Hexaniobate Nanopeapods: In Situ Deposition of Magnetic-Noble Metal Nanoparticles inside Preformed Nanoscrolls

Sarah P. Gauthier
University of New Orleans, spgauthi@uno.edu

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Hexaniobate Nanopeapods: In Situ Deposition of Magnetic-Noble Metal Nanoparticles inside Preformed Nanoscrolls

A Thesis

Submitted to the Graduate Faculty of the University of New Orleans in partial fulfillment of the requirements for the degree of

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by

Sarah Gauthier

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To My Family, Friends, and Colleagues
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An *in situ* deposition procedure was developed for the nanopeapod (NPP) formation of NiAu nanoparticles inside preformed acid-exchanged hexaniobate nanoscrolls (HNB). Metal salt precursors of Ni(acac)$_2$ and HAuCl$_4$·3H$_2$O were reduced in solution under mild synthetic conditions in the presence of the preformed acid-exchanged hexaniobate nanoscrolls. Two of the surfactants used for the formation of the nanoparticles were oleylamine and triphenylphosphine oxide (TTPO). Reaction conditions were studied and modified to produce well-defined NiAu@HNB NPP systems, with monodispersed particles evenly filling and orienting within the nanoscrolls. The synthetic parameters studied were both time and temperature, with the most well-defined peapod systems being those produced from lower temperatures (100°C) and longer reaction times (60 minutes). NiAu@HNB NPPs synthesized under these conditions yielded a narrow size distribution of NiAu nanoparticles, ranging ~ 4 – 10 nm in diameter, evenly filled and oriented within the inner diameter of hexaniobate nanoscrolls (ranging ~2 μm in length).

**Keywords:** Nanoscrolls, Hexaniobate, Nanopeapods, Ni-Au, In-Situ Deposition
Chapter 1

Introduction

1.1 Nanomaterial Fundamentals: Dimensional Growth

Throughout the scope of chemical applications and study, the class of nanomaterials is a substantial field that is ever developing. In nanomaterials alone, there are basic categories which define the nano-sized material itself. Most commonly, nanomaterials are defined by dimensionality in which the component is made, as shown in Figure 1.1. Spheres, clusters, and particles are 0D, where these grow as point-like structures. Rods, fibers, wires, scrolls, and tubes, which grow along one dimension such as length, are 1D materials. Upon adding another dimension of growth, like that of films, multilayers, plates, or sheets, the material becomes 2D. Lastly, nanomaterials consisting of multiple axes growth such as cubes, flowers and other polycrystals are considered 3D [1].

Figure 1.1: Dimensional Categories of Nanomaterials. A. Growth as point-like structures (0D); B. one axis of growth such as rods, fibers, wires, scrolls, and tubes (1D); C. two axes of growth such as films, multilayers, and plates (2D); and D. three axes of growth such as cubes (3D).
1.2 Nanoparticles: Structural Characteristics

Nanoparticles themselves are considered 0D materials, in that the growth of the particles occurs from a point-like origin and continues outward in all directions. Nanoparticle (NP) is defined as a particle of any shape with dimensions of $10^{-9} - 10^{-7}$ m. NPs behave as a whole unit, thereby possessing novel physical characteristics when compared to the bulk material [2]. Physical properties of NPs are related to the composition and morphology of the structure, but some of the foremost properties include unusual electron transport, enhanced quantum yields, functionalization capabilities, and stronger magnetic response in some materials. These properties are most often a result of the large surface area of exposed atoms relative to the volume of the material. Commonly synthesized NPs include metal chalcogenides, transition metals, metal oxides, and noble metals, to name a few. By combining various classes of NPs, synergistic properties can be realized and used in a wide variety of applications, from biomedical practice, to optical and electronic fields, to environmental and industrial uses.

Synthetic strategies for NPs are divided into two categories, like all nanomaterials: the top-down method and the bottom-up method. In the top-down method, particles are formed by the breakdown of bulk material. Top-down techniques include ball milling, sonication, and other break-down methods. While these syntheses offer the benefit of bulk processing for nanomaterial formation, the resulting particles are typically unevenly distributed in size and shape.

Bottom-up approaches build NPs from the atomic level upwards. This allows for more control over size, shape, and morphology, although the yield can often be relatively
low. Bottom-up approaches to NP synthesis are subdivided into liquid-phase and gas-phase. The most common liquid-phase methods include many different strategies, such as: reduction, hydrothermal/solvothermal synthesis, precipitation, co-precipitation, sol-gel processing, microwave synthesis, sonochemical synthesis, and electrochemical template-assisted synthesis. Whereas gas-phase methods include chemical vapor deposition, precursor evaporation and pyrolysis, laser-induced evaporation and pyrolysis, thermal and microwave plasma, sputtering, laser ablation, and droplet evaporation and explosion [3]. The growth mechanism for liquid-phase synthesized NPs is based on the nucleation of the solid nanomaterial in solution. Typically, a precursor is reduced or decomposed in solution to yield zero-valent atoms. Nucleation is the point at which these atoms are at the minimum concentration for supersaturation, and they then begin to self-accumulate into small clusters. The point of supersaturation is essentially the driving force for nucleation to begin. Further growth from zero-valent atoms on this nucleation site yields the formation of particles, which can occur through Ostwald ripening or by oriented attachment [4].

Figure 1.2: Nanoparticle Nucleation. A. Generation of zero-valent atoms reaches supersaturation; B. after which self-assembly of atoms into small clusters (nucleation) occurs; and C. continued growth on nucleation site leads to particle formation.
Figure 1.2 describes the process of NP nucleation and growth. After nucleation, growth of the NPs can occur through Ostwald ripening or by oriented attachment. In the case of Ostwald ripening, the mechanism for crystal coarsening has been described in terms of growth of large particles at the expense of smaller particles. Ostwald ripening typically occurs when supersaturation is low. Alternatively, oriented attachment is considered the self-organization of particles with a common crystallographic orientation, thereby eliminating two high-energy surfaces by crystallographic fusion [5]. The characterization methods employed for synthesized NPs vary based on the material's composition, which itself can differ widely according to desired needs. Most of the significant methods used are those that analyze size, morphology, and topography; elemental composition; optical, electronic, and magnetic properties; crystal structure and even thermal stability, to name a few. A schematic for NP characterization is shown in Figure 1.3.

**Figure 1.3: Nanoparticle Characterization.** NPs can be characterized based on A. concentration, B. size and morphology, C. crystal structure, D. elemental composition, E. thermal stability, F. magnetic properties, G. electronic properties, and H. optical properties, respectively.
Conventional microscopy techniques which measure NP size and morphology are transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Furthermore, Raman, UV-Vis, X-ray photoelectron (XPS), and elemental dispersive (EDS) spectroscopy are all spectroscopic methods used for compositional and quantitative measures. Dynamic light scattering (DLS) is used to measure optical scattering properties; cyclic and linear sweep voltammetry are used to analyze electronic properties; thermal stability of the particles is measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC); and vibrating sample magnetometer (VSM) and superconducting quantum interference device (SQUID) are employed for studies of magnetic properties [6]. However it should be noted that this list is not a limit of characterization methods used for NP analysis.

1.3 Nanoscrolls versus Nanotubes: Rolling Up Layered Materials

In the category of 3D nanomaterials, both scrolls and tubes have distinct morphologies that allow for unique properties. Particularly, a nanoscroll (NSc) is a continuous roll of a lamellar structure; on the other hand, a nanotube (NT) is an enclosed hollow cylinder of a layered material. Like scrolls, tubes can be multi-walled in structure, as depicted in Figure 1.4.
Many different layered materials form NScs and NTs, such as graphene, carbon, carbon nitride, hexagonal boron nitride, TiO$_2$, V$_2$O$_5$, some layered perovskite types, and many more; furthermore, it could be assumed that under precise conditions, any lamellar structure should be capable of producing scrolls or tubes [7].

The physical properties of NScs and NTs include high surface area, functionalization capabilities, tailored growth, electronic conductivity, and protective sheathing for encapsulation of other nanomaterials. With these physical qualities, the applications of NScs and NTs varies widely across many categories – from electronics, optoelectronics, magnetic data storage, sensors, biomedical drug delivery systems, to solar energy and environmental remediation [8, 9].

Synthetic strategies for NScs and NTs are again divided into the two categories of top-down methods and bottom-up methods. In top-down methods, scrolls and tubes are most often synthesized by exfoliation, cleavage, and / or intercalation of lamellar structures. Additionally, sonication and laser thinning are also used to pry apart layered materials for the formation of sheets, tubes, and scrolls. Bottom-up approaches, which are
not as commonly utilized, include solution phase growth, chemical vapor deposition, and electron beam lithography. While not typically employed, these approaches may afford more control over the morphology and topography of sheets, tubes, and scrolls. Figure 1.5 illustrates the top-down synthetic approach for NScs and NTs [10].

**Figure 1.5: Top-down Exfoliation Method for Nanoscroll Formation.**

A. Layered material is exfoliated into individual sheets, which scroll under appropriate conditions in order to reduce mechanical strain, producing C. nanoscrolls and nanotubes.

After formation of NScs and NTs, common characterization techniques used are TEM, SEM, and AFM for determination of morphology and topography, XRD for crystal structure analysis, and Raman spectroscopy, UV-Vis spectroscopy, XPS, and EDS for composition and quantitative measures [10].

**1.4 Nanopeapod Formation: Inclusion of Nanoparticles within Nanoscrolls**

Due to the enclosed nature of NScs, they can provide sheathing and support for other nanomaterials, such as quantum dots, particles, or even wires and rods. Additionally, the inclusion of NPs offers additional physical properties and molecular functionalities [11]. The architectural combination of NPs inside of a NSc is known as a nanopeapod (NPP). This ordered arrangement can provide both mechanical and chemical stability while fostering NP and NSc interactions. The cooperative properties of the NPP is a result of the geometric assembly of the building units in addition to the intrinsic properties of each component [11]. The designed interface between the different components can produce novel features and properties, such as unusual electron transport, improved quantum yields, functionalization capabilities, and even stronger magnetic response in some materials [11].
As such, the geometry of the NPP composite structure affords numerous fundamental and practical applications in catalytic processes [12], magnetic data storage [13], optical devices, sensors [14], and templates [15] for other assemblies.

Previous syntheses for the preparation of NPPs have included microwave reactions [16], pulsed electrodeposition in combination with solid state reaction [17], pulsed liquid-injection with chemical vapor deposition [18], vapor–liquid–solid growth [19], Rayleigh-instability induced encapsulation via atomic layer deposition [20], wet-chemical method by selective etching [21], electrodeposition inside preformed nanotubes [22], Galvanic displacement of electrodeposited multi-segmented nanowires [23], and sacrificial template route [24].

While these synthetic approaches for NPPs are effective in terms of morphological control, phase purity, and crystallinity, combining NPs within NScs in a well-defined manner is not always clear-cut [11]. Difficulties remain in the synthetic strategies for precise control over NPPs with monodisperse particles evenly filling and orienting within the scrolls. Additionally, some of these previously listed methods can be costly, tedious, and not easily employed in bulk synthesis.

Other methods such as encapsulation and in situ deposition, as previously reported by our group [11, 15, 26, 27], allow for more precise control in the synthesis of NPPs. In the encapsulation method, the lamellar structure is pulled apart (exfoliated) into sheets and scrolled while in the presence of preformed NPs. This allows for the capture of the NPs into the rolled interior of the NSc. Alternatively, in situ deposition involves the solution-phase deposition of NPs inside preformed NScs. The in situ method also produces NPs in the inner
diameter of NScs. Figure 1.6 shows both mechanisms for the encapsulation and *in situ* deposition methods for the synthesis of NPPs.

**Figure 1.6: Comparison of In-Situ Deposition and Encapsulation Methods for Nanopeapod Formation.**

A. Encapsulation method exfoliates lamellar structure and scrolls while in the presence of preformed NPs; B. *In situ* deposition method employs solution-phase deposition of NPs inside preformed NScs.

Building on previous methods reported by our group [11, 15, 26, 27], a facile and mild protocol for the synthesis of NPP composites was developed using an *in situ* deposition method. During this wet synthesis, preformed hexaniobate (HNB) NScs were treated with metal salt precursors of Ni and Au; subsequently the precursors were reduced in solution under mild synthetic conditions in the presence of oleylamine and triphenylphosphine oxide to form NPP systems.

The objective in synthesizing ferromagnetic and noble metal composite NPs inside preformed HNB NScs was to obtain well-defined and monodisperse nanocomposites. Another overlying goal behind the development of this method is that essentially if any
reduction method of NPs can be grown in solution, HNB NScs could serve as a template for chain growth of said NPs to form NPPs. The realization of this goal can lead to the combination of many different compounds, where the properties of the nanomaterials can be tailored to suit desired requirements.

Reaction conditions were studied and modified to produce well-defined NiAu@HNB NPP systems, with monodispersed particles evenly filling and orienting within the NScs. The synthetic parameters studied were both time and temperature, with the most well-defined peapod systems being those produced from lower temperatures (100°C) and longer reaction times (60 minutes).
1.5 References:


Chapter 2

Synthesis of Ni-Au@HNB NPPs: In Situ Deposition in Preformed Nanoscrolls

2.1 Introduction

In situ growth methods have been established in our group for the fabrication of NPPs with pure gold NPs deposited in preformed HNB NScs [4]. There is also an interest in preparing materials by this approach that exhibit magnetic properties. The objective was then to fabricate ferromagnetic and noble metal composite NPs inside preformed HNB NScs. Such materials would be of interest in applications as anisotropic magnetic components [9], photocatalytic composites [8], and possibly as biomedical devices [10]. Herein methods for the fabrication of NiAu@HNB NPP with well-defined NPs are presented.

2.2 Experimental

2.2.1 Solid State Synthesis of K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17}

Potassium hexaniobate was synthesized according to the procedure as reported previously by our group [1]. K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17} was synthesized by the solid state reaction of K\textsubscript{2}CO\textsubscript{3} and Nb\textsubscript{2}O\textsubscript{5}, in the molar ratio of 1.0:1.4. The starting materials were ground and pre-heated together in an alumina crucible at 900°C for 1 hour, after which the reaction was ground again intermittently. The reaction was then heated again at 1050°C for 48 hours. The resultant white powder of K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17} was washed multiple times with DI water and ethanol, and it was allowed to dry overnight in an oven at 75°C. The crystal structure of K\textsubscript{4}Nb\textsubscript{6}O\textsubscript{17} was then characterized by powder X-ray diffraction (XRD).
2.2.2 Hydrothermal Synthesis of $H_xK_{4-x}Nb_6O_{17}$

Acid-exchanged $K_4Nb_6O_{17}$ ($H_3K_{4-x}Nb_6O_{17}$) was obtained by treating 1.0 g of $K_4Nb_6O_{17}$ with 8 mL HNO$_3$ (6M). The solution was placed in a Teflon liner inside of a stainless-steel autoclave, which was heated at 80°C for 2 days. The product was washed multiple times with DI water and ethanol, and it was allowed to dry overnight in an oven at 75°C. The crystal structure of $H_xK_{4-x}Nb_6O_{17}$ was then characterized by XRD.

2.2.3 Solvothermal Synthesis of Multi-Walled Nanoscrolls (NScs)

Hexaniobate nanoscrolls (HNB NScs) were synthesized by a method as reported previously by our group [2]. First, 0.1g of $H_xK_{4-x}Nb_6O_{17}$ was added to 0.15 g (0.19 mmol) TBAOH, 5 mL oleylamine (~15 mmol), and 8 mL toluene. The solution mixture was allowed to stir magnetically for 1 hour in a Teflon liner, which was then transferred to a stainless-steel autoclave. The autoclave was heated at 220°C for 6 hours, and then it was allowed to cool to room temperature. The product of HNB NScs was washed with ethanol several times, and it was allowed to dry overnight in an oven at 75°C. The dried sample was then characterized by XRD.

2.2.4 In Situ Deposition of NiAu@HNB Nanopeapods (NPPs)

The nanopeapods were synthesized through the *in situ* deposition of Ni and Au precursors in preformed hexaniobate nanoscrolls, by methods adapted from the literature [3, 4]. First, 0.128 g (0.5 mmol) of Ni(acac)$_2$ and 0.083 g (0.3 mmol) of triphenylphosphine oxide were dissolved in 7mL of oleylamine by stirring the mixture at 45°C. The resulting Ni mixture produced a viscous green solution that became less opaque upon dissolution.
Meanwhile, 0.059 g of HAuCl₄·3H₂O (0.15 mmol) and 0.1 g of HNB NScs were dissolved in 2 mL benzyl ether, 2 mL hexanes, and 8 mL ethanol. This Au-HNB mixture was added to the pre-heated Ni solution to form a yellow/brown solution. The entire reaction was stirred vigorously with a magnetic stir bar, and it was heated under various reaction parameters, as given in Table 2.1.

Upon heating the solution, the mixture turned deep violet in color. After reaction, the mixture was allowed to cool to room temperature. The resulting solution was centrifuged 3 times with ethanol for 5 minutes at 6000 rpm to remove excess solvents, free nanoparticles, and unreacted components. The precipitate appeared as a deep violet powder, and it was kept damp with minimal EtOH for storage and further characterization. The NiAu@HNB product was then characterized for its crystal structure by XRD. The morphology of the nanopeapod sample was analyzed using transmission electron microscopy (TEM), while the elemental composition was determined using energy dispersive spectroscopy (EDS).

### 2.3 Characterization of Ni-Au@HNB NPPs

XRD measurements were collected using a Philips X'Pert X-ray diffractometer with monochromatized Cu Kα radiation, with an accelerating voltage and current of 40 kV and
40 mA. The morphology of the nanopeapods was analyzed using a JEOL 2010 TEM at an accelerating voltage of 200kV, equipped with a Gatan CCD camera. EDAX Genesis EDS (used concurrently with TEM) was used to measure the elemental composition of the samples.

2.4 Results

2.4.1 Synthesis of $K_4Nb_6O_{17}$ and $H_xK_{4-x}Nb_6O_{17}$

Potassium hexaniobate was synthesized through a solid state reaction by the grinding of $K_2CO_3$ and $Nb_2O_5$ (molar ratio of 1.0 to 1.4), followed by pre-heating at 900°C for 1 hour. The reaction mixture was then intermediately ground, and replaced in the furnace at 1050°C for 48 hours. The white powder of $K_4Nb_6O_{17}$ was allowed to cool to room temperature. It was washed with DI water and ethanol in order to remove any unreacted materials, and it was then allowed to dry overnight in a drying oven (75°C). The product was characterized by XRD, as given below in Figure 2.1a. The prominent (040) reflection of $K_4Nb_6O_{17}$ appeared at 9.5° two theta, while characteristic reflections of (220) at 23.2°, (002) at 27.8°, (0 10 0) at 31.8°, and (400) at 46.6° are also seen. Weaker reflections of (0k0) appeared, with (020) at 4.8° and (060) at 14.3° 2theta.
Once $K_4Nb_6O_{17}$ was characterized, 1 g of the material was treated hydrothermally with 8 mL $HNO_3$ (6M) in a Teflon-lined Parr bomb at 80°C for 48 hours. The acid-exchanged product of $H_xK_{4-x}Nb_6O_{17}$ was washed with DI water and ethanol to remove excess acid, and it was allowed to dry overnight. The degree of acid-exchange was characterized by XRD, as given below in Figure 2.1b. The (040) reflection shifted from 9.5° to 11.1° for $H_xK_{4-x}Nb_6O_{17}$, indicating the partial exchange of $H_3O^+$ in place of $K^+$ cations.

### 2.4.2 Synthesis of Hexaniobate Nanoscrolls

With the successful acid-exchange of hexaniobate, nanoscrolls were synthesized by a solvothermal method as described earlier by our group [2]. Initially 0.1 g of $H_xK_{4-x}Nb_6O_{17}$ was mixed with 0.15 g TBAOH (0.19 mmol), 5 mL oleylamine (~15mmol), and 8 mL...
toluene. The reaction was stirred for 1 hour to ensure mixing and dissolution, then the reaction was transferred to a Teflon-lined Parr-bomb. The reaction was heated at 220°C for 6 hours, allowed to cool to room temperature, and washed with ethanol. The HNB NScs were then dried overnight, and the product was characterized by XRD as shown in Figure 2.1c. The product was assigned reflections based on previous literature results [5]. The presence of multiple low-angle peaks between 3° – 12° 2theta indicated the scrolled nature of the original \( H_xK_{4-x}Nb_6O_{17} \). These 4 peaks could relate to the (0k0) reflections that are common to the parent compound of \( K_4Nb_6O_{17} \). A broad (040) reflection appeared at \( \sim 9.7° \), which would relate to \( d_{040} = 9.1\text{Å} \). Other broad low-angle reflections are seen at \( \sim 4.7° \) and \( \sim 6.8° \), either of which could possibly relate to the (020) reflection. While another broad low-angle reflection is seen at 11.1°, this reflection may also be related to the (060). A weak (220) reflection is seen at \( \sim 23.2° \), while a sharp reflection of (002) is seen at \( \sim 27.8° \), and the (400) reflection appeared at 46.6° 2theta.

2.4.3 In Situ Deposition of NiAu Nanoparticles in Preformed Hexaniobate Nanoscrolls
The NiAu@HNB NPPs were synthesized under various reaction conditions, as listed in Table 2.1, from a modified literature procedure [3, 4]. NiAu@HNB XRD, shown in Figure 2.2a-d, again showed the low-angle reflections common to $\text{H}_x\text{K}_{4-x}\text{Nb}_6\text{O}_{17}$ NScs; additionally, the measurements also showed the appearance of Au and Ni reflections beginning at $\sim 38.1^\circ$. The peak seen at $38.1^\circ$ relates to Au (111), with a reflection at $44.5^\circ$ equivalent to both Au (200) and Ni (111). However, there is no peak seen for the Ni (200) reflection. It could be inferred at $76.5^\circ$ 2theta that the presence of broad peaks in Synthesis 3 and 4 relate to both Au (311) and Ni (220). XRD data confirms the crystal structure of at least Au metal in the presence of HNB NScs, while supporting the possibility of Ni metal.

Figure 2.2: X-Ray Diffraction Data – NiAu@HNB NPPs. a. Synthesis 1 – 200°C for 30 minutes; b. Synthesis 2 – 175°C for 30 minutes; c. Synthesis 3 – 150°C for 60 minutes; d. Synthesis 4 – 100°C for 60 minutes; e. HNB multi-walled nanoscrolls; f. Ni reference; and g. Au Reference.
After analyzing the crystal structure of the starting materials and the as-synthesized NiAu@HNB NPPs, the morphology and monodispersity of the NPPs were studied using TEM. The resultant micrographs are shown in Figure 2.3. TEM images show the presence of ordered NPs inside the inner diameter of HNB NScs, indicating the in situ deposition of the Ni and Au metals. However some of the synthetic procedures resulted in poor filling of the niobate scrolls with polydispersed particles. From syntheses 1 – 4, nanopeapod synthetic procedures were optimized as a result of the poor filling, large nanoparticle size range, and the condition of the nanoscrolls (as seen in Figure 2.3a-c).

**Figure 2.3: Transmission Electron Microscope Images – NiAu@HNB NPPs.**

- **a.** Synthesis 1 – 200°C for 30 minutes;
- **b.** Synthesis 2 – 175°C for 30 minutes;
- **c.** Synthesis 3 – 150°C for 60 minutes;
- **d.** Synthesis 4 – 100°C for 60 minutes.
With the resulting data from XRD and TEM analyses, the NiAu@HNB NPPs were also analyzed by EDS to ensure elemental composition. The EDS data is given in Figure 2.4, with measurements taken in two separate areas of the sample (NiAu@HNB 1).

**Figure 2.4: Elemental Dispersive Spectroscopy Data – NiAu@HNB NPPs.**

* a. Synthesis 1 – 200°C for 30 minutes, first area of sample; b. Synthesis 1 – 200°C for 30 minutes, second area of sample.

Multiple Ni and Au peaks appeared in both areas of EDS measurements, in addition to Nb, K, and O. Peaks from Cu and Fe are due to Cu grids used for the sample preparation, while carbon is due to surfactant on the surface of the NScs and NPs. Quantitative calculations of both areas in Synthesis 1 are shown in Figure 2.5 and yielded a weight percent ratio of 0.04% Ni to 0.01% Au. EDS confirms the presence of both Ni and Au, as well as Nb, supporting the formation of NiAu@HNB NPPs.
Figure 2.5: Quantitative Elemental Composition – NiAu@HNB NPPs. Quantitative calculations of both areas in Synthesis 1 yielded a weight percent ratio of 0.04% Ni to 0.01% Au.

With characterization methods combined, XRD, TEM, and EDS all support the formation of NiAu@HNB NPPs. XRD data indicates the characteristic crystallinity of the samples. TEM images also lend great insight into the actual morphology of the peapod systems in terms of filling and dispersity from the NPs. Finally EDS confirms the composition of the NPPs.

2.5 Discussion
2.5.1 Synthesis of Hexaniobate

Multi-Walled Nanoscrolls – Crystal Structure Evaluation

Both parent compounds of \( K_4\text{Nb}_6\text{O}_{17} \) and \( H_xK_{4-x}\text{Nb}_6\text{O}_{17} \) were characterized based on X-ray diffractometry. Similarly, the scrolled \( H_xK_{4-x}\text{Nb}_6\text{O}_{17} \) nanosheets were investigated by XRD in order to qualitatively elucidate the changes in crystal structure.

In the initial synthesis of HNB NScs, XRD data in Figure 2.1c shows multiple low angle reflections which are commonly seen in the scrolled layered material of \( H_xK_{4-x}\text{Nb}_6\text{O}_{17} \), as described previously by Hu and coworkers [5]. The presence of multiple low-angle peaks between 3° – 12° 2theta indicated the scrolled nature of the original \( H_xK_{4-x}\text{Nb}_6\text{O}_{17} \), while the high-angle reflections are more characteristic of the parent compound, as shown in Table 2.2. These 4 peaks could relate to the \((0k0)\) reflections that are common to the parent compound of \( K_4\text{Nb}_6\text{O}_{17} \). The most distinctive peak of this compound family is the \((040)\) reflection, typically found in the range of ~9 – 12° 2θ. According to a previous study by Bizeto and Constantino [6], \( d_{020} = 15.8 \text{ Å} \) and \( d_{040} = 8.0 \text{ Å} \) for \( H_xK_{4-x}\text{Nb}_6\text{O}_{17} \). In the first and most intense peak, the position at 4.7° correlates to \( d = 18.8 \text{ Å} \). It is likely that the first peak is the presence of TBA\(^+\) ions with both \( H_3O^+\) and water molecules, which is described in literature [7]. The second peak at 6.8° yields \( d = 13.0 \text{ Å} \), and this is more closely related to the literature value of \( d_{020} = 15.8 \text{ Å} \). A broad \((040)\) reflection appeared at ~9.7°, which would give \( d_{040} = 9.1 \text{ Å} \), similar to \( d_{040} = 8.0 \text{ Å} \) for \( H_xK_{4-x}\text{Nb}_6\text{O}_{17} \). While another broad low-angle reflection is seen at 11.1°, this reflection may also be related to the \((060)\). A weak

<table>
<thead>
<tr>
<th>Position (°2θ)</th>
<th>( hkl ) reflection</th>
<th>( d)-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7</td>
<td>TBA(^+), ( H_3O^+ ), ( H_2O )</td>
<td>18.8</td>
</tr>
<tr>
<td>6.8</td>
<td>(020)</td>
<td>13.0</td>
</tr>
<tr>
<td>9.7</td>
<td>(040)</td>
<td>9.1</td>
</tr>
<tr>
<td>23.2</td>
<td>(220)</td>
<td>3.8</td>
</tr>
<tr>
<td>27.8</td>
<td>(002)</td>
<td>3.2</td>
</tr>
<tr>
<td>46.6</td>
<td>(400)</td>
<td>1.9</td>
</tr>
</tbody>
</table>
(220) reflection is seen at ~23.2°, while a sharp reflection of (002) is seen at ~27.8°, and the (400) reflection appeared at 46.6° 2theta.

Generally, the presence of multiple low-angle reflections can be a qualitative indication that $H_{x}K_{4-x}Nb_{6}O_{17}$ has exfoliated and possibly scrolled. Due to the large amount of modification from the parent compound to the resulting nanoscrolls, XRD data may be difficult to interpret. Additionally, the TBAOH and oleylamine intercalated into the scrolls likely cause lower-angle shifts in the $H_{x}K_{4-x}Nb_{6}O_{17}$ reflections, and may even be presenting their own individual peaks. However, in higher angle reflections, the HNB NScs seem to retain the characteristic reflections of the parent compound $K_{4}Nb_{6}O_{17}$.

### 2.5.2 Modifying In Situ Reaction Conditions – Temperature and Time

An in situ deposition method of noble metal NPs inside preformed HNB NScs was initially reported by our group [4]. Similarly, a procedure for synthesizing NiAu NPs was described by She et al [3]. In combining the two previously reported methods, the synthesis of NiAu@HNB NPPs was developed and fine-tuned to produce well defined and monodisperse nanocomposites. An overlying goal behind the development of this method is that essentially if any reduction method of NPs can be grown in solution, HNB NScs could serve as a template for chain growth of said NPs to form NPPs. The realization of this goal can lead to the combination of many different compounds, where the properties of the nanomaterials can be tailored to suit desired requirements.
In order to complete the goal of HNB NScs as NPP templates in the case of NiAu NPs, fine tuning of synthetic procedures was necessary. Maintaining control over the magnetic-noble metallic NP morphology can be difficult due to the large mismatch of the lattice parameters of Ni and Au [3]. Based on the reaction conditions listed in Table 2.1, heat reduction to 100°C and time increase to 60 minutes, without inert atmosphere, was determined to be the optimal conditions. In general reduction NP syntheses, particle formation is facilitated by inert atmospheres, especially to avoid oxidation of metal precursors. While an inert atmosphere (Ar\textsubscript{(g)}) was used in Syntheses 1 and 2, none was used in Syntheses 3 and 4 due to the more stable nature of both Ni and Au precursors. The synthesis of the NiAu NPs required the preheating of Ni(acac)\textsubscript{2} and TPPO (triphenylphosphine oxide) in oleylamine. The necessity of the preheating can be attributed both to the viscous nature of oleylamine at room temperature and to the formation of small Ni nuclei which facilitates NP growth. With a lowered synthesis temperature and increased reaction time (Synthesis 4), the NPPs produced were more well-defined, with better filling of the HNB NScs and more monodisperse NiAu NPs, as seen in both XRD and TEM data.

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Temperature</th>
<th>Time</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200° C</td>
<td>30 min</td>
<td>Ar\textsubscript{(g)}</td>
</tr>
<tr>
<td>2</td>
<td>175° C</td>
<td>30 min</td>
<td>Ar\textsubscript{(g)}</td>
</tr>
<tr>
<td>3</td>
<td>150° C</td>
<td>60 min</td>
<td>None</td>
</tr>
<tr>
<td>4</td>
<td>100° C</td>
<td>60 min</td>
<td>None</td>
</tr>
</tbody>
</table>
2.5.3 X-Ray Diffraction Analysis – NiAu@HNB NPPs

With the adjustment in synthetic approach across Synthesis 1 – 4, XRD data (Figure 2.2a-d) supports the formation of more well-defined NPP systems. XRD analysis of Synthesis 1 (Figure 2.2a) shows broad peaks with low intensity for Au (111) and Au (200)/Ni (111); while Synthesis 2 (Figure 2.2b) shows a higher intensity for Au (111) and Au (200)/Ni (111) and the appearance of a broad peak for Au (220).

In Synthesis 3 and 4 (Figure 2.2c-d), sharper peaks with higher intensities are seen for all high angle reflections beginning at 28.1° through 80° 2theta. The sharper peaks and higher intensities indicate a more crystalline nature of the NiAu NPs. In all 4 syntheses (Figure 2.2a-d), characteristic low angle reflections are still seen for HNB NScs at 3° – 28° 2theta, supporting the presence of a scrolled lamellar structure.

From Synthesis 1 to Synthesis 4, the decrease in temperature and increase in time facilitates more crystalline and monodispersed NPs and better crystallinity of the HNB NScs.

2.5.4 Transmission Electron Microscopy Imaging – NiAu@HNB NPPs

Images obtained from TEM (Figure 2.3a-d) also supports the formation of more well-defined NPP systems due to the modified synthetic approaches of Synthesis 1 – 4. Synthesis 1 (Figure 2.3a) shows the formation of NiAu@HNB NPPs, with NPs located in the inner diameter of the NScs. However NiAu NP shape ranges from oblong/square to spherical, with large size distributions of ~ 8 – 22 nm. This could be due to the NPs forming too quickly (30 minutes). Sheets of HNB are also seen in Synthesis 1, indicating that the
NSCs may not have been fully preformed before the in situ deposition. The scrolls may have even been affected by the higher temperature (200°C) of the reaction.

Images of Synthesis 2 (Figure 2.3b) evidence poor filling of the scrolls with most particles forming outside of the scrolls. The particles range widely in size, with diameters of ~ 6 – 25 nm; additionally, the HNB scrolls were of various sizes with some curved edges, indicating again poor scroll morphologies, which would have affected filling. The poor filling and wide size distribution of the NPs can also be attributed to the high temperature (175°C) and short time (30 minutes) of the reaction, whereby NPs formed too quickly and unevenly.

In Synthesis 3 (Figure 2.3c), the NPPs are seen with a better filling ratio than Synthesis 2; however, the NPs are not uniformly distributed within the scrolls. A majority of the particles can be seen outside of the HNB NScs, agglomerating together in particular regions. The size of the NPs ranges less drastically, from ~ 5 – 15 nm in diameter. The NScs appear to have a better morphology in the lower temperature (150°C) and increased time (60 minutes) of Synthesis 3, while still showing some irregularities in shape.

Lastly, the NPPs shown from Synthesis 4 (Figure 2.3d) are more uniformly defined and dispersed. While some free NPs are seen outside of the NScs and aggregated in some regions, the majority of the scrolls are filled almost completely with ordered chains of NiAu NPs. The size distribution of the NPs is much narrower than previous syntheses, ranging ~ 4 – 10 nm in diameter. The NScs in general appear in better condition, with more linear morphologies, and evenly spaced inner diameters. Overall, the synthetic parameters of lowered temperature (100°C) and increased time (60 minutes) produced the most
uniformed NiAu@HNB NPPs, as evidenced by TEM images. This supports the indications also given by XRD that across synthetic procedures 1 – 4, more crystalline and monodispersed NPs are formed. This in turn improves the in situ deposition of NiAu NPs within HNB NScs, being more evenly distributed and more narrow in size range.

2.5.5 Elemental Dispersive Spectroscopy – NiAu@HNB NPPs

Used concurrently with TEM, elemental analysis was utilized to confirm the presence of Ni, Au, and Nb in the NiAu@HNB NPPs. EDS data collected from Synthesis 1 is shown in Figure 4; furthermore, two separate areas of the sample were analyzed, given in Figure 4a and 4b. In the first area of Synthesis 1 (Figure 2.4a), elements which appear are: C, O, K, Fe, Ni, Cu, Nb, and Au. The strong peak related to C is likely due to sample preparation and some of the surfactant from the NPPs; furthermore, peaks for both Fe and Cu are due to the grid used to view the sample. The presence of O, K, and Nb are attributed to the HNB NScs; and lastly, a strong peak for Ni at ~1.5 keV and multiple peaks for Au at ~2 (shared with Nb), 10, and 11.5 keV are seen.

Again in the second sample area of Synthesis 1 (Figure 2.4b), the same list of elements is shown. However this portion of the sample shows two clear peaks related to Ni at ~1.5 and 7.5 keV, with only very low intensity Au peaks, ranging from ~9 – 13.5 keV. One intense peak is shared by both Nb and Au (~2 keV), while other low intensity peaks of Nb can be seen past 16 keV. Based on the quantitative data obtained from both areas of EDS measurements shown in Figure 5, the weight percent ratio of Ni to Au is 0.04% to 0.01%. The initial protocol has the Ni to Au precursors in a ratio of 0.5mmol to 0.15 mmol. When considering the in situ deposition, a relative amount of Ni and Au could be lost due to the
formation of free NPs which would be washed off at the end of the synthesis. Considering both areas of measurement, EDS confirms the presence of both Ni and Au, as well as Nb, supporting the formation of NiAu@HNB NPPs, and revealing the basic ratios of Ni to Au formed.

**Conclusions**

An *in situ* deposition procedure was developed for the well-defined nanopeapod (NPP) formation of NiAu nanoparticles inside preformed acid-exchanged hexaniobate nanoscrolls. Metal salt precursors of Ni(acac)$_2$ and HAuCl$_4$·3H$_2$O were reduced in solution under mild synthetic conditions in the presence of the preformed acid-exchanged hexaniobate nanoscrolls. Reaction conditions were studied and modified in order to produce well-defined NiAu@HNB NPP systems, with monodisperse particles evenly filling and orienting within the nanoscrolls. The synthetic parameters studied were both time and temperature, with the most well-defined peapod systems being those produced from lower temperatures (100°C) and longer reaction times (60 minutes).

Overall, NiAu@HNB NPPs synthesized under the listed conditions yielded a more narrow size distribution of NiAu nanoparticles, ranging ~ 4 – 10 nm in diameter, by evenly filling and orienting within the inner diameter of hexaniobate nanoscrolls. The procedural modifications were effective in terms of improving morphological control, phase purity, and crystallinity, respectively. The relative ease of the procedure afforded even filling and orienting of nanoparticles within the scrolls, making this method less tedious and more easily employed in bulk synthesis. The product of NiAu@HNB NPP has many future applications in catalytic processes, magnetic data storage, optical devices, sensors, and templates for other assemblies.
2.7 References:


Vita

Sarah Gauthier was born in New Orleans, La., and she has been a life-long resident of Slidell, La. She obtained a Bachelor of Science in Chemistry from the University of New Orleans in 2012. In order to enrich her knowledge and understanding of the chemical sciences, she continued at the University of New Orleans to pursue a Master’s of Science in Chemistry. As a graduate student, she has held leadership roles in both chemical professional organizations in the Department of Chemistry, the Graduate Chemical Society and Alpha Chi Sigma Professional Chemistry Fraternity. During the Master’s program, she joined Dr. John Wiley’s research group in Summer 2013 in order to pursue a thesis track degree. Her research was focused on studying the nanocomposite structure of various hexaniobate nanopeapods, with the addition of ferromagnetic components.