Synthesis and Characterization of Monodisperse Ni-Co Bimetallic Nanocrystals

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SYNTHESIS AND CHARACTERIZATION OF MONODISPERSE Ni-Co BIMETALLIC NANOCRYSTALS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Zongyue Chai
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ABSTRACT

Monodisperse Ni-Co bimetallic nanocrystals have been intensively investigated during the past several decades because of their unique physical and chemical properties that are promising for a broad range of applications in emerging technologies. The precise control of shape, size, and structure of nanocrystals is critical for the desired functionality, while transmission electron microscopy (TEM) is one of the most powerful and versatile techniques to characterize the nanocrystal’s structure, morphology, and physical and chemical properties on the atomic to nanometer scales. The research of this thesis focuses on the synthesis of bimetallic Ni-Co nanocrystals and the understanding of the underlying crystal growth mechanism through advanced structural and chemical characterizations using TEM techniques. We have studied the effect of synthetic temperature, reaction time, concentration of precursors and surfactant on the nanocrystal’s morphology and structure. Throughout a series experimental attempts, an optimal set of synthesis parameters was found, which produced the controlled synthesis of Ni-Co nanocrystals with average size of 10.59±1.42 nm from the thermal decomposition reaction at 230°C for 4 h. With the help of TEM, dynamic morphology evolution of Ni-Co nanocrystals as a function of reaction time was discovered and the associated monodisperse nanocrystal growth through digestive ripening mechanism was also elucidated. We have also found that the addition of trioctylyphosphine (TOP) surfactant not only regulates the shape and size, but also causes the formation of nickel/cobalt phosphide during nanocrystal growth, which needs further investigation to clarify. The findings obtained from this research provides fundamental
understanding of crystal growth mechanism of bimetallic Ni-Co nanocrystals and may also offer useful implications for controlled synthesis of other bimetallic systems.
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1.1 Nanocrystals and Their Technological Applications

Nanomaterials have been intensively investigated during the past several decades because they display unique physical and chemical properties different from those of their bulk counterparts. Among various types of nanomaterials, nanostructured metallic systems have shown intriguing properties that are highly morphology and composition dependent. In particular, bimetallic nanocrystals are attractive not only because the unique nanoscale properties of each composing metals can be integrated to get multifunctionality within a single nanocrystal, but also due to the new properties arisen at the nanoscale.

Bimetallic nanocrystals have attracted tremendous attention due to their excellent performance in the applications of catalysis, chemical sensors, drug delivery, and plasmonics. For example, X. Xia et al. has synthesized bimetallic nanocrystal by alloying two active but expensive metals together via a seed-mediated growth method and demonstrated that Pd-Ru has outstanding peroxidase catalytical properties. Bimetallic nanocrystals combining two metals with distinct optical properties can show tunable plasmonic properties. Therefore, S. Han and co-workers have used this feature to design Au-Pd nanocrystals for hydrogen sensing in water, where Pd can uptake hydrogen and the Au interior can sense the change. Because bimetallic nanocrystals can be synthesized with precise shapes surface chemical and physical properties, and this engineering flexibility has enabled the design of novel therapeutics, contrast agents, and integrated systems for
the diagnosis and treatment of diseases. For example, W. C. W. Chan’s group has investigated the assembly of nanomaterials using DNA to produce low toxicity nanocrystals for biomedical applications.\textsuperscript{5} In addition, some nanocrystals serve as chemical sensors, such as, Ce$_2$O that exhibits rich oxygen vacancies, low redox potential, and high oxide ion conductivity as an ideal material for gas sensing.\textsuperscript{6}

1.2 Structures of Bimetallic Nanocrystals

The widespread applications of bimetallic nanocrystals depend on their size, structure, morphology, and composition, which are tunable through a variety of controlled synthesis and processing. Here, we describe the structure of nanocrystals in two different aspects. For individual bimetallic nanocrystals, their atomic-scale structures may include alloying (ordered intermetallic and random solid-solution), and Janus, core-shell, multi-shell, and many other distinct configurations, as shown in Figure 1.1.\textsuperscript{7} For nanocrystal assemblies on the microscale, they may display different microstructures, in both homogenous\textsuperscript{8} and heterogeneous\textsuperscript{9} arrangement, as shown in Figure 1.2. It is worth noting that despite the homogeneity or heterogeneity on the assembly scale, the composing individual nanocrystals as basic building blocks exhibit high uniformity in both size and shape, especially for the necessity of homogeneous assemblies. From this point of view, characterizing the structures of individual nanocrystals is important and prerequisite for the controllable design of functional bimetallic systems.

As for the composition of bimetallic nanocrystals, previous studies have heavily investigated the noble metal systems, which indeed exhibit excellent properties in many
aspects, but the expensive cost still remains a large obstacle for up-scale application. In this regard, we are motivated to focus on the bimetallic nanocrystals composing cheap transition metal elements for potentially cost-effective applications.

Figure 1.1. Structures of bimetallic nanocrystals: (a) random solid solution; (b) ordered solid solution; (c) subclusters with two interfaces (Janus); (d) subclusters with three interfaces; (e) subclusters with a small number of A–B bonds; (f) core-shell; (g) multishell core-shell; (h) multiple small core material coated by single shell material; (i) movable core within hollow shell material.\(^7\)
1.3 Synthesis Approach and Mechanism

1.3.1 Synthesis Approach

It is well-known that the structure-property relationship is at the center of materials science so that understanding and controlling the synthesis of nanocrystals are also essentially important. With the advancement of nanoscience and nanotechnology, significant progress has been achieved on the synthesis of bimetallic nanocrystals with...
tailored size, shape, composition, and structure, while continuous. The effort on investigating simple, stable, and inexpensive methods for the synthesis of high-quality nanocrystals has never ended. The synthesis of nanocrystals can be achieved by two main approaches, i.e., chemical methods and physical methods. Due to the easy setup, facile route, and good controllability, wet chemical methods have been widely utilized for the synthesis of nanocrystals, such as the seeded-growth method, hydrothermal method, and thermal decomposition method. In a typical thermal decomposition synthesis, diethyleneglycol (DEG) and oleylamine (OAm) are widely used as solvents that can reduce metallic precursors to produce nanocrystals in the presence of surfactants or polymers. Usually, the metal precursors cannot be decomposed at room temperature, even mixing with reducing agents. However, at high temperatures (200-300°C) thermal reduction process can easily occur. Therefore, there are two widely used routes: (i) heating the mixture directly by heating mantle or oil bath, or (ii) through the so-called “hot-injection” technique, where a “cold” solution of precursor molecules is rapidly injected into a hot coordinating alkyl solvent.

OAm, as a long-chain primary alkylamine, is widely used in the synthesis of various nanostructures. The high boiling point (~350°C) of OAm allows high-temperature conditions. OAm can act not only as a solvent for many organic and inorganic compounds but also as a surfactant and a mild reducing agent in the reaction. OAm is an electron donor at thermal reduction reaction. There are several advantages of OAm such that commercial OAm has a lower price than other pure alkylamines. Moreover, OAm can be easy to be washed off reaction products after the synthesis of nanocrystals because it is a
liquid at room temperature. The molecular structure of OAm is depicted in Figure 1.3.\textsuperscript{19} The carbon-carbon double bond (C=C) in the middle of the molecule is another unique feature, which improves its coordination with elements, in addition to the exhibited affinity to metals through its NH2 functional groups.\textsuperscript{20}

![Figure 1.3. The molecular structure of oleylamine containing a carbon-carbon double bond (C=C) in the middle.\textsuperscript{19}](image)

S. Liu and co-workers proposed a plausible reaction pathway of the thermal decomposition synthesis, where Nickel (II) acetylacetonate (Ni(acac)\textsubscript{2}), as a precursor, is reduced to Ni by oleylamine,\textsuperscript{21} as shown in Figure 1.4. At the beginning of the reaction, Ni(acac)\textsubscript{2} is coupled with OAm to form the Ni-OAm complex, which is then reduced to Ni0 by the extra OAm in the solution. Following the same reaction pathway, other transition metal elements, such as Fe and Co, can also be synthesized to nanocrystals with the help of OAm.\textsuperscript{22,23} With oleic acid (OAc) and trioctylyphosphine (TOP), Ni nanocrystals
with size in a range of 8-16 nm were produced.\textsuperscript{24} The role of OAm and TOP in the thermal decomposition of Ni(acac)\textsubscript{2} was reported by Carencio et al.\textsuperscript{18} The TOP surfactant can offer better size control. In addition, previous investigations have proven that higher reaction temperatures (e.g., > 240°C) are favored for the formation of the hcp-Ni phase, while lower temperatures tend to yield fcc-Ni nanocrystals.\textsuperscript{25}

Figure 1.4. Schematic diagram showing the mechanism of thermal decomposition synthesis of Ni nanocrystals.\textsuperscript{21}

Bimetallic nanocrystals comprising at least one transition element have been successfully synthesized using OAm as a reaction medium. Chaubey et al.\textsuperscript{26} synthesized 20 nm FeCo nanocrystals with OAm and OAc, using Fe(acac)\textsubscript{3} and Co(acac)\textsubscript{2} as a precursor. In another research,\textsuperscript{27} Co-Ni nanocrystals with various compositions (Co\textsubscript{50}Ni\textsubscript{50} and Co\textsubscript{80}Ni\textsubscript{20}) were produced using OAm in a triple ligand mixture (solvent, surfactant, reductant) together with OAc and TOP. Several investigations have indicated that the transition metal precursors M(acac)\textsubscript{2} (M = Ni, Co) were firstly decomposed at 200°C to produce intermediate production (M-TOP complexes), which would be further decomposed at 240°C, which leads to the formation of Co and Ni nuclei in the mixture.\textsuperscript{27}
These early works have demonstrated the feasibility of thermal decomposition synthesis of bimetallic nanocrystals using transition metal precursors in general, which will be employed as a primary method in this thesis.

1.3.2 Synthesis Mechanism

In the regime of crystal growth, several theoretical models have been proposed to describe the processes of nucleation and growth of nanocrystals, including nucleation mechanisms, such as LaMer mechanism, Fink-Watzky two-step mechanism; and growth mechanism, such as Ostwald ripening and digestive ripening, coalescence and orientated attachment, as well as intra-particle growth. In this section, we focus on the discussion of LaMer mechanism, Ostwald ripening, and digestive ripening.

LaMer mechanism. In 1950, LaMer studied the synthesis of sulfur sols from the decomposition of \( \text{NaS}_2\text{O}_3 \), consisting of two steps, i.e., the thiosulfate decomposition to free sulfur, and then sulfur sols formation in solution. Through the LaMer mechanism, the nucleation and growth are separated into three stages, where the concentration of monomers is plotted as a function of time, as shown in Figure 1.5. The Stage I shows the increase of free monomers upon the decomposition of precursors in the reaction media. The Stage II shows the critical concentration, above which the nucleation will occur extremely rapidly, so-called “burst-nucleation.” This nucleation rate is described as “effectively infinite”, and after this point, there is almost no nucleation occurring because of the lower concentration of monomers than this critical value. The Stage III indicates the rapid decrease of monomer concentration in the solution to a certain stable value for the
continuous growth of nuclei. The following growth stage is controlled by the diffusion of the monomers through the solution.

Figure 1.5. Schematic diagram showing LaMer mechanism (I) the increase in concentration of free monomers; (II) concentration of monomers over critical value; (III) the concentration decrease as monomers are consumed due to growth.\textsuperscript{30}

**Ostwald ripening.** Ostwald ripening was first proposed in 1900. It was initially developed to explain the coarsening and growth of larger oil droplets at the expense of smaller ones because of the diffusion of individual oil molecules from the latter to the former through the solvent. The mechanism of growth is caused by the change in solubility of nanocrystals depending on their size, which is described by the Gibbs-Thomson equation

\[
C_r = C_b \cdot \exp\left(\frac{-2\gamma v}{r k_B T}\right)
\]
where $C_r$ is crystal solubility, $C_b$ is the bulk concentration of monomers, $\gamma$ is interface energy, $v$ is the molar volume of the bulk crystal, $r$ is crystal radius, $k_B$ is Boltzmann constant, $T$ is temperature. Small crystals perform the high solubility, and monomers move from small crystals to big ones due to the concentration gradient. Small crystals will re-dissolve into solution hand help large crystals grow. The growth process of Ostwald ripening is depicted in Figure 1.6. The surface growth of nanocrystals is continued by the deposition of monomers on the existing nuclei. These monomers are in turn formed as a result of either the continuing reaction or the dissolution of the already-formed nuclei that are smaller than a critical size.

![Figure 1.6](image)

Figure 1.6. Schematic representation of Ostwald ripening. The diagram contains four representative stages following the arrow directions to illustrate the change in the size of nanocrystals upon the growth in the solution through the dissolution and deposition of monomers.\textsuperscript{31}
**Digestive ripening.** Digestive ripening is seemingly the inverse process of Ostwald ripening. In this ripening mechanism, as small nanocrystals grow, the large ones redissolve into the solution, make a uniform distribution of nanocrystals size when reaching a stable balance between the dissolution and deposition. The surface energy of the nanocrystals will influence this nucleation and growth process. The surface layer of larger nanocrystals will redissolve and help the growth of smaller ones.\textsuperscript{28} J. R. Shimpi and co-workers\textsuperscript{31} proposed plausible digestive ripening processes in three steps, as shown in Figure 1.7. (I) The existing weakly bound ligands, surfactants, and solvent molecules are replaced, and the newly added ligands bind to the surfaces of the polydisperse nanocrystals. These stronger ligands result in an interesting consequence that the larger nanocrystal will break into smaller ones. (II) The break of larger nanocrystals (especially those larger than 10 nm) leads to the narrow size distribution and the formation of ligand-metal complex species on the nanocrystal surface. Shimpi et al.\textsuperscript{31} explained this process that the ligands will attack nanocrystals defect sites where the chemical reactivity is high. (III) When they are refluxed in a relatively high boiling point solvent with surface-active ligands, the nanocrystal size distribution becomes narrower. Meanwhile, there are several pieces of evidence in the literature supporting this mechanism.\textsuperscript{32-34} Ultimately, equilibrium gets established between the surface etching and redeposition processes, and the entire nanocrystal system reaches an optimum size with excellent monodispersion.\textsuperscript{31}
Figure 1.7. Schematic representation of the digestive ripening. Step I: formation of polydisperse nanocrystals. Step II: modification of both small and large nanocrystals. Step III: formation of nearly monodisperse nanocrystals.\textsuperscript{31}

In actual applications, different nanocrystals may follow different mechanisms, and sometimes even the same nanocrystal system may conform to more than one model due to different synthetic paths. Comparing the well-known Ostwald ripening, digestive ripening process is highly effective to produce monodisperse nanocrystals but much less understood for its fundamental mechanism. From this perspective, more attention needs to be paid for a better understanding of nucleation and growth mechanism on the fundamental level and from the microscopic point of view.\textsuperscript{28}
1.4 Characterization for Nanocrystals

1.4.1 Transmission Electron Microscopy

In modern material science research, transmission electron microscopy (TEM) is one of the most powerful and versatile techniques for the characterization of materials structure, morphology, and physical and chemical properties on the atomic to nanometer scales. Figure 1.8 shows the schematics of the components of a TEM, including the electron gun, electromagnetic lenses, and various electron detectors and spectrometers. As shown in Figure 1.8, the electron beam is generated from the gun, focused by a series of lenses. When the electron beam transmits the sample, it generates different types of electron scattering. By collecting the different electron signals, images can be obtained in TEM mode or scanning transmission electron microscopy (STEM) mode. High-resolution TEM (HRTEM) can resolve the materials structures with atomic resolution using the phase contrast, which is related to sample thickness and microscope defocus but less sensitive to identify an element. In contrast, STEM can provide more information about the sample because the scanning modality is fundamentally different from the TEM image formation under static parallel beams. For example, the annular dark-field (ADF) STEM image is formed by collecting the scattered electrons at certain angles rather than the direct-beam electrons. In this way, high angle annular dark-field (HAADF) STEM images can be acquired with the contrast proportional to the atomic number ($\sim Z^{1.7}$) of the specimen, which offers a directly interpretable imaging method with spatial resolution on the atomic scale.
Figure 1.8. Schematic diagram showing the structure of a TEM, including core components of electron source, lenses, and detectors.\textsuperscript{51}
For example, H. Shan and co-workers\textsuperscript{36} have studied core-shell structured Pd-Pt nanocrystals using HRTEM. As shown in Figure 1.9 (a) shows, the atomics arrangement is easily resolved within a single nanocrystal. However, the image cannot provide more information about the elemental distribution of these nanocrystals. As a comparison, HAADF-STEM was also used to study the same Pd-Pt core-shell nanocrystals as Figure 1.9 (b). It is obvious that the edges and corners of the nanocrystal show brighter contrast than the central region, which indicates the existence of a heavier element Pt on the shell of the nanocrystal, while the interior is the Pd rich region with relatively lower contrast.

![Figure 1.9. The atomic structure of single Pd-Pt core-shell nanocrystal illustrated by (a) HRTEM and (b) HAADF-STEM images. Scale bar is 2 nm.\textsuperscript{36}](image)

**1.4.2 Analytical Spectroscopy**

The limitations of only using TEM or STEM imaging are apparent since they can solely help to distinguish the distribution of light and heavy elements in nanocrystals but
not able to identify specific elements given that no prior knowledge is available about the composing elements. In order to know the elemental distribution identities and their spatial distribution, analytical spectroscopy techniques are necessarily needed. However, energy dispersive x-ray spectroscopy (EDS) can identify the chemical fingerprints from the characteristic x-ray peaks to offer chemical sensitive information. For example, X. Xia and co-workers\textsuperscript{37} have investigated Pd-Pt core-shell nanocrystals using the HAADF-STEM image, and the EDS mapping image is shown in Figure 1.10. Figure 1.10 (a) shows distinct contrast from Pt on the shell and Pd at the center of the nanocrystal, while the EDS mapping clearly approves the chemical identities of Pd and Pt elements on the core and shell elemental of the nanocrystal, respectively.

Figure 1.10. characterization of a single Pd-Pt core-shell nanocrystal by STEM-EDS. (a) HAADF-STEM image and electron diffraction pattern recorded from the Pd-Pt core-shell nanocrystal; (b) EDS mapping of the same nanocrystal.\textsuperscript{37}
Electron energy-loss spectrometers (EELS) is another effective method to identify elemental identity and distribution in nanocrystals. In contrast to EDS, EELS use the energy loss of inelastically scattered electrons from the transmitted incident electron beam, which provides characteristic energy-loss edges corresponding to the ionization energies of the probed atoms. Therefore, EELS can identify not only elemental identify but also their chemical valence states and electronic structure. Besides, EELS outperforms EDS for analyzing the light elements.\textsuperscript{35} For example, M. Rossell and co-workers\textsuperscript{38} investigated Ba\textsubscript{0.03}Sr\textsubscript{0.97}TiO\textsubscript{3} nanocrystals and mapped the atomic-resolution elemental distribution by the STEM-EELS, as shown in Figure 1.11.

Figure 1.11. STEM image of a single Ba\textsubscript{0.03}Sr\textsubscript{0.97}TiO\textsubscript{3} nanocrystal along with the STEM-EELS mapping of Ti (green), Sr (blue), and Ba (red) elements.\textsuperscript{38}
1.4.3 In Situ TEM

Unlike traditional TEM, in situ TEM is a novel method to study dynamic structural evolution in different conditions, which can give enable a powerful way to characterize the real-time changes in materials. For example, M. Gocyla et al.\textsuperscript{39} have investigated the structure and morphological changes as well as the transformation mechanism of PtNi\textsubscript{x} octahedral nanocrystals using in situ TEM at heating conditions. As shown in Figure 1.12, the morphology of an individual PtNi\textsubscript{1.5} nanocrystal is changed from the octahedron shape at the beginning of the in situ heating experiment to spherical shape after heating to 500°C.

![HRTEM image series of PtNi\textsubscript{1.5} nanocrystal showing obvious structural evolution upon in situ heating from 50°C to 500°C.\textsuperscript{39}](image)

Figure 1.12. HRTEM image series of PtNi\textsubscript{1.5} nanocrystal showing obvious structural evolution upon in situ heating from 50°C to 500°C.\textsuperscript{39}

As demonstrated in this section, TEM based imaging and spectroscopy methods are powerful to characterize the structure, morphology, and chemistry of bimetallic nanocrystals to be studied in this thesis. We will have to select the most suitable method according to specific samples and scenarios.
1.5 Research Scope and Objectives

In this thesis, we will focus on the synthesis and characterization of bimetallic nanocrystals made from transition metals. More specifically, the focused system is Ni-Co bimetallic nanocrystals. We choose the thermal decomposition method to synthesize monodisperse bimetallic Ni-Co nanocrystals with uniform shape and size through systematic control of multiple synthetic parameters, such as reaction time, reaction temperature, the concentration of precursor, and addition of surfactant. We will use TEM-based techniques to characterize the morphology, structure, and chemical composition of synthesized nanocrystals at different conditions. The overarching objective is to understand the fundamental growth mechanism of bimetallic Ni-Co nanocrystals, which can further guide the rational design and controlled synthesis of bimetallic nanocrystals in a broader range.
As mentioned in Chapter 1, this research focuses on the study of synthesis of monodisperse bimetallic nanocrystals. This chapter will discuss the experimental methods and procedures, including the synthesis and characterization of bimetallic nanocrystals. Specifically, the first part of this chapter describes the synthesis of nanocrystals, including the synthesis approach, the selection of surfactant, and the experimental setup, procedures, and parameters used for the synthetic experiments. The second part of this chapter describes the characterization of synthesized nanocrystals using various electron and x-ray based techniques. The equipment, technical specifications, and experimental setup and parameters used in this study are given in details as well.

2.1 Synthesis of Bimetallic Ni-Co Nanocrystals

2.1.1 Synthesis Approach

Many approaches have been developed to synthesize bimetallic nanocrystals, especially the wet-chemical routes, such as thermal decomposition (including hot-injection, and heating-up), polyol process, hydrothermal, electrochemical reductions, and sol-gel technique. In this work, our synthetic procedure employs thermal decomposition because it is convenient and controllable. Long-chain primary alkylamine, such as oleylamine, acts as both a solvent and a reduction agent at elevated temperatures. Furthermore, during the reaction procedure, we can add different surfactants.
into the solution to control shape, size, and dispersion. The entire reactions are carried out under the Ar atmosphere.

### 2.1.2 Selection of Surfactant

For general purposes, surfactants are very common in nanocrystal synthesis. For example, S. Choi and co-workers used W(CO)$_6$ in PtNi synthesis in order to get octahedral nanocrystals.$^{44}$ In a typical thermal decomposition synthesis of Ni-Co nanocrystals, Ni (II) and Co (II) precursors are reduced at a high temperature from a mixture containing amine or carboxylic acid.$^{45}$ In this case, the synthesis goes through complex reactions due to the uncertainty of intermediates, which makes a controllable synthesis difficult or impossible. It cannot produce monodisperse nanocrystals with a broad range of sizes because of the nature of ligands. Therefore, we need to add a surfactant that can control the nanocrystal growth and its size distribution. In this study, we use trioctylphosphine (TOP) in the synthesis of Ni-Co nanocrystals.

### 2.1.3 Synthesis Setup, Procedures, and Parameters

In this research, we use thermal decomposition approach for synthesis with a series of modified recipes based on several previous studies.$^{18,46}$ The organic chemicals used in this study include oleylamine (OAm, C$_{37}$H$_{75}$N, TCI American, >50% ), oleic acid (OAc, C$_{18}$H$_{34}$O$_2$, Fisher Chemical, 98%), benzyl ether (BE, C$_{14}$H$_{14}$O, Acros Organics, 99%), diethylene glycol dimethyl ether (DE, C$_{10}$H$_{20}$O, Acros Organics, 99%), and octadecene (C$_{12}$H$_{24}$, Acros Organics, 90%). The surfactants are trioctylphosphine (TOP, C$_{24}$H$_{51}$P,
Acros Organics, 96%) and tungsten hexacarbonyl (W(CO)₆, Acros Organics, 99%). The precursors are nickel acetylacetonate (Ni(acac)₂, C₁₀H₁₄NiO₄, Acros Organics, 96%) and cobalt acetylacetonate (Co(acac)₂, C₁₀H₁₄CoO₄, Acros Organics, 96%). In a typical synthesis procedure, metal precursors, organic solvents, reduction agents and surfactant were mixed and put into a three-neck flask, which was placed inside a heating mantle. The mixture was heated to an elevated temperature, degassed at 100°C, and then heated to the desired reaction temperature for a specific reaction time. The whole procedure was carried out under Ar atmosphere to avoid any possible oxidation.

The synthesis is carried out in a 100 ml three-neck flask, and a heating mantle is used to heat the flask. The temperature is monitored by a thermometer from the solution within the flask. The mixture is under magnetic stirring with the stirring speed kept constant during the synthesis. After heating, the solution is immediately removed from the mantle and then centrifuged after cooling down to room temperature. The mixture is centrifuged with 3 ml hexane and 12 ml ethanol for several times until the upper layer solution becomes transparent. After centrifugation, the sample is separated from the solution and dried in a vacuum oven in order to remove residual ethanol. Finally, the samples redispersed in hexanes to protect them from oxidation. The experimental setup is shown in Figure 2.1.
We have employed three synthetic routes in this study in order to clarify the effect of reaction time, temperature, surfactant, and concentration on the synthesis of bimetallic Ni-Co nanocrystals. The first route is to use OAm and OAc as reducing agents and surfactant without adding any additional surfactant. The amount of metal precursors, reaction time and temperature are varied in a series of experiments, while the amount of organic solvents is the same. Specific synthetic parameters are shown in Table 2.1.
Table 2.1. Experimental parameters for synthesis of Ni-Co nanocrystals with oleylamine.

<table>
<thead>
<tr>
<th>No.</th>
<th>(\text{Ni(acac)}_2) (mg)</th>
<th>(\text{Co(acac)}_2) (mg)</th>
<th>OAm (ml)</th>
<th>OAc (ml)</th>
<th>DE (ml)</th>
<th>Octadecene (ml)</th>
<th>Reaction Time (min)</th>
<th>Reaction Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>200</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>300</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>400</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>30</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
<td>400</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>60</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>400</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>60</td>
<td>230</td>
</tr>
<tr>
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<td>400</td>
<td>400</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>120</td>
<td>230</td>
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<tr>
<td>7</td>
<td>400</td>
<td>400</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>30</td>
<td>270</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
<td>400</td>
<td>0.7</td>
<td>0.7</td>
<td>5</td>
<td>5</td>
<td>60</td>
<td>270</td>
</tr>
</tbody>
</table>
The second route is to use OAm as the reducing agent with addition of the surfactant TOP. The amount of TOP surfactant and reaction time are varied in a series of experiments, while the amount of metal precursors, organic solvents, and reaction temperature are kept the same. Specific synthetic parameters are shown in Table 2.2.

Table 2.2. Experimental parameters for synthesis of Ni-Co nanocrystals with surfactant TOP

<table>
<thead>
<tr>
<th>No.</th>
<th>Ni(acac)$_2$ (mg)</th>
<th>Co(acac)$_2$ (mg)</th>
<th>OAm (ml)</th>
<th>TOP (ml)</th>
<th>Reaction Time (min)</th>
<th>Reaction Temperature (°C)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>64</td>
<td>10</td>
<td>0</td>
<td>0.5</td>
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</tr>
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<td>2</td>
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<td>64</td>
<td>10</td>
<td>0.8</td>
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<td>230</td>
</tr>
<tr>
<td>3</td>
<td>64</td>
<td>64</td>
<td>10</td>
<td>0.8</td>
<td>2</td>
<td>230</td>
</tr>
<tr>
<td>4</td>
<td>64</td>
<td>64</td>
<td>10</td>
<td>0.8</td>
<td>3</td>
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</tr>
<tr>
<td>5</td>
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<td>64</td>
<td>10</td>
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<tr>
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<td>64</td>
<td>10</td>
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<tr>
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<td>64</td>
<td>10</td>
<td>1.2</td>
<td>2</td>
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<tr>
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<td>64</td>
<td>64</td>
<td>10</td>
<td>1.2</td>
<td>3</td>
<td>230</td>
</tr>
<tr>
<td>9</td>
<td>64</td>
<td>64</td>
<td>10</td>
<td>1.2</td>
<td>4</td>
<td>230</td>
</tr>
</tbody>
</table>
The third route is to use OAm and OAc as reducing agents with addition of the surfactant W(CO)$_6$. The amount of W(CO)$_6$ surfactant and reaction time are varied in a series of experiments, while the amount of metal precursors, organic solvents, and reaction temperature are kept the same. Specific synthetic parameters are shown in Table 2.3.

Table 2.3. Experimental parameters for synthesis of Ni-Co nanocrystals with surfactant W(CO)$_6$

<table>
<thead>
<tr>
<th>No.</th>
<th>Ni(acac)$_2$ (mg)</th>
<th>Co(acac)$_2$ (mg)</th>
<th>OAm (ml)</th>
<th>OAc (ml)</th>
<th>BE (ml)</th>
<th>W(CO)$_6$ (mg)</th>
<th>Reaction Time (min)</th>
<th>Reaction Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>0</td>
<td>60</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>20</td>
<td>2</td>
<td>1</td>
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<tr>
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<td>20</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>60</td>
<td>45</td>
<td>250</td>
</tr>
</tbody>
</table>

2.2 Characterization of Bimetallic Ni-Co Nanocrystals

2.2.1 X-Ray Diffraction

X-ray diffraction (XRD) uses x-rays to characterize the crystal structure and phase composition of a material. The working principle of XRD is shown in Figure 2.2,47 in which x-ray tube generates an x-ray radiation beam which passes through the Soller slits.
The x-ray beam passing through slits strikes the specimen and is further diffracted to form a convergent beam at the receiving slits, and then the detector collects the signal.\textsuperscript{48}

Figure 2.2. Instrument and working principle of XRD: (a) schematic of x-ray diffractometer, (b) theory of X-ray diffraction at the Bragg condition.\textsuperscript{47}

XRD occurs at the condition satisfying the Bragg’s law, which is used to determine the angle of diffraction beam off a sample:

\[ n\lambda = 2dsin\theta \]

where \( n \) is the order of reflection, \( \lambda \) is the wavelength of the incident wave (specifically in this research, we use Cu K\( \alpha \) source with \( \lambda=0.15406 \) nm), \( d \) is the interplanar spacing between the planes of atoms, and \( \theta \) is the glancing angle. Figure 2.2 (b) depicts the x-ray reflection process.\textsuperscript{49} In this research, it is primarily used for identification of phase, composition, and crystallinity. The Rigaku Ultima IV diffractometer was utilized to test samples in the form of powders, which is suitable for our nanocrystal samples. The synthesized samples were placed on a glass plate that does not generate any signal. XRD
was tested from 25° to 80° at a rate of 0.2°/s. We also use samples mixed with standard graphite to calibrate the XRD results.

### 2.2.2 Transmission Electron Microscopy

As mentioned in Chapter 1, TEM is a powerful tool to characterize the nanocrystal samples. In this research, TEM was performed using the Hitachi H9500 TEM with 300 kV acceleration voltage and Hitachi SU9000 STEM with 30 kV accelerating voltage, as shown in Figure 2.3.

In a typical TEM sample preparation, Ni-Co nanocrystals were dispersed in hexane, because the non-polar hexane solvent makes metallic nanocrystals uniformly dispersed. Then, several droplets of the nanocrystal suspension are placed onto a 3 mm diameter, 300 mesh Cu TEM grid. After the hexane completely evaporated, the TEM grid was loaded onto a TEM holder, and then the holder was inserted into the TEM column. Before the observation of samples, the TEM column alignment is needed, which makes TEM generate clear images without much optical aberrations, ensuring the accuracy in determining the crystal structure information. This process includes, but not limited to, checking condenser lens aperture centering, condenser lens stagnation correction, setting eucentric height, voltage center alignment, and objective lens stagnation correction. When all alignments are accomplished, we can begin to take TEM images from the region of interest. Besides the regular imaging, TEM can also operate in the electron diffraction mode. Under this mode, selected area electron diffraction (SAED) patterns can be taken, which is used to determine the crystal structure of the sample.
Scanning TEM (STEM) is another operation mode, which provides additional analytical information about the sample. For example, unlike normal TEM, the high angle annular dark-field (HAADF) STEM provides the contrast proportional to atomic numbers (~Z\(^{1.7}\)), which offers more directly interpretable crystal structure information. In addition, analytical spectroscopy techniques, such as EDS, can be acquired to determine the elemental information of the sample. In this research, we use Hitachi SU9000 STEM, which is convenient to operate in both bright-field and HAADF modes with simultaneous EDS functions.

Figure 2.3. Electron microscopes and material characterization instrumentation. (a) Hitachi H9500 TEM, and (b) Hitachi SU9000 STEM.

Electron diffraction is an indispensable function of TEM and one of the most useful characterization methods for nanocrystals. In a typical SAED pattern, it contains a series
of bright spots, which indicates the crystal structure satisfying the electron diffraction at Bragg conditions. In the cases of polycrystalline diffraction, these bright spots consist of a series of diffraction rings, and the diameter of each ring represents a different interplanar $d$ spacing in nanocrystals. Therefore, we can use SAED to identify the crystal structure and the corresponding phase composition of the sample, which can also be directly compared with XRD results.

For better analysis and comparison, we can perform rotational average to convert a two-dimensional diffraction pattern to a one-dimensional diffraction intensity profile, which contains the equivalent structural information and can be directly compared with the XRD spectrum. The detailed procedures of rotational average are shown in Figure 2.4.50 Firstly, the diffraction pattern intensity is integrated across the full $2\pi$ range along r direction (Figure 2.4 (a)), so a radially averaged intensity profile is drawn, such as shown in Figure 2.4 (b). Then the background can be subtracted using power-law model. Finally, the intensity profile is shown in Figure 2.4 (d), which is similar to XRD spectrum. The whole procedure can be done within the Digital Micrograph software package. In Figure 2.4 (b-d), the horizontal axis represents the reciprocal distance $1/d$, which is directly related to the $d$ spacing. Bragg’s law shows the relationship between $d$ and $\theta$. Therefore, when the horizontal axis can be converted from $1/d$ to $2\theta$, so that the electron diffraction intensity profile can be directly compared with the XRD result.
As introduced in Chapter 1, EDS is a useful analytical technique to reveal the information about chemical composition and elemental distribution using the characteristic x-rays generated by the intershell electron transfer within the sample, as shown in Figure 2.5. The energy-dispersive X-rays indicate fingerprints for identification of specific elements. Hitachi SU9000 STEM equips with an EDS detector to collect simultaneous analytical spectrum along with HAADF-STEM imaging. Therefore, after high-resolution TEM imaging performed on Hitachi H9500, we can also conduct STEM-EDS characterization using Hitachi SU9000 to obtain the correlated chemical composition and elemental mapping from the same sample.
Figure 2.5. Principle of energy dispersive X-ray spectroscopy within a transmission electron microscope.\textsuperscript{52}
CHAPTER THREE
RESULTS AND DISCUSSION

The research of this thesis focuses on the synthesis of bimetallic Ni-Co nanocrystals and the understanding of the underlying crystal growth mechanism through advanced structural and chemical characterizations using transmission electron microscopy (TEM). This chapter begins with discussing the effect of synthetic temperature, reaction time, concentration of precursors and surfactant on the nanocrystal’s morphology and structure. Throughout a series experimental attempts, an optimal set of synthesis parameters was found. With the help of TEM, dynamic morphology evolution of Ni-Co nanocrystals as a function of reaction time was discovered and the associated monodisperse nanocrystal growth through digestive ripening mechanism was also elucidated. The details are described in the following sections.

3.1 Effect of Precursor Concentration, Reaction Time, and Temperature

Our first series of synthesis of monodisperse Ni-Co bimetallic nanocrystals was conducted through thermal decomposition of Ni and Co precursors in oleylamine and oleic acid without additional surfactant, based on the reported recipe by S. Sharma et al.27 The synthetic parameters of our experiments are listed in Table 2.1. First, we investigated the effect of precursor concentration on nanocrystal synthesis by adding different amount of Ni(acac)₂ and Co(acac)₂ of 200 mg, 300 mg, and 400 mg. After 30 min reaction, we only obtained Ni-Co nanocrystals for the synthesis with 400 mg metal precursors, whereas the other two syntheses were not successful. Besides, increasing the reaction time or raising
the reaction temperature did not work. According to the LaMer nucleation mechanism, the nucleation process only starts when the concentration of monomers reaches a critical value. Therefore, our results indicate that 400 mg Ni and Co precursors exceed the critical concentration for successful synthesis of Ni-Co nanocrystals. The synthesized Ni-Co nanocrystals can be successfully centrifuged from solution after the reaction, as shown in Figure 3.1.

![Figure 3.1](image.png)

Figure 3.1. (a) TEM image and (b) SAED pattern of Ni-Co nanocrystals synthesized with 400 mg Ni and Co precursors at 250°C for 30 min.

Second, we investigated the effects of reaction time and temperature on the nanocrystal size and morphology, because the uniform and monodisperse nanocrystals are desired in this thesis. We synthesized Ni-Co nanocrystals using 400 mg metal precursors at temperature of 230°C, 250°C, and 270°C, with various reaction times. Figure 3.2 shows TEM images of Ni-Co nanocrystals synthesized via different reaction times and
temperatures. In Figure 3.3, each row of samples is obtained at the same reaction temperature but increasing reaction time. Comparing the samples with the same reaction temperature, the average size of nanocrystals slightly increases as reaction time extends. Comparing the sample with the same reaction time, the average size increases as reaction temperature increases. In order to get more accurate comparison in size distribution, the quantitative analysis on statistical size distribution analyses have been carried out, as shown in Figure 3.3. The statistical results illustrate the same tendency as observed in TEM images in Figure 3.2, indicating that the average size of nanocrystals increase with the increase of both reaction time and temperature. This trend is more clearly represented in Figure 3.4, which depicts the average size as a function of both time and temperature. However, high temperature synthesis (i.e., 270°C) tends to cause polydisperse size distribution due to the continued nanocrystal growth following the Ostwald ripening (Figure 3.3 (c)). On the other hand, low temperature synthesis (i.e., 230°C) typically leads to more monodisperse size distribution, although much longer time may be required to achieve it. Based on these experiments, we determine that the temperature of 230°C would be a suitable reaction temperature for optimized synthesis of Ni-Co nanocrystals.
Figure 3.2. TEM images of Ni-Co nanocrystals synthesized at various conditions: (a) 230°C, 60 min; (b) 230°C, 120 min; (c) 250°C, 30 min; (d) 250°C, 60 min; (e) 270°C, 30 min; (f) 270°C, 60 min.
Figure 3.3. The statistical analysis of size distribution for the synthesized Ni-Co nanocrystals with various reaction time and temperature: (a) 230°C; (b) 250°C; (c) 270°C.

Figure 3.4. The average size of Ni-Co nanocrystals as a function of both time and temperature, extracted from data shown in Figure 3.3.
3.2 Effect of Surfactant

Another series of synthesis of monodisperse Ni-Co bimetallic nanocrystals was conducted through thermal decomposition approach with addition of different types of surfactants to clarify the effect of surfactant on nanocrystal size and morphology. Oleylamine plays a role of surfactant in thermal decomposition; however, if there are other stronger surfactants existing in the system, oleylamine will no longer be the main factor.\textsuperscript{17} In nanocrystal synthesis, trioctylphosphine (TOP) can effective control size of nanocrystal, because TOP has a specific structure where P group binding with Ni and Co surface sites forms a layer that inhibits nanocrystal growth and protects nanocrystals from agglomerating, so that small and monodisperse Ni-Co bimetallic nanocrystals would form.\textsuperscript{45} In addition, W(CO)\textsubscript{6} is extensive used in octahedral nanocrystals synthesis, because when W(CO)\textsubscript{6} is heated, it will decompose and release CO gas, which not only provides a reducing atmosphere but also inhibits crystal growth. Therefore, we selected TOP and W(CO)\textsubscript{6} to investigate the effect of different surfactants on nanocrystal synthesis.\textsuperscript{44} Figure 3.5 (a–c) shows the typical TEM images of Ni-Co nanocrystals which were synthesized in at 230\degree C for 30min with oleylamine, with surfactant TOP, and with surfactant W(CO)\textsubscript{6}, respectively. As seen from Figure 3.5 (a), it is easy to know that without adding surfactant, the nanocrystals will continue growing and result in an irregular shape and very broad size distribution. Figure 3.5 (b) shows that the nanocrystals have a regular-shaped morphology and exhibit a much narrower size distribution, when TOP was added during synthesis. Figure 3.5 (c) shows the Ni-Co nanocrystals with addition of W(CO)\textsubscript{6} during synthesis. Comparing with Figure 3.5 (a) without any surfactant, the nanocrystal size and morphology
are more uniform in Figure 3.5 (c), suggesting that the surfactant W(CO)₆ is also useful to control nanocrystal growth. However, the size of Ni-Co nanocrystals is relatively larger than those synthesized with TOP, and the size distribution also less monodisperse. The results suggest that TOP is the most suitable surfactant to control the size and morphology of Ni-Co nanocrystals in our designated synthetic approach.

Figure 3.5. TEM images of Ni-Co nanocrystals synthesized at 230°C (a) with oleylamine, (b) with surfactant TOP, and (c) with surfactant W(CO)₆.

3.3 Dynamic Evolution of Structure, Morphology, and Phase

Previous research and this current study have both shown that TOP is a powerful surfactant to control the size and morphology of Ni-Co bimetallic nanocrystals. In this section, we will investigate the dynamic evolution of structure, morphology, and phase during nanocrystal growth as a function of time and the influence of concentration of TOP on this process. The amount of TOP surfactant and reaction time are varied in a series of experiments, while the amount of metal precursors, organic solvents, and reaction temperature are kept the same. The TEM images of Ni-Co nanocrystals synthesized with 0.8 ml or 1.2 ml TOP after 1 h, 2h, 3h, and 4h are shown in Figure 3.6, and the
corresponding experimental parameters are shown in Table 2.2. It is found that TOP has played an important role to induce quite significant changes in the resulting nanocrystals. Firstly, when no TOP was added into the solution (Figure 3.5 (a)), the reaction speed is very fast. After 30 minutes, all precursors were used up and the nanocrystal size was large. But when TOP was included in the thermal decomposition reaction, the speed of reaction was slowed down. Even after reacting for 1 h, the sample was still in the intermediate state where only ultrafine nanoclusters were formed in the solution. As reaction time increases, these nanoclusters start to merge and grow into nanocrystals with finite size and irregular shape after 2 h reaction (Figure 3.6 (b) and (f)). Further, the nanocrystals would transform their morphologies into more regular shapes (such as after 3 h reaction shown in Figure 3.6 (c) and (g)), and then gradually lead to more homogeneous side distribution (such as after 4 h reaction shown in Figure 3.6 (d) and (h)). This reaction procedure is suggested to follow the digestive ripening mechanism. It is also found that adding TOP also has obvious effect on the size of nanocrystals. With the help of TOP, nanocrystal size is much smaller than those without TOP, while increasing the concentration of TOP from 0.8 ml (Figure 3.6 left-hand column) to 1.2 ml (Figure 3.6 right-hand column) result in a decrease in the size of Ni-Co nanocrystals, as well as a slight change in the nanocrystal shape. We have reproductively observed that in presence of higher concentration of TOP, the nanocrystals are devoid of well-defined facets and become almost completely spherical (Figure 3.6 (h)). The influence of the reaction time and surfactant concentration are believed to depend on the ligand-nanocrystal interaction, such as that between TOP and Ni-Co, and it is evident that addition of such new ligands may change original ripening mechanism.
Figure 3.6. TEM images of Ni-Co nanocrystals synthesized at various conditions: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h with 0.8 ml TOP; (e) 1 h, (f) 2 h, (g) 3 h, (h) 4 h with 1.2 ml TOP.
In order to accurately analyze the size distribution as a function of reaction time, the quantitative analysis of nanocrystal size distribution was carried out for the images displayed in Figure 3.6. With the help of ImageJ software, it is convenient to separate individual nanocrystals and measure the size of each nanocrystal. With the measurement of numerous nanocrystals, the statistical information including the average size and the standard deviation can be obtained, as shown in Figure 3.7. For the synthesis with 0.8 ml TOP (Figure 3.7 (a)), the average nanocrystal size is gradually decreased from 13.71±2.85 nm at 2 h to 11.54±1.49 nm at 3 h and then to 10.59±1.42 nm at 4 h. Meanwhile, the size distribution also becomes narrower as indicated by the smaller standard deviations. For the synthesis with 1.2 ml TOP (Figure 3.7 (b)), the statistical data also shows the same changing trend in the evolution of size and size distribution, i.e., as reaction time increases, the average size gradually decreases, and the size distribution become narrower. The statistical data also confirms that the growth of Ni-Co nanocrystals in this synthesis follows the digestive ripening, because the larger nanocrystals become small while the smaller one grow larger to reach eventually the homogeneous size distribution. The side-by-side comparison of statistical nanocrystal size distribution as a function of time between different TOP concentrations shown in Figure 3.8 also draws the conclusion that the size of nanocrystals synthesized with higher concentration of TOP is smaller than that with lower TOP concentration, both of which cause the slight decrease in the size of nanocrystals at prolonged reaction time, following the digestive ripening mechanism.
Figure 3.7. The statistical analysis of size distribution for the synthesized Ni-Co nanocrystals after various reaction time with different surfactant concentration of (a) 0.8 ml TOP, and (b) 1.2 ml TOP.

Figure 3.8. The size distribution of Ni-Co nanocrystals as a function of reaction time with different concentrations of TOP. The data is obtained from Figure 3.7.
X-ray diffraction (XRD) is an essential method to identify the phase composition of crystalline materials. We also used XRD to examine the phase composition of the synthesized Ni-Co nanocrystals, as shown in Figure 3.9. After carefully calibrating using the standard graphite as a calibration reference, as shown in Figure 3.9 (b) and indexing the XRD pattern of the synthesized sample, the characteristic peak positions were found to be deviated from the sole FCC Ni-Co alloy phase, indicating that other unexpected compound phases may exist in the sample. These phases are suggested to be Ni-Co phosphides, as shown in Figure 3.9 (a). This presenting issue needs to be further investigated and clarified. Moreover, we also analyzed the average size of nanocrystals using Scherrer equation, which is expressed as

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

where, \(\tau\) is the average size of the ordered domain, \(K\) is a dimensionless shape factor, the shape factor has a typical value of about 0.9, \(\lambda\) is the X-ray wavelength (here we use \(\lambda = 0.154056\) for Cu Kα), \(\beta\) is the line broadening at half the maximum intensity or full width at half maximum (FWHM), and \(\theta\) is the Bragg angle.

From the XRD profile in Figure 3.9 (a), we measured the (111) peak position to be 41.14°, with the corresponding FWHM of 0.840, These values were used to calculate the average size of nanocrystals, which is estimated to be 10.2 nm by Scherrer equation. This result is in a close agreement with the statistical measurement from TEM images (10.59 nm).
Figure 3.9. XRD patterns of (a) Ni-Co nanocrystals synthesized with 0.8 ml TOP after 4 h reaction, and (b) the same Ni-Co sample mixed with standard graphite for calibration.

To confirm the unexpected phase revealed by XRD, we also conducted selected area electron diffraction (SAED) associated with TEM characterization. Figure 3.10 (a) shows a typical SAED pattern obtained by TEM. Following the method introduced in Chapter 2, we carried out the rotational average for the SAED pattern to identify phase composition for the same sample. The diffraction pattern was integrated across the full $2\pi$ range along the $r$ direction (Figure 3.10 (a)), so a radially averaged diffraction intensity profile was drawn, as shown in Figure 3.10 (b). After subtracting the background using the power-law model, the pure diffraction intensity profile was obtained, as shown in Figure 3.10 (c). Further, according to the Bragg’s law, the reciprocal lattice spacing ($d$) can be converted to the Bragg angle $2\theta$ as the horizontal axis, for an easier direct comparison with XRD patterns.
Figure 3.10. Procedures for rotational average of SAED: (a) SAED pattern of the sample synthesized with 0.8 ml TOP and after 4 h reaction; (b) diffraction intensity profile after rotational integration; (c) diffraction intensity profile after background subtraction.

The processed SAED and XRD results were plotted together in Figure 3.11. Both XRD and SAED profiles show the consistent result that the nanocrystals contain Ni-Co phosphides (main peak located at ~41°) in addition to the desired Ni-Co phase (main peak located at ~44°).
Figure 3.11. Comparison of characteristic diffraction peaks in XRD and rotational-averaged SAED, along with standard phases as indexing references.

To further reveal the element distribution in the nanocrystals, we also did elemental mapping using energy dispersive X-ray spectroscopy (EDS) associated with STEM imaging. Figure 3.12 shows the STEM image and the corresponding EDS mapping in the same area. Figure 3.12 (b-d) shows the distribution of Ni, Co, and P elements in the nanocrystals, which clearly proves that all three elements are exited in the sample and that these elements are not distributed homogeneously. In particular, the P map shown in Figure 3.11 (d) indicates that phosphorus likely appears on the surface (or shell) of the
nanocrystals. The mixed elemental map shown in Figure 3.12 (e) provides a direct visualization to show that nanocrystals are heterogeneous in composition.

Figure 3.12. Elemental mapping of nanocrystals synthesized with TOP after 4 h reaction: (a) STEM image; and elemental mapping of (b) Ni, (c) Co, (d) P, and (e) mixed map of the nanocrystals.

Based on all characterizations of XRD, SAED, and EDS, it is evident that two phases exist in the synthesized nanocrystals, i.e., the desired Ni-Co phase and the unexpected (Ni-Co)$_2$P phase. However, the reason for the formation of the phosphide phase is unclear and need further investigation.

### 3.4 Mechanism of Digestive Ripening

In order to further understand the dynamic evolution of morphology and structure during the nanocrystal growth process, especially to clarify when and how the metal
Phosphides are formed in nanocrystals, we carried out the SAED analysis on multiple nanocrystal sample synthesized at various reaction time in the range of 1–4 h, as shown in Figure 3.13.

Figure 3.13. Phase evolution as a function of reaction time revealed by rotational-averaged SAED profiles (left) and the corresponding TEM images (right).

After synthesis for 1 h, the reaction product was a large amount of ultra-small crystalline nanoclusters that were nucleated from the solution but had not transferred into
nanocrystals. At this stage, the intermediate products show pure FCC Ni-Co phase without any phosphides. However, starting from reaction for 2 h, the formation of Ni-Co phosphides has started, along with the formation of nanocrystals with finite size and shape. With further extended reaction time to 3 h and 4 h, the coexistence of both phases continue to remain, which suggests that the formation of phosphides is likely related to the addition of TOP during the nanocrystal growth, since the phosphorus would compound with Ni-Co metals when ligands are attached to the surface of nanocrystals to regulate their shapes.

This unexpected phosphide formation occurred during the nanocrystal growth is not uncommon. Previous studies have pointed out that during reaction process, the TOP will also decompose and be reduced to phosphorus that may react with nanocrystal. Besides, J. R. Shimpi\textsuperscript{31} proposed that in larger nanocrystals, the ligands prefer to attack these large nanocrystals at the defect sites where chemical reactivity is higher than other around regions. Owen\textsuperscript{53} classified the ligand-nanocrystal surface interaction into three types, viz., L, X, and Z. Specifically, amines and phosphines/phosphine oxides interaction with the nanocrystal surface by forming coordinate covalent bonds are categorized as L-type, which is accountable for the synthesis in this research. Based on the prior knowledge and the obtained information from our characterizations, we propose a model to illustrate the nanocrystal growth process and the underlying mechanism for the digestive ripening, as shown in Figure 3.14. This model can explain the formation of Ni-Co nanocrystals as well as the Ni-Co phosphides formed by the reaction with TOP. Although this is a persuasive model that well fit to our observations, further in-depth investigation will be needed to validate this hypothesis.
Figure 3.14. The proposed model of the Ni-Co nanocrystal growth and underlying mechanism of digestive ripening.
4.1 Conclusions

The research in this thesis has investigated the synthesis of monodisperse Ni-Co bimetallic nanocrystals and the structure characterization using TEM-based techniques. In order to get monodisperse Ni-Co bimetallic nanocrystals, various synthetic parameters were studied, including reaction time, reaction temperature, type of surfactants and their concentrations, based on the thermal decomposition method. By careful characterization of the morphology, structure, and chemistry of the obtained nanocrystals using TEM imaging, diffraction, and spectroscopy methods, we have provided a better understanding of the dynamic nanocrystal growth process and the underlying growth mechanism. The key findings are summarized below.

(1) We have found that the size of nanocrystals increases with the increase of reaction temperature, and the nanocrystal growth continues with extended reaction time, indicating that the growth of nanocrystals follows the Ostwald ripening. The experiments indicate that when the reaction temperature is lower than 230°C, the precursor-oleylamine complex monomers may not be decomposed to form Ni-Co nanocrystals, which implies that 230°C would be optimized temperature for controlled synthesis of monodisperse nanocrystals.

(2) We have revealed that the addition of surfactants plays an important role in the control of nanocrystal shape and size. Specifically, trioctyolphosphine (TOP) was
found to be a powerful surfactant for the synthesis of monodisperse Ni-Co bimetallic nanocrystals. With the help of TOP, the growth of nanocrystals follows the digestive ripening mechanism, in which both the size and the size distribution decrease as a function of reaction time, resulting in monodisperse morphology with average size of ~10.59 nm after 4 h reaction. Increasing the concentration of TOP leads to slightly decrease of average size of nanocrystals, i.e., forming ~9.31 nm when TOP is increased from 0.8 ml to 1.2 ml.

(3) We have discovered from both XRD and SAED results that the synthesized nanocrystals consist of two coexisted phases, i.e., Ni-Co and (Ni-Co)\(_2\)P. It is suggested that the formation of phosphides is likely related to the addition of TOP during the nanocrystal growth, since the phosphorus would be decomposed and then compound with Ni-Co metals when ligands are attached to the surface of nanocrystals to regulate their shapes during digestive ripening.

4.2 Future Work

Following the current work presented in Chapter 3, we expected to further confirm the detailed information of the phosphide phase and figure out a feasible and effectively way to control and eliminate the formation of the phosphide phase during the nanocrystal growth. Based on our proposed model shown in Figure 3.14, we hypothesize that the control of TOP concentration and reaction temperature will be effective approaches to limit the formation of (Ni-Co)\(_2\)P. We also infer that post-synthesis heat-treatment may also
change the phase composition and structure heterogeneity of the nanocrystals. Therefore, we propose the following plans for the future work.

1. Investigate the detailed chemical information of phosphide phase by using other characterization methods such as Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Investigate the effect of TOP concentration and reaction temperature on the formation of metal phosphide phase.

3. Investigate the morphology and structure evolution as a function of temperature using in situ heating TEM experiments.
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