacial tension gradient is imposed by the localized higher concentration of ethanol from the interface. At room temperature, one droplet of pure ethanol is added into the water and at the same time, this small area of ethanol causes the interfacial tension gradient (the difference of interfacial tension between hexane/water and hexane/ethanol is 50.38 - 22.31 = 28.0 mN/m, respectively [46, 47]). The force induced by this interfacial tension gradient pushes Pt NPs to migrate toward the area of higher interfacial tension (hexane/water) and form a dense film layer. However, this large interfacial tension gradient may result in a non-uniform film. In this work, a modification of the regular film making procedure was used. First, pre-mixed 2 mL ethanol with 10 mL water (2 mL EtOH + 10 mL H₂O) and made 16 % (v/v %) ethanol aqueous solution. Then added another 3 mL ethanol into the water-ethanol mixture. This process lowers the interfacial tension gradient compared to directly adding ethanol into pure water. By adding 16 % (v/v %) of ethanol into water, the interfacial tension of hexane/water decreases from 50.38 mN/m to \sim 20 mN/m, respectively. [46] The latter interfacial tension gradient (interfacial tension difference of hexane/16% ethanol aqueous sol and air/ethanol is ~ 20 - 22.31 \approx 0 mN/m) is much smaller than previous (interfacial tension difference of hexane/water and air/ethanol is 50.38 - 22.31 = 28.07mN/m). Figure 3.13 (a) shows if ethanol is added directly to the aqueous Pt colloid solution, a relatively large interfacial tension gradient area (28.07 mN/m) is produced.

This large interfacial tension gradient pushes Pt NPs migrate to the opposite side (away from ethanol) and forming a dense, non-uniform film. However, if 16% (v/v %) aqueous ethanol mixes with Pt colloid and then added extra ethanol, it creates a much smaller surface tension gradient (~ 0 mN/m) area. Pt NPs migrate slower and aggregate to uniform film because of the smaller interfacial tension gradient (Figure 3.13 (b)).



Figure 3.13 Schematic illustration of the interfacial tension gradient's influence on the self-assembly of the Pt NPs at water/ hexane interfaces. (a) Adding ethanol directly into the water solvent creates a relatively large interfacial surface tension gradient, forming a non-uniform and dense film. (b) Pre-mixing ethanol with Pt colloidal aqueous sol and then adding the rest ethanol creates a relatively smaller interfacial tension gradient and forms a more uniform film.
3.4 Conclusion

Large area, uniform films of 5-6 nm diameter Pt nanoparticles self-assembled into 30-40 nm diameter aggregates have been prepared at the interface of two immiscible phases: an aqueous Pt colloidal solution and hexane. This interfacial film can then be easily transferred onto a glass substrate. The method involves adding ethanol into an aqueous Pt nanoparticle dispersion, and simultaneously, Pt nanoparticles in the water were extracted to the water/hexane interface, forming a black thin film. The closepacked structures and monolayer property of these thin films were verified by transmission electron microscopy (TEM) and atomic force microscope (AFM) characterizations. A fundamental understanding of the film fabrication mechanism is vital to apply this film making method to other materials. This work addressed and discussed three aspects that relate to film formation: the formation of Pt NP film at hexane/water interface is driven by the reduction in the interfacial energy of the system, ethanol addition lowers both the surface charges on Pt NPs (or lowers the ζ -potential of Pt colloidal aqueous solution to -30mV) and the NPs adsorption barrier, pushes particles moving from water phase to the hexane/water interface, and the low interfacial tension gradient enables the assembly to uniform films. This film making method offers an easy and widely applicable way for preparing samples for destructive measurements, i.e., the ultra-fast time resolved optical pump/X-ray probe XRD measurement. The film made by the above method is an appropriate sample for repeating pump-probe experiment on enough equivalent spots to get enough data to study the solid-state diffusion and newphase formation process.

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Chapter 4

AN UNUSUAL LATTICE EVOLUTION OF Pt NANOPARTICLES CAUSED BY THE INTERACTION OF OXYGEN WITH PLATINUM SURFACES

4.1 Introduction

The formation and characterization of uniform Pt films and the mechanism of film formation were discussed in Chapter 3. During the course of this study, an unusual evolution of the lattice parameter of the Pt nanoparticles with time was noted. This observation and its origin will be discussed in this chapter.

Atoms at the surface of a finite material have different physical and chemical properties from interior atoms because they have fewer direct neighbors. Particles with a large fraction of atoms at the surface have a low mean coordination number and, therefore, finite size effects. [1] Ideally, if the material has an infinite size, it should show a perfectly periodic structure. In reality, however, no material has an infinite size. Size-sensitive effects, which arise from the effect of the boundaries (e.g. there exists boundaries between the surface and the bulk), present in finite size effects. In bulk or macroscopic systems, the finite size effect is negligible because the number of surface atoms is an insignificant fraction of the total. In this size regime all system properties can be usefully characterized as either extensive or intensive in the volume. [3]

When a solid is elastically deformed, work is performed against both volume and surface forces. Under most conditions the volume term will strongly dominate over the surface term. However, as nanostructured materials have significantly large surfaceto-volume ratios, the surface term can become important as a consequence of finite size effect and induce a bulk stress that elastically changes the equilibrium lattice spacing, leading to a size-dependent lattice change behavior. [4] Considering a spherical solid particle of radius R with an isotropic surface stress (*f*), the influence of the surface stress on it generates a pressure Δp : [5]

$$\Delta p = 2f/R \tag{1}$$

This equation is called the Laplace-Young Equation and Δp is the Laplace pressure. The particle bulk reacts to this pressure by an internal strain which is reflected by a change of lattice parameters. The magnitude of strain and the relative change in lattice parameters ($\Delta a/a_0$) (*a* and a_0 are the strained and bulk lattice parameters) are dependent on the bulk modulus (B) and can be estimated by Equation 2: [4-9]

$$\frac{\Delta V}{V_0} = 3\frac{\Delta a}{a_0} = 3\frac{a - a_0}{a_0} = -\frac{\Delta p}{B}$$
(2)
$$\frac{\Delta a}{a_0} = \frac{a - a_0}{a_0} = -\frac{2f}{3BR}$$
(3)

In most cases, the surface stress in metal nanoparticles is positive, [4-7] and Equation 3 predicts a lattice parameter contraction in direct proportion to the reciprocal of the grain size. However, lattices expansion [10-13] or even non-monotonic behavior [3, 14-18] of some metal nanoparticles can also be found. Moreover, for nanoparticles of the same metal, disparate lattice change behavior was observed in different investigations. [14] For example, Pd particles at smaller grain sizes (< 8 nm) showed lattice expansion with an inverse particle size dependence, [19] whereas lattice contraction is reported for grain sizes > 8 nm. [20] Non-monotonic evolution of the lattice parameter was reported in nanoparticles of Pt, [3] Ni, [14-16] Fe, Cu, Ag, and W. [4, 14, 17, 18] Several interpretations of these inconsistencies have been reported. For example, Unruh et al. claimed that a combination of microstructure dependent compressive (due to the 2D particle surface) and tensile stresses (due to the formation of intergranular material during sintering and grain growth) acting on the Pt nanoparticles leads to the nonmonotonic evolution of the Pt lattice parameter. [3] Another possible explanation of the lattice expansion of Pt nanoparticles by Tillmann et al. suggests that an expansion of the lattice parameter of Pt nanoparticles, which is the Pt–Pt next-neighbor distances at the particle surface, may originate from an amorphous oxide on the nanoparticle surface and/or dissolution of oxygen on subsurface sites. [21] Miller and co-workers found an expanded lattice parameter of surface oxidized Pt nanoparticles contracts after treatment in a H₂ reducing atmosphere. [22] Most of the above studies showed an expanded Pt lattice, and when a contracted lattice has been reported, the lattice parameter change is approximately proportional to the inverse particle size as predicted by the Laplace-Young Equation. [23-28] There are few investigations about the lattice evolution with the absence of a size dependence in nanoscale materials and a reasonable and unifying explanation has not yet emerged.

In this chapter, uniform Pt monolayer films prepared according to Chapter 3 were used as samples. Then the crystal structure of these Pt NP 2D films was characterized by using X-ray diffraction (XRD), giving access to their size and lattice parameter. The evolution of the lattice constant and the Scherrer size of Pt NPs were examined for a long time period (~ 1 week) and the results show that the lattice parameters of Pt NPs increased over time (while remaining smaller than the bulk value) with no obvious change in grain size. Furthermore, the surface oxidation evolution of Pt film was studied using high-resolution X-ray photoelectron spectroscopy (XPS). With the combination of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results, this chapter will give a proposed explanation for the unusual lattice evolution behavior of Pt nanoparticles.

4.2 Experimental Section

4.2.1 Preparation of Pt nanoparticles (Pt NPs)

The nanostructured Pt samples were prepared according to Chapter 3. See details in Section 3.2.1.

4.2.2 Preparation of Pt NPs monolayer film

The Pt NPs monolayer films were prepared according to Chapter 3 (see details in section 3.2.1.3), only the material and dimensions of substrates were different.

Samples to be used for XRD were prepared on glass slides with dimensions: $2.5 \times 1.5 \times 0.1$ cm. Samples to be used for XPS were deposited on boron nitride (BN) substrates with dimensions: $2.5 \times 1.5 \times 0.1$ cm.

4.3 Results and discussion

4.3.1 Lattice parameter and the size relationship studied by XRD

Figure 4.1(a) shows the TEM images of the Pt nanoparticles. Most of these Pt nanoparticles have approximately spherical shape and exhibit relatively uniform diameters of about 40~50 nm. The aggregate particle size distribution of as-prepared Pt nanoparticles was also measured by dynamic light scattering (DLS) (Figure 4.1(b)). The mean particle size estimated from the histogram as shown by Figure 4.1(b) was 40 nm, which was consistent with the TEM size. A TEM image of the Pt film (Figure 4.1(c)) shows the ~ 40 nm particles formed a dense film, with the voids having a typical size equivalent to 1~8 nanocrystals. The optical photo of the Pt film on a glass substrate, lying on top of a white paper with a symbol "Pt", shown in the Figure 4.1(c) inset, further proved that the Pt film surface has no visible cracks and indicates the film is thin.

The crystal structure of Pt NPs of the 2-D film was characterized by XRD to obtain particle size and lattice parameter information. The lattice parameters of Pt (111) were calculated by combining Bragg's law (Equation (4)) with the known crystal structure of the Pt nanoparticles, i.e. face centered cubic.

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{4}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
(5)



Figure 4.1 TEM images and the particle size distributions. (a) As-prepared Pt nanoparticle (b) Pt nanoparticle size (diameter) distribution measured by Dynamic Light Scattering. (c) Pt monolayer film (inset was the photo of Pt film deposited on glass).

Here λ is the X-ray wavelength (Cu K_{a1} : 1.54056 Å), θ the X-ray incidence angle of the peak, h, k, *l* are the Miller indices of the Bragg planes (h, k, l for Pt (111) is 1, 1, 1), d is the interplane distance and *a* is the lattice parameter. The interplane distance is determined by Bragg's law and with the Miller indices of Pt (111), the lattice parameter can be computed from Equation 5. Pt NPs Scherrer size (diameter) can be calculated from the Debye-Scherer formula.

$$D_{hkl} = \frac{K\lambda}{B_{hkl}\cos\theta}$$

where D_{hkl} is the crystallite size in the direction perpendicular to the lattice planes, hkl are the Miller indices of the planes being analysed, K is a crystallite-shape factor (K = 0.9 for spherical particle), λ is the wavelength of the X-rays (Cu K_{a1} : 1.54056 Å), B_{hkl} is the width (full-width at half-maximum) of the X-ray diffraction peak in radians and θ is the Bragg angle.

Before carrying out the XRD measurement, an unevaporated layer of residual hexane/water covered the Pt film, acting as a separator between the air and the Pt film surface. (ref. Chapter 3: section 3.2.1.3 Preparation of Pt NPs monolayer film). The film samples were immediately placed in the diffractometer after they were made and still protected by a hexane/water layer and the diffraction patterns then represent the evolution of the particle lattice parameter with time following exposure to air. Figure 4.2 displays the evolution in the diffraction peak (Pt (111)), the Scherrer particle size, and the apparent lattice constant of the Pt NPs as a function of the time. In Figure 4.2(a), 0 hours in the legend means the time when the surface of Pt film directly exposed to the air. Several basic experimental observations from Figure 4.2 are as follows: first, the XRD results show that apart from the initial measurement, the half maximum width of the (111) diffraction lines has no obvious change, but the peak positions of (111) diffraction lines shift to smaller angles (corresponding to an increase in the lattice parameter), without a change of the grain size, for the Pt NPs film sample in air from 0 hours to 190 hours (Figure 4.2(a)). Second, the Pt NP grain size only showed a small fluctuation at the beginning and remained essentially constant (~ 175 Å in diameter) over a long air exposure time (~ 190 hours) (Figure 4.2(b)). (Note: The Scherrer size showed in Figure 4.2 (b) is much larger (17.5 nm) than Scherrer size ($\sim 6-7$ nm) in Chapter 3, which was derived from XRD patterns (Figure 3.3 (b) and Figure 3.6 (c)). The inconsistency of the Scherrer sizes may due to the different concentration or sizes of Pt seeds solution. The seeds solution which was used to prepare Pt NPs in Chapter 4 were not freshly made. It was just the same mother seed solution of preparing Pt NPs in Chapter 3. However, these two experiments have a time interval of more than 6 months. The seeds may aggregate to larger particles and affected the following Pt NPs sizes



Figure 4.2 Evolution in (a) Pt (111) diffraction peak as a function of time (Pt NPs film in air for 0 (red), 0.75 (blue), 5 (orange), 22.5 (green), 70 (purple) and 190 (grey) hours). The dotted line (black) represents the bulk Pt (111) position. (b) the Scherrer particle size and (c) Pt lattice parameter as a function of time. Symbols are data points and red dotted line is fit to the data. Blue dotted line is the lattice parameter of the bulk Pt.

and further reflected to the difference of Scherrer sizes.) Here the particle size (~ 175 Å) determined from XRD patterns was crystallite size (or "grain size"). The Pt clusters are polycrystals and composed of many small Pt seeds (individual crystallites), which has the size of ~ 200 Å. This is the reason that sizes in Figure 4.2(b) is almost 2 to 2.5 times smaller than Pt

cluster size ($\sim 40 \sim 50$ nm) which is determined from TEM before. Third, unlike the grain size evolution, the value of the Pt lattice parameter exhibited a significant increase during the first couple of hours, changing to a slower increase at later times. The lattice

parameters for these Pt nanoparticles are always smaller than the bulk lattice value (a = 3.9239 Å) (Figure 4.2(c)). The XRD results shows the lattice expansion cannot be attributed to a size change (lattice change behavior is not size dependent). One plausible factor that might be responsible for expanding the Pt lattice is surface oxidation and/or subsurface oxygen incorporation, [21, 22] because the evolution of the lattice depends on the duration of exposure to air.

To support the above hypothesis, X-ray photoelectron spectroscopy was used to study the surface properties of the Pt NP films.

4.3.2 XPS investigation of the causes for the lattice expansion

XPS is a surface sensitive spectroscopy, which can be used to obtain information about the oxidation states of the Pt nanoparticles. Figure 4.3(a) displays a serious of XPS spectra in the Pt 4f region of the Pt film which was exposed to air from 0 hours to 205 hours. The XPS spectra were analyzed using the XPSPEAK41 software [29] with a fitting routine which decomposes each spectrum into individual mixed Gaussian-Lorentzian peaks using a Linear background. The deconvolution of the Pt 4f peaks was performed using doublets with spin orbit splitting energy of 3.3 eV and the intensity ratio Pt $4f_{7/2}$: Pt $4f_{5/2} = 4:3$; [30, 31] these XPS data analyses are listed in Table 4.1. The Pt 4f electron spectra are well-resolved with three doublets with Pt 4f_{7/2} binding energies of among 71.4, 72.1 and 76.0 eV and Pt 4f_{5/2} between 74.7, 75.4 and 79.3 eV. The peaks at lower binding energies (71.4 and 74.7 eV) are due to Pt (0), while the higher binding energy component is due to the oxidation state of Pt (II) (72.1 and 75.4 eV) (such as PtO) and a higher oxidation state of Pt (IV) (76.0 and 79.3 eV) species such as PtO₂. [29, 32-34] Representative examples of the fits of samples at 0 hours and 205 hours are shown in Figure 4.3(b). The existence of Pt (IV) suggested some Pt (II) was further oxidized to Pt (IV) when exposed to air for longer times. Figure 4.3(b) also shows some extend of inhomogeneous broadening (FWHM) of oxidation state of Pt (0) (e.g. Pt (II)), which was due to the close proximity of existing peaks, i.e. some extend of unresolved Pt (II) and Pt (0). [35]



Figure 4.3 (a) Peak evolution of Pt 4f XPS spectra of Pt film as a function of time. Pt film was exposed in air from 0 hours to 205 hours. (b) Fitting examples of Pt film exposed in air for 0 hours (top) and 205 hours (bottom). (c) Evolution of Pt (II) +Pt (IV) to Pt (0) ratio as a function of air exposure time.

Figure 4.3(a) shows that exposure of the Pt film surface to air up to 9 days (~205 hours) made the shape of the Pt 4f peaks more asymmetric and broader, while the peak positions moved to higher binding energy. This would suggest that the Pt NPs got partially oxidized and a fraction of the Pt atoms shifted oxidation state from Pt (0) to Pt (II). Quantitative analysis of the integrated areas under the deconvoluted peaks in the XPS spectra yielded the results summarized in Table 4.1. The relative area corresponding to the oxidized Pt (Pt (II) + Pt (IV) phases) was 51.0% when the Pt film was in air for 0 hours, while in the case of a Pt film in air for 205 hours, the percent of the oxidized Pt (Pt (II) + Pt (IV) phase) phase increased to 75.0%. In order to find out the oxidation is only happened at the surface of Pt NP film or the whole part of Pt NPs,

Table 4.1 Binding energies and relative integrated area for each species of Pt at different exposed time from Pt 4f XPS spectra

Exposed to Air	Species	Binding Energy (eV)	Relative integrated
(hrs)			area (%)
0	Pt (0)	71.4, 74.7	49.0
	Pt (II)	72.1, 75.4	31.4
	Pt (IV)	76.0, 79.3	19.6
0.25	Pt (0)	71.5, 74.8	43.8
	Pt (II)	72.2, 75.5	34.0
	Pt (IV)	76.0, 79.3	22.2
0.5	Pt (0)	71.5, 74.8	42.3
	Pt (II)	72.2, 75.5	35.8
	Pt (IV)	76.0, 79.3	22.5
	Pt (0)	71.5, 74.8	41.5
0.75	Pt (II)	72.2, 75.5	36.5
	Pt (IV)	76.0, 79.3	22.0
1	Pt (0)	71.5, 74.8	41.6
	Pt (II)	72.2, 75.5	37.1
	Pt (IV)	76.0, 79.3	21.3
1.25	Pt (0)	71.5, 74.8	37.8
	Pt (II)	72.2, 75.5	40.4
	Pt (IV)	76.0, 79.3	21.8
17	Pt (0)	71.7, 75.0	36.2
	Pt (II)	72.4, 75.7	38.4
	Pt (IV)	76.0, 79.3	25.4
30	Pt (0)	71.7, 75.0	31.1
	Pt (II)	72.4, 75.7	43.9
	Pt (IV)	76.2, 79.5	25.0

45	Pt (0)	71.7, 75.0	29.0
	Pt (II)	72.4, 75.7	41.5
	Pt (IV)	76.0, 79.3	29.5
89	Pt (0)	71.7, 75.0	28.9
	Pt (II)	72.4, 75.7	41.9
	Pt (IV)	76.0, 79.3	29.2
115	Pt (0)	71.7, 75.0	27.4
	Pt (II)	72.4, 75.7	43.6
	Pt (IV)	76.0, 79.3	29.0
205	Pt (0)	71.7, 75.0	25.0
	Pt (II)	72.4, 75.7	45.2
	Pt (IV)	76.0, 79.3	29.8

the oxidation penetration depth will be discussed as follows.

Sampling Depth is defined as the depth from which 95% of all photoelectrons are scattered by the time that they reach the surface (3 λ). Most λ are in the range of 1 - 3.5 nm for Al K_{α} radiation. So, the sampling depth (3 λ) for XPS under these conditions is 3-10 nm. [36] The Pt NP film is monolayer, which has a depth of ~ 40 nm (the diameter of the Pt NP). Approximately 10 nm/40 nm (= 25%) of the Pt NP film can be detected by XPS. Therefore, at 0 hrs, only 25% × 50% (= 12.5%) Pt NPs at the film are oxidized.

In order to see the Pt oxidation evolution more clearly, the evolution of the (Pt (II) + Pt (IV)/Pt (0) ratio with the time of Pt film exposure to air is shown in Figure 4.3(c). The ratio is 1.14 at 0 hours, indicating that at the beginning, half of the Pt exist as Pt (0) in the Pt monolayer sample. The existence of Pt (II)/Pt (IV) before apparent air exposure should be attributed to the Pt NPs preparation and washing, which were not conducted in an oxygen-free environment. Upon longer O_2 exposure, the oxidation species of Pt (II) + Pt (IV)) content increased quickly.

The variations in the lattice parameters can be explained as follows: First, the surface stress in metals is usually positive. The reason for positive surface stresses can be explained by the bond-order behavior of the metallic bond. [37] Pauling [37] mentioned that in a metal, the strength of a bond increases continuously as the coordination number of the atom decreases. The increased strength per bond results in a decreased bond length for lower coordination numbers. As a consequence of this, the less coordinated atoms at the surface favor shorter bond lengths than the more coordinated atoms in the bulk. This means that the surface atoms, because they are restrained by the bulk, are in a state of tension, which directly translates to a positive surface stress. [4] The positive surface stress causes a contracted lattice parameter as suggested by the Laplace Equation. Second, when the Pt film was exposed in air, the surface Pt nanoparticles were slowly oxidized (evidence from the XPS results). In case of surface Pt atoms bond to oxygen and/or oxygen is dissolved on subsurface sites of the nanoparticles (Pt (0) is oxidized to Pt (II) shown from XPS results), resulting the neutralizing the compressive surface stress. This neutralizes of the compressive surface stress finally causes the increasing of Pt-Pt next-neighbor spacings at the Pt nanoparticle surface and also the increasing of lattice parameters in the nanoparticle core. [21] This above hypothesis of expanded Pt lattice parameters was observed after Pt NP film was exposed to air and caused by the Pt NP film surface oxidation agrees well with Miller et. al., [22] who have observed that the expanded lattice parameter of surface oxidized Pt NPs contracted after treatment in a H₂ reducing atmosphere.

Figure 4.4 shows the evolution of the lattice parameters of Pt nanoparticles as a function of Pt (II)/Pt (0) ratio. It shows that the lattice parameter increases with increasing Pt (II)/Pt (0). The oxidation of Pt at the surface of the films apparently neutralizes the compressive surface stress effect which expanded the Pt-Pt next-neighbor distances and finally releases the lattice contraction.



Figure 4.4 Relationship of (Pt (II) + Pt (IV))/Pt (0) ratio and Pt lattice parameter. Symbols are data points.

4.4 Conclusion

In this chapter, an unusual lattice parameter evolution of Pt nanoparticles incumbent upon Pt NPs monolayer film formation was described. X-ray diffraction (XRD) showed that the initial Pt lattice parameter showed a significantly contracted value compared to the bulk value; it slowly relaxed without pronounced changes of the particle size. X-ray photoelectron spectroscopy (XPS) provided information about the Pt NPs' surface states as a plausible explanation for the lattice relaxation. XPS showed that Pt NP film surfaces were slowly oxidized and probably formed Pt-O bonds. The formation of the oxide bond may produce tensile stresses, which neutralize the compressive surface stress and lead to the lattice expansion. This surface oxidation of Pt film may be responsible for the abnormal Pt nanoparticles lattice evolution during the film formation.

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Chapter 5

THE STRUCTURE TRANSITION OF FCC-Ni AND HCP-Ni₃C

5.1 Introduction

Nickel nanoparticles are widely studied due to their important magnetic [1,2] and catalytic properties. [3,4] Ni has three possible crystallographic phases, i.e. facecentered cubic (fcc), hexagonal close-packed (hcp) and body-centered cubic (bcc). At ambient conditions (P, T), fcc Ni is the stable phase, and colloidal synthesis routes for producing this phase have been reported by many research groups. [1, 5-9] In contrast, the hcp and bcc structures are metastable phases, and can only be prepared under special circumstances. A series of reports have suggested that both fcc and hcp Ni NPs can be synthesized by thermal reduction of Ni (II) salts with reducing agents in an organic solvent, for example, reduction of nickel chloride (NiCl₂) with KBH₄, [10] nickel acetate (Ni(CH₃COO)₂) with tetraethylene glycol, [11] nickel oleate complex with an organic amine, [12] and so on. In these studies, the thermodynamically stable fcc Ni is formed at a relatively low reaction temperatures below about 240 °C and the metastable hcp-Ni appeared at higher reaction temperatures (above 250 °C). The reported formation of the metastable phase at higher temperature than that of the stable phase, seems unusual. In addition, experimental reports of the magnetic properties for hcp Ni are inconsistent. [10-19] For example, Chinnasamy et al. [11] claimed that hcp Ni is nonmagnetic; Han et al. [12] reported the ferromagnetic properties of hcp Ni, and Jeon et al. [13] reported antiferromagnetic behavior of hcp Ni.

In 2006, Leng et al. [20] first claimed that the hexagonal phase obtained via the solution route was not metallic hcp-Ni but the hexagonal nickel carbide (Ni₃C); hexagonal nickel carbide is characterized as an interstitial solid solution of carbon in

(a) hcp-Ni



Figure 5.1 Crystal structures of (a) hexagonal hcp-Ni and (b) rhombohedral Ni₃C, highlighting the similarities between the structures and the location of the interstitial carbon in Ni₃C. Nickel atoms are represented by large red spheres, and carbon atoms are represented by small blue spheres. Adapted from Reference. [26] **Copyright (a) 2011 American Chemical Society**.

the metallic hcp-Ni. [21] The hexagonal phase has been characterized as Ni carbide by some investigators using powder X-ray diffraction, [20, 22-26] while several others identified the hexagonal phase as metallic hcp-Ni. [10,13,15,19,27] This controversy apparently arises because the structure of hcp-Ni is quite similar to that of Ni₃C (Figure 5.1). [26] Ni₃C has a rhombohedral structure with interstitial carbon in an hcp-Ni lattice, but its structure can be approximated by a hexagonal sub cell that is nearly identical in size to that of hcp Ni. [21] In other words, the XRD patterns of metallic hcp-Ni and Ni₃C are very similar. Meanwhile, similar to the magnetic properties of hcp Ni, the

magnetism of Ni₃C observed in experiments also ranges from nonmagnetic to ferromagnetic due to the residual unreacted fcc Ni and carbon vacancies in the samples. [20, 22, 23, 28, 29] Therefore, it remains an open question whether the hexagonal phase obtained via the solution route is metallic hcp-Ni or nickel carbide. The clarification of this question will help develop advanced materials consisting of Ni NPs.

Due to the small difference in the lattice energies of the fcc and hcp phases of Ni, [30, 31] the structures of Ni can be tuned among these phases by varying the temperature and pressure. Through a thorough study of the fcc-Ni and hcp-Ni₃C transition process and the corresponding intermediates involved in this, the identification of the hexagonal phases to be the Ni₃C may be possible. In this chapter, the reduction of Ni (II) by the polyol process is described. The product nanoparticles were characterized by X-ray diffraction (XRD). The formation of the hexagonal nickel carbide and the mechanism were proposed, and an unidentified cubic phase was inferred to be cubic nickel carbide, which is an intermediate product of the carburization of metallic fcc-Ni to the hexagonal nickel carbide.

5.2 Experimental Section

5.2.1 Synthesis of Ni nanoparticles (Ni NPs)

Fcc-Ni and hcp-Ni₃C nanocrystals were made via the polyol method. The polyol method is a versatile liquid-phase method utilizing high boiling and multivalent alcohols to make nanoparticles. Here, the polyol acts as both reducing agent and solvent. [32]

Nickel (II) acetate tetrahydrate $(Ni(CH_3COO)_2 \cdot 4H_2O)$ (1.06g, 98%, Sigma-Aldrich) (4.26 mmol, 250 mg Ni) was placed in a 250-mL three-neck round-bottomed flask. Subsequently, 100 mL triethylene glycol was added along with a magnetic stir bar and the flask was fitted with a thermometer (right neck), condenser (middle neck), and a glass tube (left neck); N₂ gas was purged for 20 minutes through the glass tube and inserted into the solution to remove the dissolved oxygen in triethylene glycol. The flask was then put into a microwave reactor and heated to 100 °C for 5 minutes by microwave irradiation to dissolve the Ni(CH₃COO)₂·4H₂O powder in triethylene glycol (conc.: 42.6 mM). The solution was then heated to 250°C, and within 2 minutes the color of the solution turned from light green to black, indicating Ni (II) was reduced to Ni (0). During the whole heating process, N₂ is continuously purged to provide an inert atmosphere to protect the Ni NP products from being oxidized. The products were isolated after different dwell times (5 min, 30 min, 60 min and 120 min) by holding the temperature constant at 250 °C. After reached the desired dwell time, the flask, which was containing the black suspension, is removed from the microwave oven. The flask was quenched in an ice bath to room temperature (within approximately 5 min) and then synthesized particles were washed by centrifugation with distilled water. To clean the particles (remove unreacted salts), the above prepared suspension was centrifuged at 10,000 rpm for 15 minutes, the supernatant was removed, and the solid was re-dispersed in deionized water. The above cleaning steps were repeated for another two times. At the end, the nanoparticles were re-dispersed in ethanol in a crystalizing dish and then the crystalizing dish containing the particle suspension was put into an oven (temp. \sim 80 °C) to dry particles in air for several hours.

5.2.2 The microwave reactor

In this work, microwave irradiation was used as the heating power. The model of the microwave was a BP-125/50 (from Microwave Research and Applications, Inc.), and the reaction chamber of which was is fitted with magnetic stirring, reflux condenser, and an optical fiber temperature controller. The microwave power is generated by 1,000 W magnetrons, with frequency 2.450 GHz. This microwave reactor was operated with a CAL 9500P programmable process controller (from CAL Controls Inc.), which allows the microwave to follow a programmed protocol. In order to generate the scheduled heating ramps, the power is continuously supplied and automatically modulated by the process controller. The whole set-up is shown in Figure 5.2.



Figure 5.2 Microwave reactor for Ni nanoparticle synthesis

The microwave reactor can be programmed with steps for temperature and times with the controller, and the transition from one temperature to the next only took less than a minute.

5.3 Results and discussion

Figure 5.3 shows X-ray diffraction (XRD) profiles of the product NPs after dwell times of 5 min, 30 min, 60 min, and 120 min at 250 °C, together with the standard diffraction profiles of metallic fcc and hcp-Ni and hexagonal nickel carbide (Ni₃C). For the samples synthesized at 250 °C for 5 min, the diffraction pattern was indexed as that for the metallic fcc-Ni with a lattice parameter of $a_0 = 3.5298$ Å (standard fcc Ni: $a_0 = 3.53$ Å [33]). For the samples synthesized at 250 °C for 30 min, diffractions peaks of



Figure 5.3. XRD patterns of product NPs isolated with the dwell time are (a). t = 5 min, (b). t = 30 min, (c). t = 60 min and (d). t = 120 min at 250 °C. The calculated XRD line positions of (e) fcc-Ni (ref. 33) (f) metallic hcp-Ni (ref. 34) and (g) hcp-Ni₃C (ref. 21) are also shown for comparison. Symbols represent: **I**, fcc-Ni; \odot , hexagonal Ni₃C; and ∇ , cubic Ni-C phase, which is proposed to be an intermediate cubic nickel carbide.

a hexagonal phase (marked by open circles in the figure) and a cubic phase (marked by open triangle in the figure) appeared, and fcc-Ni peaks still can be observed. When further extending the dwell time to 60 min, the hexagonal phase and the unidentified cubic phase became more intense and obvious, and fcc-Ni peaks still can be observed. For the sample synthesized at 250 °C for 120 min, diffractions peaks of the hexagonal phase have the strongest intensity; these were attributed to either a phase possessing the hcp-Ni lattice with lattice parameters of $a_0 = 2.648$ Å and $c_0 = 4.334$ Å (standard hcp Ni: $a_0 = 2.66$ Å and $c_0 = 4.32$ Å) or the superlattice hcp-Ni₃C (rhombohedral structure with interstitial carbon in an hcp-Ni lattice (Figure 5.1(b))) with $a_0 = 4.586$ Å and $c_0 =$ 13.00 Å (standard Ni₃C: $a_0 = 4.553$ Å and $c_0 = 12.92$ Å). From the calculated lattice constants above, the hexagonal phase could not be unambiguously identified as the metallic hcp-Ni or the hcp-Ni₃C. Figure 5.3 also shows the transition of fcc-Ni phase to hcp phase (hcp-Ni or Ni₃C). When heated at 250 °C for 5 min, only fcc-Ni resulted (Figure 5.3(a)). When the dwell time was extended to 30 min, the hexagonal phase (hcp-Ni or Ni₃C) started to form; at t = 60 min and even at 120 min, the peak intensities of the fcc phase were decreased while the peak intensities of the hcp phase were increased, meaning part of the fcc-Ni NCs was transformed to hcp phase. The unidentified cubic phase appeared at t = 30 min, and became obvious at t = 60 min, finally disappearing at t = 120 min. This abnormal cubic phase behavior may be attributed to the fact that it is an intermediate product. In order to further study the transition of the fcc phase to the hcp phase and the cubic intermediate, peaks at the 2θ range of $(35^\circ, 55^\circ)$ were fitted (the fitting model is SPVII (Split - Pearson 7) with Rigaku PDXL software) [35] and shown in Figure 5.4.

Figure 5.4 shows that at 250 °C, the peak at $2\theta = 44.4^{\circ}$ gets broad and asymmetric from t = 5 min to 30 min, which is due to the variation of the solid composition, i.e. the variation concentration gradients in non-stoichiometric compounds. [36] At t= 60 min, a peak appeared at $2\theta = 44.2^{\circ}$ (the evolution of the compositional variation), attributed to the intermediate cubic phase. The amount of this intermediate



Figure 5.4. Fitted XRD patterns of product NCs isolated with the dwell time are (a). t = 5min, (b). t = 30 min, (c). t = 60 min and (d). t = 120 min at 250 °C. in the 2 θ range of (35°, 55°). Black dotted lines mark the bulk hcp-Ni₃C phase, while red dotted lines mark the bulk fcc-Ni phase.

cubic phase decreased and finally vanished with further extending the dwell time to 120 min; at the same time the hexagonal phase was obtained at the $2\theta = 44.7^{\circ}$. This most intense peak position shifted from $2\theta = 44.4^{\circ}$ to $2\theta = 44.7^{\circ}$, indicating the Ni phase changes from metallic fcc Ni to the intermediate cubic phase to the final hexagonal phase. However, the peak at 51.7°, which was attributed to fcc Ni (200), still persisted, suggesting the major products were the hexagonal phase nanoparticles, and a minor

amount of fcc Ni nanoparticles were still left. With the evidence of the evolution of the intermediate phase, which showed an asymmetric broad peak (often characterizing solid solutions with significant compositional variation) at the beginning and split into two sharp peaks and finally returned to one hexagonal peak, it is reasonable to propose that the hexagonal phase is superlattice hcp-Ni₃C. [37]

To determine the mechanism of the above process, i.e. the transformation of the fcc Ni to the hcp Ni₃C, and to further prove the product is hcp Ni₃C instead of hcp Ni, the strongest peak of the XRD spectrum was fitted and presented in Figure 5.5. The fitting model is a symmetric Pearson VII function plus a linear background in order to determine the peak position and width [38]. The Pearson Type VII peak function is a Lorentz function raised to a power and contains four parameters, i.e. xc (center, xc > 0), A (area, A > 1), w (width, w = 1) and mu (profile shape factor, initial mu = 2). In the interpretation of the nickel carbide formation, metallic nickel was assumed to be formed at first and then its carburization occurred. The validity of the assumption was demonstrated by the change of the product phase depending on the reaction time, as shown in Figure 5.3-Figure 5.5. Figure 5.5 shows that only metallic fcc-Ni was obtained from the synthesis at 250 °C for 5 min; when the reaction time increased from 5 min to 30 min, the broadening of the major peaks in the XRD pattern may be due to the slow diffusion of 'active C atoms' into the fcc Ni to form the meta-stable cubic nickel carbide (Ni-C alloy). This cubic nickel carbide should be characterized as an interstitial solid solution of carbon in fcc-Ni; it appears as an intermediate product from the fcc-Ni to the hexagonal nickel carbide. The source of 'active C atom' was proposed to be CO, and this was discussed in previous work. [24, 39, 40] The CO formed by decomposition of acetate [39, 41] at high temperature. When hydrocarbons such as triethylene glycol are used as solvents, the active carbon from adsorbed CO diffuses and deposits into the fcc-Ni. [42] Since the carbon atoms diffuse more slowly through nickel carbide than through nickel (the evidence is the observation of the cubic Ni_xC intermediate), [43] the initial carbide fcc-Ni_xC formation proceeds more rapidly than the formation of the final product hcp-Ni₃C. [43] The schematic illustration of this process is shown in Figure 5.6.



Figure 5.5. Fitted XRD patterns of product NCs isolated with the dwell time are (a). t = 5 min, (b). t = 30 min, (c). t = 60 min and (d). t = 120 min at 250 °C. in the 2θ range of (42.5°, 45.5°). Black dotted lines mark the bulk hcp-Ni₃C phase; red dotted lines mark the bulk fcc-Ni phase; blue dotted lines mark the meta-stable intermediate fcc-Ni_xC.



Figure 5.6 A schematic illustration of the transition of fcc-Ni to hcp-Ni₃C mechanism. At first, CO, produced by decomposition of nickel acetate, is adsorbed on the surface of fcc-Ni NCs, then the active carbon from adsorbed CO diffuses and deposits into the fcc-Ni, and finally form the superlattice hcp-Ni₃C structure.

The progressive shift of peak positions toward lower angles and the broadening of the peak as reaction time increases are clearly evident. This is consistent with the argument that the expansion of the unit cell is due to interstitial carbon incorporation as a function of reaction time. [26]

Although at t = 60 min the Ni₃C peaks have largest intensity, the fcc-Ni peaks still persisted ($2\theta = 44.2^{\circ}$), indicating that one cannot get pure hcp-Ni₃C NPs simply by extending the reaction time. A reasonable next step was to try a higher temperature, to check whether pure hcp Ni₃C could be obtained. Figure 5.7 shows the XRD pattern for samples heated to 275°C from t = 30 min to t = 60 min; surprisingly, still a mixture of the fcc Ni and hcp Ni₃C was obtained and the cubic phase peak intensity even gets larger. It appears that simply increasing the temperature form pure hcp Ni₃C, and at 275°C, fcc-Ni and hcp Ni₃C coexist and the peak intensity of fcc-Ni becomes stable. This result is shown more obviously in Figure 5.8, the fitted XRD patterns of the most



Figure 5.7. XRD patterns of product NCs isolated with the dwell time (a). t = 30min, (b). t = 45min, (c). t = 60min at 275°C. The XRD profile of (d) fcc-Ni (ref. 33) and (e) hcp-Ni₃C (ref. 21).



Figure 5.8. Fitted XRD patterns of product NCs isolated with the dwell time (a). t = 30 min, (b). t = 45 min, (c). t = 60 min at 275 °C. in the 2 θ range of (35°, 55°). Black dotted lines mark the bulk hcp-Ni₃C phase, while red dotted lines mark the bulk fcc-Ni phase.
intense peak range obtained from Figure 5.7 in the 2θ range of $(35^\circ, 55^\circ)$. The asymmetry of peak at $2\theta = 44.7^\circ$, and the existence of the $2\theta = 51.7^\circ$ are all the evidence of the coexistence of fcc-Ni and hcp Ni₃C.

5.4 Conclusion

This chapter discussed the transition process of fcc-Ni and hcp-Ni₃C. The Ni NPs obtained from a polyol process, i.e., the reduction of nickel (II) acetate in triethylene glycol, have been identified using XRD. The hexagonal phase turned out to be a superlattice hexagonal nickel carbide, Ni₃C. The transition of the fcc-Ni to hcp-Ni₃C mechanism is proposed as follows: The metallic fcc-Ni NPs are formed by reduction of nickel (II) acetate 250 °C at first, and then carburization into hexagonal nickel carbide occurs; a cubic nickel carbide is probably formed as an intermediate. The previously reported syntheses of the metallic hcp-Ni were carried out in the organic solutions such as amines, glycols, and so on, where the reaction temperature was usually above 250 °C. Under such reaction conditions, it is possible that some organic reagents may decompose and produce CO gas and provided the 'active C' and formed Ni₃C. Thus, a reasonable conclusion was made that the hexagonal phase in the previous work is the hcp-Ni₃C instead of metallic hcp-Ni.

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Chapter 6

SYNTHESIS OF Cu_xNi_y CORE/SHELL NANOPARTICLES OF VARYING COMPOSITION

6.1 Introduction

The Cu-Ni system is important and popular in various fields, e.g. corrosionresistant structural materials, [1] welding [2] and magnetic devices. [3-5] Cu-Ni is also chosen as an ideal diffusion couple to study the solid-state diffusion and new phase formation based on the following considerations. First, the Cu-Ni system forms solid solutions at all compositions and has a simple solid-liquid miscibility gap. This is because Cu and Ni both crystallize in the face-centered cubic (fcc) structure, have similar atomic radii (< 15% difference), electronegativities, and valences. [6] Second, copper precursors are preferentially reduced over nickel salts because of the more positive standard reduction potential of Cu (II) ($\varepsilon_{Cu^{2+}/Cu^{0}}^{o} = 0.337$ V) [7] relative to Ni(II) ($\varepsilon_{Ni^{2+}/Ni^{0}}^{o} = -0.25$ V). [8] The difference in reduction potentials in mixtures of metal precursors makes metallic Cu nanoparticles form first from a mixed Cu²⁺/Ni²⁺ solution and serve as the seeds for the subsequent nucleation and growth of Ni metal, resulting in a core – shell structure. [9] This preparation procedure is generally called the one-pot co-reduction process. Third, the powder XRD peaks of Cu and Ni are well separated, so it is easy to distinguish the phases.

The synthesis of pure nanoparticles of elemental nickel and copper are relatively challenging due to the instability of Cu and Ni in ambient atmosphere, which makes them prone to oxidation. One common method is the polyol process, using a polyalcohol at elevated temperature (ethylene glycol–EG, for example) as both solvent and reducing agent, to produce metal and bimetallic nanoparticles from cationic precursors. [10-21]

In this process, the polyol can also act as protective agent to avoid particles agglomeration. [10-26] Also, soluble polymers (e.g. polyvinyl pyrrolidone (PVP)) are often added as surface protective agents (besides polyol molecules) to ward off particle aggregation. In the absence of PVP, particles are generally obtained in the micrometer size range. [27-29] However, the above process poses two problems: first, in order to get a stable colloid, PVP was often added, but it is difficult to remove the polymer on the particle surface completely (a clean surface of uniform films are needed in this thesis to provide samples for pump-prob measurements (see Introduction section).) by simple washing; second, high temperatures (usually the boiling temp. of the polyol: i.e., ~196 °C for ethylene glycol) and long reaction times are needed to ensure completion of reaction. In the case of a Cu/Ni synthesis, high reaction temperatures and long reaction times, can lead to the reduced Cu and Ni atoms diffusing and forming an alloy. Therefore, it might be important to prepare Cu_xNi_y core/shell nanoparticles at lower temperature and without adding soluble polymers.

In this chapter, the synthesis, characterization and study of Cu_xNi_y core/shell nanoparticles of varying composition is described. The nanoparticles were obtained via a one-pot co-reduction process, starting from copper acetate and nickel acetate as precursors, sodium hypophosphite (NaH₂PO₂), or hydrazine (N₂H₄) as reducing agent, and using microwave irradiation as the heat source. The as-synthesized Cu_xNi_y core/shell nanoparticles were characterized by X-ray powder diffraction (XRD), and the formation of uniform films was explored, with the film fabrication method discussed in chapter 3.

6.2 Experimental Section

6.2.1 Materials.

Copper (II) acetate monohydrate $(Cu(CH_3COO)_2 \cdot H_2O)$, nickel (II) acetate tetrahydrate 98% $(Ni(CH_3COO)_2 \cdot 4H_2O)$, ethylene glycol (99.8% HOCH₂CH₂OH, anhydrous) and sodium hypophosphite monohydrate $(Na_2H_2PO_2 \cdot H_2O)$ were all

purchased from Sigma-Aldrich. Hydrazine monohydrate 98% ($N_2H_4 \cdot H_2O$) was purchased from Alpha Aesar. Sodium hydroxide (NaOH) was purchased from Fisher. All chemicals were used as received. All the reactants (except for NaOH) were dissolved in ethylene glycol (EG) to make up a certain concentration of the corresponding EG solution, respectively.

6.2.2 Cu_xNi_y core/shell NP formation with Na₂PO₂ as the reducing reagent6.2.2.1 Preparation of Cu NPs

10 mL of 0.08 M $Cu(CH_3COO)_2 \cdot H_2O$ precursor solution was made by dissolving 0.16 g copper (II) acetate monohydrate $(Cu(CH_3COO)_2 \cdot H_2O)$ (0.8 mmol) in 10.0 mL of ethylene glycol (EG) and heating to 80 °C with vigorously stirring for 5 minutes forming a blue solution. 10 mL of 0.08 M $Cu(CH_3COO)_2$ solution, and 10 mL of 0.12 M sodium hypophosphite monohydrate $(Na_2H_2PO_2 \cdot H_2O)$ (0.1275 g, 1.2 mmol) EG solution were added to a 250 ml three-neck flask. The total volume of the reaction solution was kept at 100 mL by adding EG. The above mixture was purged with N₂ gas for 20 minutes to remove oxygen gas dissolved in EG. Then the mixture solution (Cu (II) conc. 8 mM) was placed in a microwave oven, heated from room temperature (~ 22°C) to 100 °C within 1 minute and was vigorously agitated by bubbling N₂ gas through the solution for another 30 minutes at this temperature. The color of the solution turned from blue to orange to brown within 10 minutes. After 30 minutes, a stable dark brown colored colloidal dispersion was formed.

6.2.2.2 Preparation of Ni NPs

10 mL of 0.08 M Ni(CH₃COO)₂·H₂O precursor solution was made by dissolving 0.20 g nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) (0.8 mmol) in 10.0 mL of ethylene glycol (EG) and heating to 80 °C with vigorously stirring for 5 minutes forming a green solution. 10 mL of 0.08 M Ni(CH₃COO)₂ solution, and 10 mL of 0.12 M sodium hypophosphite monohydrate (Na₂H₂PO₂·H₂O) (0.1275 g, 1.2 mmol)

EG solution were added to a 250 ml three-neck flask. The total volume of the reaction solution was kept at 100 mL by adding EG. The mixture was purged N₂ gas for 20 minutes to remove oxygen gas dissolved in EG. Then the mixture solution (Ni (II) conc. 8 mM) was placed in a microwave oven, heated from room temperature ($\sim 22^{\circ}$ C) to 175 °C within 1 minute and was vigorously agitated by bubbling N₂ gas for another 15 minutes at the temperature of 175 °C. The color of the solution mixture turned from green to grey to black within 5 minutes and a black colloidal dispersion was obtained. The black colloidal solution was heated for another 10 minutes to make sure most of the Ni (II) was reduced to Ni (0).

6.2.2.3 Preparation of different composition of Cu_xNi_y core/shell NPs

Cu₁Ni₁: 10 mL of 0.08 M Cu(CH₃COO)₂·H₂O precursor solution was made by dissolving 0.16 g copper (II) acetate tetrahydrate $(Cu(CH_3COO)_2 \cdot H_2O)$ (0.8 mmol) in 10 mL of ethylene glycol (EG) and heating to 80 °C with vigorously stirring for 5 minutes forming a blue solution. Separately, 10 mL of 0.08 M Ni(CH₃COO)₂·4H₂O precursor solution was made by dissolving 0.20 g nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) (0.20 g, 0.8 mmol) in 10 mL of ethylene glycol (EG) and heating to 80 °C with vigorously stirring for 5 minutes forming a green solution. (Cu-Ni mole ratio: 1 : 1)

Cu₁Ni₂: 10 mL of 0.08 M Cu(CH₃COO)₂·H₂O precursor solution was made by dissolving 0.16 g copper (II) acetate tetrahydrate $(Cu(CH_3COO)_2 \cdot H_2O)$ (0.8 mmol) in 10 mL of ethylene glycol (EG) and heating to 80 °C with vigorously stirring for 5 minutes forming a blue solution. Separately, 10 mL of 0.16 M Ni(CH₃COO)₂·4H₂O precursor solution was made by dissolving 0.40 g nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) (1.6 mmol) in 10.0 mL of ethylene glycol (EG) and heating to 80 °C with vigorously stirring for 5 minutes forming a green solution. (Cu-Ni mole ratio: 1 : 2)

Cu₁Ni₃: With the same method, 10 mL of 0.08 M Cu(CH₃COO)₂·H₂O (0.16 g, 0.8 mmol) precursor solution and 10 mL of 0.24 M Ni(CH₃COO)₂·4H₂O (0.6 g, 2.4 mmol) precursor solution were made separately. (Cu-Ni mole ratio: 1 : 3)

Cu₂Ni₁: With the same method, 10 mL of 0.16 M Cu(CH₃COO)₂·H₂O (0.32 g, 1.6 mmol) precursor solution and 10 mL of 0.08 M Ni(CH₃COO)₂·4H₂O (0.2 g, 0.8 mmol) precursor solution were made separately. (Cu-Ni mole ratio: 2 : 1)

of $Cu(CH_3COO)_2 \cdot H_2O$ precursor solution, 10 mL of 10 mL Ni(CH₃COO)₂·4H₂O precursor solution, and 10 mL of varying amount of sodium hypophosphite monohydrate (Na2H2PO2·H2O) (Na2H2PO2·H2O added for making Cu₁Ni₁: 0.255 g, 2.4 mmol; Cu₁Ni₂: 0.3825 g, 3.6 mmol; Cu₁Ni₃: 0.51 g, 4.8 mmol; Cu₂Ni₁: 0.3825 g, 3.6 mmol.) solution were added into a 250 ml three-neck flask. The total volume of the reaction solution was kept at 100 mL by adding EG. The above mixture was purged with N_2 gas for 20 min to remove oxygen gas dissolved in the EG. The various solutions (Cu₁Ni₁: Cu (II) conc. 8 mM, Ni (II) conc. 8 mM; Cu₁Ni₂: Cu (II) conc. 8 mM, Ni (II) conc. 16 mM; Cu₁Ni₃: Cu (II) conc. 8 mM, Ni (II) conc. 24 mM; Cu₂Ni₁: Cu (II) conc. 16 mM, Ni (II) conc. 8 mM) were placed in a microwave oven, heated from room temperature (~ 22°C) to 100°C within 1 minute, and vigorously agitated by bubbling N₂ gas through the solution for another 30 minutes, to completely reduce Cu (II) to Cu (0). Then the temperature was increased to 175°C and kept constant for another 15 mins under a N₂ atmosphere, to completely reduce Ni (II) to Ni (0). The final black suspension was quenched with an ice water bath to room temperature. To purify the particles, the cleaning processes were the same as described for the Pt and Ni nanoparticles (details in Chapter 3, 3.2.1.2 and Chapter 5, 5.2.1) After the cleaning steps, the particles were dispersed in ethanol in a crystalizing dish, and then this crystalizing dish, which containing particles and ethanol was put into an oven (temp. $\sim 80^{\circ}$ C) to dry under air overnight.

6.2.3 Cu_xNi_y core/shell NP formation with N_2H_4 and aqueous NaOH as the reducing reagent

6.2.3.1 Preparation of Cu NPs

0.16g copper (II) acetate monohydrate $(Cu(CH_3COO)_2 \cdot H_2O)$ (0.8 mmol) was first completely dissolved in 10.0 mL of ethylene glycol (EG) by heating to 80 °C and vigorous stirring for 5 minutes, to form a blue precursor solution. 10 mL of 8 mM copper (II) acetate (0.8 mmol) precursor solution was mixed with another 80.0 ml of EG and was then added to a 250 ml three-neck flask and purged with N₂ gas for 20 minutes, to remove oxygen gas dissolved in EG. 0.8 mL liquid N₂H₄·H₂O (16 mmol, 20 equivs. based on Cu (II)), and 10 mL of 0.8 M NaOH (0.32 g, 8 mmol, 10 equivs. based on Cu (II)) aqueous solution were injected into the above mixture (Cu (II) conc. 8 mM, total volume: 100 mL) and was vigorously agitated by bubbling N₂ gas through the solution at room temperature (~ 22 °C) for 30 minutes. The color of the solution turned from blue to light yellow to dark green shortly after the hydrazine hydrate was added and to brown within 2 minutes. After 30 minutes, a stable dark brown colored colloidal dispersion had formed.

6.2.3.2 Preparation of Ni NPs

0.2 g nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) (0.8 mmol) was first completely dissolved in 10.0 mL of ethylene glycol (EG) by heating to 80 °C and vigorous stirring for 5 minutes, to form a green Ni (II) precursor solution. 10 mL of 8 mM nickel (II) acetate (0.8 mmol) precursor solution was mixed with another 80.0 ml of EG and was then added to a 250 ml three-neck flask and purged with N₂ gas for 20 minutes, to remove oxygen gas dissolved in EG. 0.8 mL liquid N₂H₄·H₂O (16 mmol, 20 equivs. based on Ni (II)), and 10 mL of 0.8 M NaOH (0.32 g, 8 mmol, 10 equivs. based on Ni (II)) aqueous solution were injected into the above mixture (Ni (II) conc. 8 mM, total volume: 100 mL) and was heated to 100 °C. The mixture was vigorously agitated by bubbling N₂ gas through the solution at 100 °C for 15 minutes. The color of the solution mixture turned from yellow to brown to black within 5 min. After 15 minutes, approximately 20 - 30 of diameter \sim 1-2 mm aggregated clumps were floating on a grey colored colloidal dispersion.

6.2.3.3 Preparation of Cu_xNi_y core/shell NPs of varying compositions

Cu₁Ni₁: Cu NPs were first prepared according to the procedure of Section 6.2.3.1, changing the amount of N_2H_4 ·H₂O and NaOH to 1.6 mL liquid N_2H_4 ·H₂O (32 mmol) (N_2H_4 : Cu : Ni = 40 : 1 : 1) and 10 mL 1.6 M NaOH (0.64 g, 16 mmol) (NaOH : Cu : Ni = 20 : 1 : 1) aqueous solution, respectively. In a separate vial, 0.2 g nickel (II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) (0.8 mmol) was first completely dissolved in 10 mL of ethylene glycol (EG) by heating to 80 °C and vigorous stirring for 5 minutes, to form a blue Ni (II) precursor solution. 10 mL nickel (II) precursor solution was quickly injected into above 90 mL of EG solution containing Cu NPs and extra N₂H₄ and NaOH. The solution was then heated to 100 °C for 15 minutes, reducing Ni (II) to Ni (0) (Cu-Ni mole ratio: 1 : 1).

Another three different samples (Cu₁Ni₂, Cu₁Ni₃, Cu₂Ni₁) were prepared according to the above procedure, varying the Cu(CH₃COO)₂·H₂O / Ni(CH₃COO)₂·4H₂O ratio (mole/mole): 1/2, 1/3, and 2/1 (weight/weight: 0.16g / 0.4g, 0.16g / 0.6g, and 0.32g / 0.2g) and the amount of N₂H₄·H₂O and NaOH: 2.4 mL, 0.96 g; 3.2 mL, 1.28 g; and 2.4 mL, 0.96g; respectively.

The prepared Cu_xNi_y particles were cleaned by washing with distilled water, followed by centrifugation, and finally the particles were dispersed in ethanol in a crystalizing dish, and then this crystalizing dish, which containing particles and ethanol was put into an oven (temp. ~ 80 °C) to dry under air overnight.

6.3 Results and discussion

6.3.1 The reduction pathway

The reduction process of metal precursors to neutral metal particles includes the electrons transfer from a reducing agent to the metal and the schematic chemical reaction is as follows:

$$mMe^{n+} + nRed \rightarrow mMe^{0} + nOx$$
 (1)

The driving force of the above reaction is the difference between the standard reduction potential of the two half-cell reactions, E_{cell}^o . The magnitude of E_{cell}^o determines the value of the equilibrium constant of the reaction, K, according to the well-known Nernst equation.

$$\ln K = \frac{nFE_{cell}^o}{RT} \tag{2}$$

where K is the equilibrium constant, R is the gas constant, 8.31 joules/mole K, F is Faraday's constant, 96,485 C/mole, and T is the absolute temperature.

The reduction reaction is thermodynamically possible only if the difference between the standard reduction potentials of the two half-cell reactions, E_{cell}^{o} , is positive. Table 6.1 lists half reactions and reductive potentials of two metals: Cu, Ni and two reducing agents: NaH₂PO₂, N₂H₄. These two different reactions (with addition of two different reducing agents) will be discussed one by one.

6.3.2 Sodium hypophosphite was used as the reducing reagent

In a typical polyol process, the polyol (such as ethylene glycol) acts not only as a reaction medium but also as a reducing agent. However, in the case of Cu/Ni core/shell nanoparticle synthesis, the reducing ability of ethylene glycol is insufficient to reduce the copper and nickel ions below the boiling temperature of EG (196°C). [13, 32] NaH₂PO₂·H₂O was therefore introduced as a reducing agent. NaH₂PO₂·H₂O is generally used in aqueous chemical reduction for the preparation of copper or nickel particles [34, 35]. It acts as the reducing agent and the half reaction represented by the equation: [34]

$$H_3PO_{3(aq)} + 2H^+ + 2e^- \rightleftharpoons H_3PO_{2(aq)} + H_2O$$
(3)

In an acidic condition, the oxidation from $H_3PO_{2(aq)}$ to $H_3PO_{3(aq)}$ releases electrons. The released electrons can be utilized to reduce copper ions as shown in the equation:

$$Cu^{2+} + 2e^{-} \rightarrow Cu \tag{4}$$

The formation of a core/shell structure was attributed to the different standard reduction potential of copper and nickel. The reduction reaction of Ni (II) to Ni (0) is given by:

$$Ni^{2+} + 2e^{-} \rightarrow Ni$$
 (5)

The standard reduction potentials of Ni (II) to Ni (0) is -0.25 V, and the difference between (3) and (5) is 0.249 V, the value is much smaller than that between (3) and (4) (0.839 V), respectively. The more positive reduction potential of Cu (II) relative to Ni (II) explains the Cu_xNi_y core/shell NPs synthesis conditions, which is the transformation of copper acetate to elemental Cu was observed to precede (at 100 °C for 30 min) the transformation of nickel acetate to elemental Ni (at 175 °C for 15 min).

The products of the chemical processes described above were characterized by XRD. Figure 6.1(a). shows XRD patterns of Cu_xNi_y NPs made via reduction by NaH₂PO₂. Although the only metal precursor added for the top diffraction pattern was $Cu(CH_3COO)_2$, there are no peaks corresponding to metallic $Cu((111): 43.3^\circ, (200): 50.4^\circ)$), but the peaks that appear at 39.5° and 42.7° are assigned to the (012) and (006) planes of Cu_2O , [36] confirming that all Cu NPs were oxidized to Cu_2O in the absence of nickel acetate. However, the series of Cu_xNi_y diffraction patterns only show Cu and Ni peaks, without any discernable Cu_2O peaks. A plausible interpretation is that the later produced Ni NPs consisted of Cu_xNi_y core/shell structures with the Ni shell protecting the Cu core from oxidation.

Half Reaction	\mathcal{E}^o/V vs. SHE
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	0.340 [7]
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.25 [8]
$H_3PO_{3(aq)} + 2H^+ + 2e^- \rightleftharpoons H_3PO_{2(aq)} + H_2O$	-0.499 [31]
$N_{2(g)} + 4H_2O + 4e^- \rightleftharpoons 4OH_{(aq)} + N_2H_{4(aq)}$	-1.160 [32]

Table 6.1 Half reactions and corresponding standard reduction potential.



Figure 6.1. XRD patterns for (a). Cu, Cu₂Ni₁, Cu₁Ni₁, Cu₁Ni₂, Cu₁Ni₃, Ni NPs synthesized by NaH₂PO₂ reduction; $2\theta = 40^{\circ}$ to 100° ; (b). enlargement of the $2\theta = 41^{\circ}$ to 46° range. Black dotted lines mark the peak positions expected for pure Ni, while red dotted lines mark those expected for pure Cu.

Figure 6.1(b). enlarges the most intense peak area of Figure 6.1(a). and shows that both Cu peak position and Ni peak position of Cu_xNi_y core/shell structure are very close to pure Cu and pure Ni peak positions. A more careful inspection of the Cu and Ni position in Cu_xNi_y (Cu₁Ni₁, Cu₁Ni₂, Cu₁Ni₃) was shown in Table 6.2, with the strongest peak of the XRD spectrum was fitted. The fitting model is a symmetric Pearson VII function plus a linear background in order to determine the peak position and width. [37] Table 6.2 clearly shows a shift of the peak position of Ni to smaller angles ($2\theta = 44.50^{\circ}$, 44.43° , and 44.25° for Cu₁Ni₃, Cu₁Ni₂, and Cu₁Ni₁, respectively) as the Ni ratio is decreased, suggesting some degree of alloying happened. This suggests that some degree of interdiffusion has happened at 175 °C, though not too much. Changing the relative proportions of the metal salts allowed the Cu : Ni ratio to be varied and to obtain different composition of Cu_xNi_y core/shell nanoparticles.

Quantitative analysis of the Cu_xNi_y core/shell nanoparticle's composition was carried out, to make sure that the compositions of the products meet expectations. In order to determine each Cu_xNi_y core/shell nanoparticle's composition, Wavelength Dispersive X-Ray Fluorescence Spectroscopy (WDXRF) was used. The result Cu/Ni mole ratio matches the Cu, Ni precursor addition mole ratio. Using Cu_1Ni_1 as an example, the content ratio of Cu/Ni (mass%): 50.4/49.6. After converted to mole ratio, $Cu/Ni: 0.79/0.84 \sim 1/1$.

6.3.3 Hydrazine as the reducing reagent

Another widely used reducing reagent chosen for the synthesis of copper and nickel nanoparticles is hydrazine (N₂H₄). [38-42] Typically, appropriate amounts of metal precursors, i.e., copper acetate and nickel acetate, were dissolved directly in ethylene glycol. Then, an excess of hydrazine (N₂H₄ : Cu : Ni = 40 : 1 : 1) and aqueous NaOH solution (NaOH : Cu : Ni = 20 : 1 : 1) were added in sequence. At room temperature, Cu NPs were formed after 30 minutes; Ni NPs were only formed after stirring for 15 minutes at a temperature of 100°C. The reduction reactions are the following: [38]

Table 6.2. Peak positions $(2\theta/^{\circ})$ of Cu and Ni in Cu_xNi_y NPs fitted peaks from Figure 6.1(b).

Cu _x Ni _y	$Ni/(2\theta/^{\circ})$	$\operatorname{Cu}/(2\theta/^{\circ})$
Cu		
Cu ₁ Ni ₁	44.25	43.43
Cu ₁ Ni ₂	44.43	43.45
Cu ₁ Ni ₃	44.50	43.45
Ni	44.50	

$$2Cu^{2+} + N_2H_4 + 4OH \rightarrow 2Cu + N_2 + 4H_2O$$
(6)

$$2Ni^{2+} + N_2H_4 + 4OH^{-} \rightarrow 2Ni + N_2 + 4H_2O$$
(7)

The hydrazine reductions happened at much lower temperature (Cu (II) to Cu (0): ~22°C, Ni (II) to Ni (0): ~100°C) than the reactions using NaH₂PO₂ as the reducing agent (Cu (II) to Cu (0): ~100°C, Ni (II) to Ni (0): ~175°C). N₂H₄ is a more powerful reducing agent than NaH₂PO₂ (standard reduction potential of N₂H₄ (-1.16 V) vs. NaH₂PO₂ (-0.499 V)), which is reflected in the reaction rate.

Figure 6.2(a). shows XRD patterns of products Cu_xNi_yNPs formed by the above reactions, made with N₂H₄/NaOH as the reducing agent. Interestingly, for the pure Cu system, all peaks were attributable to metallic Cu, without any Cu₂O peaks. Chen et. al [43] claimed that in the process of reduction of cupric chloride with hydrazine (N₂H₄) in aqueous cetyltrimethylammonium bromide (CTAB) solution, nitrogen gas released during the reduction process auto-created an inert atmosphere, and inhibited Cu NPs being oxidized to Cu₂O. Considering the above provided reactions, 0.4 mmol N₂ (that is ~ 10 ml of N₂ gas at STP) was generated by reducing 0.8 mmol Cu (II) to Cu (0). The solubility of O₂ gas in EG at 298 K and 1 atm is 7.23 × 10⁻⁵ (mole fraction). [44] Thus, 100 mL EG (1.79 mol) contains 0.13 mmol dissolved O₂ gas. According to the calculated amount of produced N₂ gas (10 mL), the amount is too small to replace dissolved O₂ gas (0.13 mmol) in EG, further prevent Cu NPs being oxidized to Cu₂O.



Figure 6.2. XRD patterns for (a). Cu, Cu₂Ni₁, Cu₁Ni₁, Cu₁Ni₂, Cu₁Ni₃, Ni NPs synthesized by N₂H₄ + NaOH at $2\theta = 40^{\circ}$ to 100° ; (b). enlargement of the $2\theta = 41^{\circ}$ to 46° range. Black dotted lines mark the peak positions expected for pure Ni, while red dotted lines mark those expected for pure Cu.

Cu _x Ni _y	Ni / $(2\theta/^{\circ})$	$\operatorname{Cu}/(2\theta/^{\circ})$
Cu		43.31
Cu ₁ Ni ₁	44.20	43.42
Cu ₁ Ni ₂	44.45	43.48
Cu ₁ Ni ₃	44.48	43.67
Ni	44.50	

Table 6.3. Peak positions (2θ /degree) of Cu and Ni in Cu_xNi_y NPs fitted peaks from Figure 6.2(b).

The reason why Cu NPs were not being oxidized to Cu₂O is still a mystery.

For the XRD diffraction patterns of Cu_xNi_y core/shell nanoparticles reduced by N₂H₄ (shown in Figure 6.2(b)), the Cu peak position moved to the higher angle compared to that of the pure Cu, suggesting the formation of the alloy structure. In order to give further evidence of the interdiffusion of Cu-Ni, a more careful inspection of the Cu and Ni peak positions in Cu_xNi_y (Cu₁Ni₁, Cu₁Ni₂, Cu₁Ni₃) is shown in Table 6.3; the strongest peak of the XRD spectrum was fitted ($2\theta = 41^{\circ}$ to 46°). The fitting model is a symmetric Pearson VII function plus a linear background in order to determine the peak position and width [37]. Table 6.3 shows an obviously shift of the peak position of Cu to higher angles ($2\theta = 43.31^{\circ}$, 43.42° , 43.48° and 43.67° for Cu, Cu₁Ni₁, Cu₁Ni₂, and Cu₁Ni₃, respectively) as the Cu ratio is decreased, suggesting alloy formation. A small modification of the original synthesis method was then made to prevent the formation of the alloy. Instead of adding the mixture of the dissolved Cu(CH₃COO)₂ and Ni(CH₃COO)₂ EG dispersions into extra EG solvent at the beginning, Ni(CH₃COO)₂ dispersion was injected after all Cu (II) was reduced to Cu (0). The XRD result of one example (Cu₁Ni₁ core/shell) is shown in Figure 6.3.

Comparing XRD patterns in Figure 6.3(a) (mixing Cu(acetate)₂ with Ni(acetate)₂ first and then adding N₂H₄/NaOH) to those in Figure 6.3(b) (initially reducing Cu(acetate)₂ to Cu NPs first with N₂H₄/NaOH and then adding Ni(acetate)₂, to make Ni shell), the positions of Cu and Ni peaks of Cu₁Ni₁ in Figure 6.3(b) are closer to those of pure Cu and Ni than in Figure 6.3(a), indicating that changing the order of the Ni(CH₃COO)₂ addition leads to less amount of alloy formation. This result is shown more clearly in Figure 6.3(d) and Figure 6.3(e). In addition, quantitative analysis of the composition of formed Cu₁Ni₁ alloy has also been done by fitting the XRD patterns of Figure 6.3(a) and (b).

Figure 6.3(c) to (f) shows the fitted XRD patterns for pure Cu; Cu₁Ni₁ core/shell NPs made by mixing Cu(acetate)₂ with Ni(acetate)₂ first and then adding N₂H₄/NaOH; or initially reducing Cu(acetate)₂ to Cu NPs first with N₂H₄/NaOH and then adding Ni(acetate)₂, to make Ni shell; and pure Ni, respectively. The fitted line positions

yielded best fit Cu lattice parameters of 0.3609 and 0.3611 nm; and best fit Ni lattice parameters of 0.3545 and 0.3533 nm for the Cu₁Ni₁ NPs in Figure 6.3 (a), (b) respectively. The line fits yielded a Cu lattice parameter of the pure Cu NPs of 0.3615 nm and the lattice parameter of pure Ni NPs is 0.3530 nm, respectively. According to Vegard's law: [45, 46]

$$a_{A_{(1-x)}B_x} = (1-x)a_A + xa_B$$

where $a_{A_{(1-x)}B_x}$ is the lattice parameter of the solid solution, a_A and a_B are the lattice parameters of the pure constituents, and *x* is the molar fraction of B in the solid solution, the composition results of the formed alloy are as follows:

a. Cu₁Ni₁ sample shown in Figure 6.3(d). The XRD pattern of this sample and the calculations of cell parameters clearly indicate the presence of two distinct phases: a copper-rich Cu-Ni alloy with a = 0.3608 nm and associated composition of Cu_{0.92}Ni_{0.08} (~92% Cu, ~8% Ni), and a nickel-rich Cu-Ni alloy with a = 0.3545 nm and associated composition of Cu_{0.18}Ni_{0.82} (~18% Cu, ~82% Ni).

b. Cu_1Ni_1 sample shown in Figure 6.3(e). The XRD pattern of this sample and the calculations of cell parameters clearly indicate the presence of two distinct phases: a copper-rich Cu-Ni alloy with a = 0.3611 nm and a composition of $Cu_{0.95}Ni_{0.05}$ (~95% Cu, ~5% Ni), and a nickel-rich Cu-Ni alloy with a = 0.3533 nm and a composition of $Cu_{0.03}Ni_{0.97}$ (~3% Cu, ~97% Ni).

From the above data, after changing the addition order of Ni(acetate)₂, the composition of Cu phase remains the same but the Ni content in the composition of Ni phase increased from 82% to $\sim 97\%$.



Figure 6.3. XRD patterns for Cu₁Ni₁ core/shell NPs made by (a) mixing Cu(acetate)₂ with Ni(acetate)₂ first and then adding N₂H₄/NaOH, or (b) initially reducing Cu(acetate)₂ to Cu NPs first with N₂H₄/NaOH and then adding Ni(acetate)₂, to make Ni shell; Fitted XRD patterns for (c) pure Cu; (d) enlargement of the $2\theta = 40^{\circ}$ to 48° range of (a); (e) enlargement of the $2\theta = 40^{\circ}$ to 48° range of (b); and (f) pure Ni. Black dotted lines mark the expected peak positions of pure Ni, while red dotted lines mark those of pure Cu.

6.3.4 The uniform film formation and ζ -potential analysis

After the preparation and subsequent purification of the Cu_xNi_y nanoparticles with water, the "cleaned" particles (Cu_1Ni_1 : ~2.2 mg, Cu_1Ni_2 : ~3.3 mg, Cu_1Ni_3 : ~4.4 mg, Cu_2Ni_1 : ~3.3 mg) were re-dispersed in 10 mL deionized water, the same concentration of 'as-prepared' Pt NPs described in Chapter 3 for assembling uniform films. Figure 6.4 shows Cu_xNi_y NPs made by the reducing agent, NaH_2PO_2 , deposited on the glass substrate. The films are optically uniform and show no big cracks. Different from the Pt colloids (after dispersing Pt NPs in water, one needed to wait for ~50 hours before making films), 1.8mM Cu_xNi_y NP colloids can be used for film formation immediately after dispersal in water. This can be attributed to the different ζ -potential evolution of Cu_xNi_y NP colloids and Pt NP colloids.

As mentioned in Chapter 3, the prerequisite condition for NPs aggregation into film is -30 mV < ζ < +30 mV. Figure 6.5(a). shows that for a long period (~20h), the ζ -potential of Cu₁Ni₁ colloid is ~ -30 mV and its absolute value is much lower than that of Pt colloid, ~-65 mV (Figure 6.5(b)), and reached the threshold of the ζ to form the film.

Except for Cu_xNi_yNPs made by reduction with NaH_2PO_2 , the set of Cu_xNi_yNPs made by $N_2H_4/NaOH$, were also tried for film formation. However, when those Cu_xNi_y particles were transferred from EG to water, Cu_xNi_y particles were not uniformly dispersed in water, which was against the pre-requisite of uniform film formation. These NPs aggregated to big clumps and were unable to assemble into uniform films.



Figure 6.4 The uniform films of (a). Cu_2Ni_1 , (b). Cu_1Ni_1 , (c). Cu_1Ni_2 , (d). Cu_1Ni_3 deposited on the glass slide made with the reducing reagent: NaH₂PO₂.



Figure 6.5 ζ -potential evolution of (a). Cu₁Ni₁ colloids and (b). Pt colloids.

6.4 Conclusion

This chapter described the use of two typical reducing reagents (NaH₂PO₂ and N₂H₄/NaOH) to reduce copper acetate and nickel acetate to Cu_xNi_y core/shell nanoparticles. Comparison of the two reducing reagents, i.e., N₂H₄/NaOH vs NaH₂PO₂ gave rise to the following considerations. N₂H₄/NaOH is a stronger reducing agent, due to its more negative standard reduction potential (N₂H₄: -1.16 V vs. NaH₂PO₂: -0.499 V) than that of NaH₂PO₂. It can reduce Cu (II) to Cu (0) at room temperature (~22°C) and Ni (II) to Ni (0) at 100°C. This temperature difference can separate formation of elemental Cu and Ni well and result in core/shell structure formation. NaH₂PO₂ is a weaker reducing agent, which reduces Cu (II) to Cu (0) at 100°C and Ni (II) to Ni (0) at 175°C. This also led to the successfully formation of CuNi core/shell NPs. The reason why Cu NPs produced with the reducing agent N₂H₄/NaOH is still a mystery and is needed to be further explored. At the end, the two sets of Cu_xNi_y core/shell nanoparticles products were evaluated for the formation of uniform films following the film preparation procedure discussed in Chapter 3.

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