CHEMICAL SYNTHESIS OF SIZE- AND SHAPE-CONTROLLED INTERMETALIC AND METAL NANOCRYSTALS

A Dissertation in
Chemistry
by
Nam Hawn Chou

© 2009 Nam Hawn Chou

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2009
The Dissertation of Nam Hawn Chou was reviewed and approved* by the following:

Raymond E. Schaak  
Associate Professor of Chemistry  
Dissertation Advisor  
Chair of Committee

Thomas E. Mallouk  
DuPont Professor of Materials Chemistry and Physics

Karl T. Mueller  
Professor of Chemistry

Sridhar Komarneni  
Distinguished Professor of Clay Mineralogy

Ayusman Sen  
Professor of Chemistry  
Head of the Department of Chemistry

*Signatures are on file in the Graduate School
ABSTRACT

The interest in using nanocrystalline inorganic solids for nanoscale devices and technologies has fueled a tremendous research effort for developing syntheses of inorganic nanocrystals. Even though much progress has been made for the development of synthetic approaches, synthetic methods to generate size- and shape-controlled nanocrystalline materials are still challenging, particularly for multi-metal and metal systems that have been less explored due to the lack of robust synthetic approaches. This dissertation presents robust and facile solution based approaches to synthesize size- and shape-controlled intermetallic and metal nanocrystals.

We have been exploring the concept of chemical conversion for synthesizing a variety of nanomaterials with size- and shape-control. In particular, this approach has shown to be an effective chemical route for synthesizing shape-and size-controlled intermetallic nanocrystals. It has been known that size-and shape-controlled intermetallic compounds are not easily attainable since intermetallic compounds normally consist of elements possessing notably different reduction potentials, reduction kinetics, and reactivity. This chemical conversion strategy utilizes a single metal as a reactive template for synthesizing more complex nanomaterials. We have shown that β-Sn nanocrystals can chemically transform into size- and shape-controlled M-Sn intermetallic nanocrystals. This chemical conversion method also affords compounds that can be hard to obtain by traditional solid state synthetic methods. We have also established general and predictive guidelines for accessing dense and hollow single crystal nanorods in M-Sn
systems. Through this study, we have realized that reaction temperature plays a vital role in maintaining the morphology of the $\beta$-Sn nanorod templates in the products.

For the synthesis of a variety of nanomaterials by the exploitation of the established chemical conversion strategy, robust and general chemical approaches have been developed for the synthesis of shape-controlled In nanoparticles by understanding reduction kinetics. Interestingly, metal precursors that have negative reduction potential vs standard hydrogen electrode have previously been synthesized by only harsh chemical and physical methods (high reaction temperatures and strong reducing agents), which can be inadequate for yielding precisely shape-controlled nanoparticles. We have shown a simple and robust kinetically controlled borohydride reduction process for synthesizing shape-controlled In nanocrystals at room temperature. By controlling the reduction rates via the rate of addition of sodium borohydride solution and controlling several reaction parameters, including reaction solvents, additives, solvents for sodium borohydride, and alcohol solutions containing metal precursors in the presence of poly(vinyl pyrrolidone), indium nanoparticles are formed that include shapes of high aspect ratio nanowires, uniform octahedra, truncated octahedra, decahedra, triangles, spheres, and star-like shapes.

We have shown that a simple kinetically controlled reduction process can also be applied to the synthesis of size- and shape-controlled Ge nanocrystals. Again, representative chemical and physical approaches have been previously developed using harsh reaction conditions (high temperatures, high pressures, and strong reducing agents). The kinetically controlled reduction process by sodium borohydride at room temperature leads to the formation of spherical Ge nanocrystals with high monodispersity, as well as
cubic shape. By varying concentration of metal precursors and reaction solvents, different sizes of germanium nanocrystals were obtained.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................ viii

LIST OF TABLES ......................................................................................................... xiii

LIST OF ABBREVIATIONS ........................................................................................ xiv

ACKNOWLEDGEMENTS ............................................................................................ xv

Chapter 1  Introduction ............................................................................................. 1

References ................................................................................................................. 9

Chapter 2  Shape-Controlled Conversion of $\beta$-Sn Nanocrystals into Intermetallic $M$-Sn ($M = \text{Fe, Co, Ni, Pd}$) Nanocrystals ......................................................... 15

2.1 Introduction ......................................................................................................... 15
2.2 Experimental Section ....................................................................................... 17
  2.2.1 Chemicals .................................................................................................... 17
  2.2.2 Synthesis of Intermetallic Nanostructures .............................................. 17
  2.2.3 Synthesis of $\beta$-Sn Nanocrystal Shapes .............................................. 18
  2.2.4 Characterization ...................................................................................... 20
2.3 Results and Discussion .................................................................................... 20
  2.3.1 Generation of Hollow Cube-Derived FeSn$_2$ Nanostructures ............. 20
  2.3.2 Size- and Shape-Dependent Reactivity ................................................. 30
  2.3.3 Extension to Other Systems .................................................................. 35
2.4 Conclusions ...................................................................................................... 40
2.5 References ........................................................................................................ 42

Chapter 3  A Library of Single-Crystal Metal-Tin Nanorods: Using Diffusion as a Tool for Controlling the Morphology of Intermetallic Nanocrystals .................. 47

3.1 Introduction ....................................................................................................... 47
3.2 Experimental Section ....................................................................................... 49
  3.2.1 Chemicals ................................................................................................... 49
  3.2.2 Synthesis of $\beta$-Sn Nanorods .............................................................. 49
  3.2.3 Synthesis of Intermetallic Nanorods ................................................... 50
  3.2.4 Characterization ...................................................................................... 51
3.3 Results and Discussion .................................................................................... 51
  3.3.1 Syntheses of a Library of Intermetallic Nanorods ............................... 51
  3.3.2 Study of Reaction Temperatures and Diffusion Rates ....................... 59
3.4 Conclusions ...................................................................................................... 64
3.5 References ........................................................................................................ 65
Chapter 4  Room-Temperature Chemical Synthesis of Shape-Controlled Indium Nanoparticles ................................................................. 69

4.1 Introduction .................................................................................. 69
4.2 Experimental Section ................................................................. 71
4.2.1 Chemicals ................................................................................. 71
4.2.2 Synthesis of In Nanowire, Octahedra, and Truncated Octahedra ...... 71
4.2.3 Synthesis of In Spheres, Decahedra, Triangles, Nanowires, and Star-Like Shapes ................................................................. 72
4.2.4 Characterization ....................................................................... 74
4.3 Results and Discussion ................................................................. 75
4.3.1 Chemical Synthesis of In Nanowires, Octahedra, and Truncated Octahedra ................................................................. 75
4.3.2 Mechanism of In nanowire Formation ........................................ 79
4.3.3 Study of Reduction Kinetics .................................................... 84
4.3.4 Optical properties and Superconductive for In nanoparticles ......... 95
4.4 Conclusions ............................................................................... 97
4.5 References ............................................................................... 98

Chapter 5  Chemical Synthesis of Shape- and Size-Controlled Ge Nanocrystals at Room Temperature ......................................................... 102

5.1 Introduction ............................................................................... 102
5.2 Experimental Section ................................................................. 104
5.2.1 Chemicals ................................................................................. 104
5.2.2 Synthesis of Spherical and Cube-like Germanium Nanocrystal ...... 104
5.2.3 Characterization ....................................................................... 106
5.3 Results and Discussion ................................................................. 107
5.4 Conclusions ............................................................................... 119
5.5 References ............................................................................... 120

Chapter 6  General Conclusions ................................................................. 123

References .......................................................................................... 128
LIST OF FIGURES

Figure 2-1: (a) TEM micrograph and SAED pattern (inset) of FeSn\textsubscript{2} nanocrystal shapes; (b) powder XRD pattern (top: experimental; bottom: simulated); HRTEM image of a single-domain FeSn\textsubscript{2} nanocrystals ........................................21

Figure 2-2: TEM micrographs of (a-e) assemblies of cube-derived FeSn\textsubscript{2} nanocrystals and (f) representative nanocrystal shapes (each \~50 nm), including hollow squares, U-shaped structures, and nanorod dimmers. Scale bars in (a-d) are 15 nm..........................................................................................22

Figure 2-3: (a) EDS data for intermetallic FeSn\textsubscript{2} nanocrystals showing a 1:2 Fe:Sn ratio; (b) EDS data for intermetallic PdSn nanocrystals showing a 1:1 Pd:Sn ratio; (c) TEM micrograph for FeSn\textsubscript{2} (both small and large nanocrystals, similar to those shown in Figure 5d); (d-e) semi-STEM elemental mapping data for the TEM micrograph in (c), clarifying that Fe (d) is present in the same areas as the Sn (e). .......................................................................................23

Figure 2-4: (a-c) TEM micrographs for Sn nanocrystals seeds (SAED pattern shown in the inset) and (d) crystal structure of $\beta$-Sn (purple represents surface atoms; gray represents interior atoms), showing the atom density on the side and top/bottom surfaces........................................................................................24

Figure 2-5: Representative powder XRD patterns for Sn (left), CoSn\textsubscript{2} (middle), and Ni\textsubscript{3}Sn\textsubscript{4} (right). CoSn\textsubscript{2} and Ni\textsubscript{3}Sn\textsubscript{4} were synthesized as described in the text ($\beta$-Sn nanoparticles reacted with Co\textsuperscript{2+} and Ni\textsuperscript{2+} with no excess NaBH\textsubscript{4}, supporting a diffusion-based mechanism). ..........................................................25

Figure 2-6: Schematic outlining a hypothesized pathway for the formation of the observed FeSn\textsubscript{2} cube-derived nanostructures via an anisotropic Kirkendall type mechanism. All structures can be derived from preferential Fe absorption on the top and bottom 100 faces of $\beta$-Sn nanocrystals cubes, with subsequent anisotropic diffusion into the structure. In (a), uniform outward diffusion from the center of the cube produces slabs (nanorods or nanoplates), which, if not held together by residual surface oxide or by FeSn\textsubscript{2} bridges, can dissociate to form free standing particles. (They often remain associated as dimmers, which follows directly from this proposed hollowing process.) In (b), diffusion initially occurs fastest from the center, hollowing out from the center to form square-shaped structures. In (c), the diffusion and hollowing process is not uniform, proceeding in one direction faster than the other (possibly caused by subtle kinetic or steric effects), resulting in partially hollow (U-shaped) structures. Several morphologies are possible, depending on subtle and as-yet uncontrollable details about how the reaction proceeds. TEM micrographs of aliquots taken during reaction show examples of reaction intermediates that are consistent with the proposed formation
pathway. Selected examples are shown to the right and labeled according to the schematic drawing that they most closely match.............................................28

Figure 2-7: (a) TEM micrograph of bimodal FeSn₂ nanocrystals (>30 nm and <15 nm) synthesized by reacting similarly bimodal β-Sn nanocrystals with Fe³⁺ under reducing conditions. The larger (>30 nm) FeSn₂ nanocubes are partially hollow, while the smaller (<15 nm) nanocrystals are dense. TEM micrographs of (b,c) β-Sn nanocrystals that are predominately rod-patterns for β-Sn nanorod and FeSn₂ nanorods are shown in (e) and (f), respectively......31

Figure 2-8: Representative sample of (a) bimodal β-Sn nanocrystals, similar to those used to make the bimodal FeSn₂ nanocrystals shown in Figure 2-7a, and (b) a mixture of spherical and cubic β-Sn nanocrystals, similar to those used to make the CoSn₃ nanocrystals shown in Figure 2-12a..............................32

Figure 2-9: TEM micrographs and SAED patterns (insets) of (a) β-Sn nanospheres (mostly >20 nm), (b) FeSn₂ nanocubes formed from the β-Sn nanospheres in (a), and (c) FeSn₂ nanocubes (~10 nm) formed from the β-Sn nanospheres (<10 nm) shown in the inset. A schematic summary (qualitative, not shown to scale) of the various β-Sn to FeSn₂ transformations in shown in (d)..........................................................................................................................34

Figure 2-10: (a-c) TEM micrographs of cube-derived PdSn nanostructures and (d) the corresponding XRD pattern (top: experimental; bottom: pattern from PDF card #4-0803). Scale bars are 20 nm in (b) and (c). .............................................35

Figure 2-11: HRTEM micrograph for the PdSn nanocrystal shown in Figure 7b, showing a single-domain PdSn nanocrystal (inset: same low-resolution TEM micrograph shown in Figure 7b)...........................................................................36

Figure 2-12: (a) TEM micrograph, SAED pattern (inset), and (b) XRD pattern (top: experimental; bottom: PDF card #48-1813) for α-CoSn₃ nanocrystals. (c) TEM micrograph, SAED pattern (inset), and XRD pattern (top: experimental; bottom: modified from PDF card #37-1197 [PtSn₃], as described in the text) for NiSn₃. ...........................................................................38

Figure 2-13: Crystal structures of β-Sn and CuAl₂-type FeSn₂ (green = Fe, purple = Sn), highlighting conserved structural features (zigzag chains of Sn atoms) that likely help to facilitate the single crystal-to-single crystal transformation....41

Figure 3-1: Large-area TEM micrograph of β-Sn nanorods used as seeds. ..............52

Figure 3-2: Powder XRD patterns for nanocrystalline intermetallics formed by reacting β-Sn nanocrystals with appropriate metal salt solutions under reducing conditions. (a) PtSn, AuSn, Ag₄Sn, and Cu₆Sn₅, (b) CoSn₃, and (c) RuSn₂. Top: experimental. Bottom: patterns from PDF card # 25-0614
Figure 3-3: Powder XRD patterns for β-Sn (left) and Ni₃Sn₄ (right). All other XRD data is shown in Figure 3-2 in the text.

Figure 3-4: TEM micrographs and SAED patterns of nanocrystalline (a) β-Sn, (b) CoSn₃, (c) Ni₃Sn₄, (d) AuSn, (e) Cu₆Sn₅, (f) Ag₄Sn, (g) RuSn₂ (200 °C), and (h) PtSn (290 °C). All reactions were carried out at 150 °C unless otherwise noted. Scale bars are 20 nm.

Figure 3-5: Larger-area TEM micrograph of RuSn₂ (200 °C).

Figure 3-6: High resolution TEM micrographs of (a) hollow single-crystal Ni₃Sn₄ nanorods and (b) dense single-crystal CoSn₃ nanorods. Scale bars are 5 nm.

Figure 3-7: High-resolution TEM micrographs showing a hollow single-crystal PtSn nanorod (top) and a hollow single crystal CoSn₃ nanorod (bottom). Scale bars are 5 nm.

Figure 3-8: TEM micrographs and SAED patterns for (a) predominantly spherical Cu₆Sn₅ at ~20 °C, (b) single-crystal Cu₆Sn₅ nanorods at 0 °C, (c) predominantly spherical AuSn at ~20 °C, (d) single-crystal AuSn nanorods at 0 °C, and high resolution TEM micrographs for single-crystal nanorods of (e) Cu₆Sn₅, (f) AuSn, and (g) Ag₄Sn. Scale bars are 20 nm in (a-d) and 5 nm in (e-g).

Figure 3-9: TEM micrographs of (a) hollow single-crystal CoSn₃ nanorods and (b) a larger-view image showing the beginning of fragmentation into smaller spherical nanoparticles. The corresponding SAED pattern is shown in (c). Scale bars are 20 nm.

Figure 4-1: TEM micrograph of indium (a) nanowires, (b) octahedra, and (c) truncated octahedra synthesized by borohydride reduction of In³⁺.

Figure 4-2: (Left) Powder XRD patterns for In nanoparticles and simulated XRD pattern for In metal; (right) higher-angle XRD data for all samples; (inset) representative SAED pattern for In nanowires.

Figure 4-3: TEM micrograph of irregularly-shaped In nanoparticles synthesized without controlling the reduction rate.

Figure 4-4: TEM images from intermediate stages of the reaction: (a) In nanowires growing off of octahedral seeds; (b,c) nanowires becoming thicker as the reaction progresses. (d) Enlarged TEM image showing the nanowire tips, which maintain the points defined by the octahedral seeds.
Figure 4-5: High-resolution TEM micrograph of an indium octahedron, showing planar spacings that match well with the 011 and 101 planes of indium metal ($d = 2.7 \, \text{Å}$). .......................................................... 81

Figure 4-6: TEM micrograph of several indium octahedra (same image as shown in the inset to Figure 4-6), highlighting the angles formed by the edges of the octahedra. These angles compare favorably with those expected from the junction of the 011 and 101 planes (see Figure 4-7). ........................................... 82

Figure 4-7: Various representations of the crystal structure of indium: (a) In, showing the unit cell; (b) expanded version of the In crystal structure, with the 011 (purple) and 101 (blue) planes highlighted (Note: the structure has been rotated 90° counterclockwise relative to its traditional orientation); (c) same orientation and coloring scheme as in (b), showing only the atoms in the 011 and 101 planes; (d) same orientation and coloring scheme as in (c), rotated and showing the 002 plane (red plane) relative to 011 and 101. ............. 83

Figure 4-8: Left: The In crystal structure in Figure 4-6c rotated to show the angle of intersection between the 011 and 101 planes. Right: TEM micrograph from Figure 4-5 showing an indium octahedron, highlighting the angles formed by the edges of the octahedra. .................................................................. 83

Figure 4-9: Proposed growth mechanism for the indium nanowires based on the preliminary data presented thus far: (a) octahedral seeds are formed from the initial reduction step; (b) slow reduction rates lead to growth of nanowires off of the tips of the octahedra in the 100, 010, and 001 directions; (c,d) the nanowires continue to grow in these directions, retaining the pointed tip defined by the octahedral seeds (see Figure 4-4). .................................................. 84

Figure 4-10: (a) TEM micrograph of spherical In nanoparticles. ......................... 87

Figure 4-11: TEM micrographs of decahedral In nanoparticles.......................... 88

Figure 4-12: TEM micrographs of triangular In nanoparticles. ......................... 90

Figure 4-13 TEM micrographs of In nanowires synthesized in ethylene glycol. ....... 92

Figure 4-14: TEM micrograph of intermediates intermittently obtained (a) at the initial stage ($t = 150s$), (b) at the middle stage ($t = 240s$), (c) at the final stage ($t = 300 s$), and (d) schematic drawing of the most likely pathway for the formation of star-like shape In nanoparticles, based on the intermediate stages observed. The inset shows the corresponding SAED pattern ......................... 94

Figure 4-15: Representative UV-visible absorption spectrum of In nanoparticles (octahedra). ........................................................................................................... 96
Figure 4-16: (a) Temperature dependent magnetization at a 8.5 Oe applied field and a 100 Oe applied field (black diamonds, bulk In; red circles, In nanowires; blue triangles, In octahedra; green squares, In truncated octahedra). ............................................................................................................97

Figure 5-1: (a) Large-area TEM micrograph of spherical Ge nanocrystals, (b) TEM image of spherical Ge nanocrystals, (c) high resolution TEM image of a single Ge nanocrystal, showing clear lattice fringes (2.00 Å), and (d) a representative SAED pattern for spherical Ge nanocrystals.................................108

Figure 5-2: Powder XRD patterns for (a) the as-prepared Ge nanocrystals and (b) Ge nanocrystals annealed at 600 °C for 1h...........................................................110

Figure 5-3: Energy-dispersive X-ray spectrum (EDS) of the as-prepared Ge nanocrystals. .........................................................................................................111

Figure 5-4: TEM micrograph of germanium nanocrystals with bimodal size distribution............................................................................................................113

Figure 5-5: TEM micrograph of germanium nanocrystals synthesized in ethanol......114

Figure 5-6: TEM micrographs of (a) cubic germanium nanocrystals (inset: high resolution TEM image) and (b) the reaction intermediates. Schematic drawing of the most likely pathway to the formation of cubic germanium nanocrystals. .........................................................................................................116

Figure 5-7: TGA/DSC scans of as-prepared Ge nanocrystals at room temperature....117

Figure 5-8: (a) Room temperature UV-visible absorbance and (b) photoluminescence (excitation wavelength of 286 nm and emission wavelength of 326 nm). ............................................................................................................118
LIST OF TABLES

Table 4-1 Summary of reaction parameters for producing various shapes of In nanoparticles. ........................................................................................................95
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP</td>
<td>Poly (vinyl pyrrolidone)</td>
</tr>
<tr>
<td>TEG</td>
<td>Tetraethylene glycol</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>Triglyme</td>
<td>Triethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectrum</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting quantum interference device</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>TOP</td>
<td>Trioctylphosphine</td>
</tr>
<tr>
<td>TOPO</td>
<td>Trioctylphosphine oxide</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively-coupled plasma mass spectrometer</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Raymond Schaak for teaching and mentoring me for five years, as well as for his support. Especially, thanks for giving me such a creative environment and for letting me choose a project. I also thank my committee members- Dr. Mallouk, Dr. Mueller, and Dr. Komarneni. I would like to thank my committee members at Texas A&M University, Dr Goodman and Dr.Hughbanks, as well as Dr. Cotton and Dr. Dunbar for teaching me inorganic chemistry.

I would like to thank Professor Peter Schiffer and Dr. Xianglin Ke for measuring and discussing superconductivity of In nanoparticles

Thanks also the entire Schaak research group for their help and support. I would like to individually thank Dr. Rob Cable, Dr. Brian Leonard, Dr. Chris Bauer, Nathan Henderson, Farah Dawood, Kendra Avery, and James Bondi for their advice and friendship.

I would like to thank my master advisor, Moo Jin Jun at Yonsei University for teaching and mentoring me. I also thank Professor Charles O’Connor for giving me the opportunity to study nanochemistry.

I would like to thank Professors Soo Min Lee and Kwang Sup Lee for encouraging me to study chemistry.

I also thank to my family for their support, love, and encouragement. Thank you!

To my wife, I could not have done without your love and support.
Chapter 1

Introduction

Colloidal nanocrystals possess intriguing features that can be different from their bulk analogues. The physical and chemical properties of colloidal nanocrystals that are often referred to as artificial atoms can be easily adjusted by their composition, crystallinity, size, structure, and shape. For example, quantum dots exhibit size-tunable band gaps and luminescence energies due to quantum size effects. These quantum dots are now widely utilized for fluorescent labels in biomedical applications. Another typical example associated with the optical properties of metals such as gold and silver nanoparticles is a wide range of tunability of the surface plasmon resonance by varying shapes and sizes. An intrinsic catalytic property can be also accessed by shape-controlled metal nanoparticles such as Pt. Unlike spherical nanoparticles, anisotropic nanoparticles have many different facets that exhibit different physical and chemical reactivity. Magnetic properties also change as a function of size and shape. For instance, magnetic nanocrystals exhibit superparamagnetism as a result of size reduction. Other properties including mechanical properties vary by controlling shapes and sizes as well. Therefore, these unique chemical and physical properties obtained with shape- and size-controlled nanocrystals can provide a variety of applications, including information storage, medical and biological imaging, and catalysis for energy and chemical applications. Furthermore, nanomaterials can be easily integrated into devices
due to their size and solubility. Accordingly, versatile and general approaches are required for the precisely controlled synthesis of nanomaterials.

Many chemical and physical methods have been developed for the synthesis of nanomaterials. These methods can be classified as either top-down approaches, which involve size reduction of bulk materials, or bottom-up approaches, which involve growth of nanoparticles from small nuclei. The most prominent examples of top down approaches are ball milling and laser ablation. These approaches, in general, require time consuming processes, as well as elaborate experimental set-ups. Again due to their harsh experimental conditions, it is difficult to control the critical parameters that are required for rigorous control of shapes and sizes. Alternative approaches for obtaining nanomaterials can be performed via bottom-up approaches that allow for great control of size and shapes of the final products.

Solution chemical approaches are widely used for the synthesis of nanoparticles due to their capability of precise control of shapes and sizes. There are many methods, including thermal decomposition of organometallic complexes, reduction of metal salt precursors, reverse micelles or micelles, co-precipitation, and solvothermal reactions. Bottom-up approaches have been developed for semiconductor, metal oxide, and single metal nanoparticles. Typical reactions are performed in high boiling point solvents in the presence of stabilizers that can passivate the surface of nanoparticles by steric effects and/or electrostatic interactions. Unlike top-down approaches, chemical methods are performed under the relatively mild conditions that can allow for control over size and shape of nanoparticles.
Solution chemical routes have several benefits over non-chemical methods for the synthesis of nanoparticles. For example, rigorous control of size and shape can be achieved via solution chemical approaches. However, several disadvantages exist for these chemical methods. In general, solution chemical methods have been only applied to a small number of materials. Even though many types of nanomaterials have been synthesized, these chemical methods are truly system-dependent, rather than general and robust approaches for all nanomaterials. Even alloy systems that are largely associated with elements of similar reactivity, reduction potentials, and reduction kinetics have been difficult to synthesize by solution chemical routes. Thus the synthesis of highly controlled nanocrystals in terms of shapes and sizes is fairly dependent on each system. It is necessary to initiate efforts to discover new chemical approaches, as well as to improve many methodologies that have been developed to produce highly controlled shapes and sizes of nanocrystals. Even though there are some chemical approaches that can be easily applied to some nanomaterials,28 it is still hard to make all nanomaterials by these chemical methods in a controllable manner, in particular for multi-metallic alloys and intermetallics with a desirable shape and size.

Since there still remain synthetic challenges, a majority of high quality nanocrystals made by solution chemical methods have been restricted to simple systems. A few systems that have been relatively well studied are single metal systems (e.g., Au, Ag, Pt, Pd, Co, Rh), metal oxide (e.g., Fe$_3$O$_4$, ZnO), and metal chalcogenides (e.g., CdS, CdSe, ZnS). These systems have been focused on for decades due to their chemical and physical properties, as well as their potential of technological applications. However, utilization of these chemical approaches to more complex systems such as intermetallics
that involve elements of notably different reduction potentials, reduction kinetics, and reactivity have been difficult. In particular, even finding the appropriate stabilizers to control the shapes and sizes of nanocrystals is not an easy task, and making it difficult to use these chemical approaches to other systems.

Alternative synthetic routes to more complex systems are necessary to efficiently produce a variety of nanocrystals in a controlled manner. The approach of chemical conversion that has been developed by our group and others can be a promising solution. In this approach, nanocrystals serve as reactive templates that are chemically transformed into various complex nanomaterials by reaction with appropriate elemental precursors in solution. The nanocrystals can be used as morphological, compositional, and structural templates.

Many types of conversion chemistry processes can be performed to synthesize a variety of nanomaterials, in particular for complex systems. Thus, many chemical reactions can be involved, including Kirkendall type diffusion that has been developed for the synthesis of hollow nanocrystals. Ion exchange reactions have been used for the synthesis of multi-segmented nanorods while retaining the nanorod shape. Another example of chemical reactions that can be used with this chemical conversion strategy is the galvanic replacement reactions that have been developed by Xia and co-workers. The galvanic replacement reactions have been used for the formation of hollow metal and alloy nanocrystals. Basically, the nanoparticles are used as sacrificial templates by reaction with metal precursors that have a more positive reduction potential. A well-studied galvanic replacement is one involving the reaction of Ag cubes with gold precursors, and gradually silver metal oxidizes to silver ions and concomitantly gold
precursors steadily reduce to gold metal on the surface of silver metal templates. Transmetallation reactions have been used for synthesizing Co/Pt alloy, which involve the reaction of cobalt nanoparticles with Pt precursors [(i.e. Pt(acac)₂] and form core/shell nanoparticles (e.g., Co/Pt) that can be further converted into intermetallic compounds upon heating. Other chemical reactions that involve this conversion chemistry include oxidation. Several hollow metal nanoparticles have been synthesized by oxidation of metal nanoparticles to metal oxides, including CoO and Fe₃O₄.

Among many interesting nanomaterials, intermetallics are important target materials since intermetallics show a variety of intriguing chemical and physical properties, including ferromagnetism, thermoelectricity, shape-memory effects, superconductivity, hydrogen storage, and high catalytic activity. Atomically ordered intermetallic compounds often exhibit improved physical and chemical properties with respect to alloy analog. One example is that FePt shows paramagnetism as an atomically disordered face-centered cubic (fcc) alloy, but when the atoms order at the level, FePt becomes ferromagnetic with a face-centered tetragonal (fct) structure. Another example is PtBi: intermetallic PtBi shows superior electrocatalytic activity relative to pure Pt. The atomically ordered crystal structure plays a critical role in the enhanced chemical and physical properties of intermetallic compounds, but compositions of intermetallic compounds, in general, fix atomic ratios that give a very narrow range of compositions. However at the nanoscale, the physical and chemical properties of these intermetallic compounds can be easily tuned by controlling particle sizes and shapes.

The following chapters describe the development of the chemical conversion approach to synthesize shape-and size-controlled intermetallics, as well as new chemical
approaches to synthesize shape-controlled metal nanocrystals for further use as templates for the formation of a variety of alloys and intermetallic compounds. The first, associated with the development of the chemical conversion approach, involves the formation of shape-controlled $\beta$-Sn nanocrystals, including nanocubes, nanospheres, nanorods, and then chemical conversion into Sn-based intermetallic compounds that consist of a variety of distinctive crystal structures. It is noteworthy to point out that size- and shape-controlled FeSn$_2$ is generated via chemical conversion strategy, but other chemical solution methods can not be applied to this intermetallic system. This result implies that the reactivity of elements involved with the formation of these intermetallic compounds is quite different chemically, thus often leading to difficulty of controlling size and shape for these intermetallic compounds. This chemical conversion approach turns out to be a useful route to synthesize new and metastable compounds as well. As such, it can be a promising alternative to other non-equilibrium approaches for the synthesis of new, metastable, and low-temperature phases. Therefore, it can open the door to the discovery of new compounds as nanocrystals.

We describe the generalization of this chemical conversion approach to obtain a variety of rod-shaped Sn-based intermetallic compounds by use of rod-shaped Sn as reactive templates. We established general and predictive guidelines for the formation of single-crystal nanorods in a large number of chemically distinct intermetallic systems. Temperature turns out to be key role in maintaining the shape of $\beta$-Sn nanorod templates in the final products. This result is associated with the diffusion characteristics of metal elements. The melting point of metal elements can serve as a rough estimate of their rate of diffusion relative to that of other elements. This is useful for establishing empirical
guidelines for the formation of intermetallic compounds at the lowest reaction temperature, as well as developing shape-controlled syntheses of a large number of technologically important intermetallic and other multi-metal nanocrystals.

For the synthesis of a variety of nanomaterials by the exploitation of the established chemical conversion strategy, it is required that shape-controlled metals are necessary as templates. Accordingly, robust and general approaches are required for the formation of metal systems with a desired shape and size, particularly for metal systems that have been less explored due to the lack of versatile and robust chemical approaches. Among several metal systems that have been less explored, many chemical and physical methods have been used for the synthesis of In nanoparticles. However, the reactions were performed under harsh reaction conditions (e.g., high temperatures and strong reducing agents), which can hinder the control of size and shape. Therefore, we have developed a simple kinetically controlled borohydride reduction process for synthesizing shape-controlled In nanocrystals at room temperature. In nanocrystals are formed with shapes of high aspect ratio nanowires, uniform octahedra, and truncated octahedra. Other shapes such as decahedra, triangular, spherical In and star-shaped In nanocrystals are formed by carefully controlling the reduction rate, as well as choosing appropriate reaction solvents to increase and/or decrease the reduction rates, along with consideration of several parameters.

A simple kinetically controlled reduction process can also be applied to size- and shape-controlled Ge nanocrystals. Ge nanocrystals exhibit a strong visible photoluminescence and can be used for biological applications and optoelectronics. Group IV semiconductors such as Ge and Si have unique advantages with respect to II-IV
semiconductor nanocrystals (e.g., CdSe, CdS), since Ge and Si nanocrystals are nontoxic to biological systems. Again, representative chemical and physical approaches that have been developed have been performed under harsh conditions (high temperatures, high pressures, and strong reducing agents). The kinetically controlled reduction process by sodium borohydride at room temperature leads to the formation of spherical Ge nanocrystal with high monodispersity, as well as cubic shape. Interestingly, the cubic germanium nanocrystals are formed via kinetically controlled in situ self assembly of small Ge nanospheres. For the formation of larger Ge nanocrystals, we examined the concentration effect of metal precursor on the particle sizes. With higher concentration of germanium tetrachloride, Ge nanocrystals with bimodal size distribution (larger particles show 10 nm mean diameter and smaller particles show 3 nm mean diameter) were obtained. Utilization of ethanol as the reaction solvent, rather than ethylene glycol, lead to the formation of 50 nm mean diameter Ge nanocrystals as well.

As mentioned earlier, the shape-controlled metal nanocrystals can be used as reactive templates for the formation of more complex nanomaterials. Preliminary data show that metastable InSn₄ can be accessed via chemical conversion approach by using preformed shape controlled In nanocrystals. This result implies that this chemical conversion approach is robust and general approach for synthesizing shape-controlled complex nanomaterials, as well as to obtain new and metastable compounds. Eventually, the tremendous potential of this chemical conversion approach, along with the development of new chemical approaches to metal nanocrystal synthesis can guide us to explore new nanomaterials with a desired shape and size for targeted properties and applications.
References


(e) Xie, J.; Zhao, X. B.; Cao, G. S.; Zhao, M. J.; Su, S. F. J. Power Sources **2005**, 140, 350.


(e) Zhang, Y.; Li,


Chapter 2
Shape-Controlled Conversion of $\beta$-Sn Nanocrystals into Intermetallic $M$-Sn ($M =$ Fe, Co, Ni, Pd) Nanocrystals

2.1 Introduction

Template-based strategies are becoming increasingly common for synthesizing nanoscale inorganic solids with complex morphologies. For example, non-reactive templates, such as colloidal crystals\(^1\) and porous alumina membranes,\(^2\) can serve as physical molds for the deposition of many types of materials. Likewise, metal nanoparticles can serve as reactive templates that help to define the shape and composition of derivative nanostructures after carrying out appropriate chemical transformations.\(^3\) Some of the many recent examples of the latter include hollow Au nanoboxes formed by templating against Ag nanocubes,\(^4\) Ag$_2$Se nanowires formed by reacting Se nanowires with a solution of AgNO$_3$,\(^5\) hollow cobalt sulfide nanospheres formed by reacting Co nanoparticles with sulfur,\(^6\) and hollow CoPt alloy nanospheres

* Reprinted in part with permission from *J. Am. Chem. Soc.*, 129 Chou, N. H.; Schaak, R. E. "Shape-Controlled Conversion of $\beta$-Sn Nanocrystals into Intermetallic $M$-Sn ($M =$ Fe, Co, Ni, Pd) Nanocrystals,” 7339, Copyright 2007 by the American Chemical Society.
formed from the reaction of Co nanoparticles with aqueous K$_2$PtCl$_6$ under reducing conditions. The strategies that utilize metal nanoparticle templates generally succeed at producing shape-controlled nanostructures with morphologies that can be difficult or impossible to prepare using other synthetic methods, including 1D nanowires, cube-shaped nanocrystals, and hollow nanostructures.

The ability to control the shape of metal nanocrystals is important because it is central to applications such as catalysis and plasmonics. For example, cubes and tetrahedra expose different crystal facets, and each shows unique catalytic capabilities that may be exploited to fine-tune catalytic activity and selectivity. Likewise, dense spheres, hollow spheres, cubes, rods, and triangles each have unique plasmonic properties, which can be fine-tuned by changing their shape. Despite significant advances in controlling the shape of metal nanocrystals, particularly through template-based strategies, rigorous shape control of multi-metal nanocrystals remains challenging. To date, there have been no examples of rigorous shape control in multi-metal intermetallic systems with elements of notably different reduction potentials, reduction kinetics, and reactivity.

Here we show that β-Sn nanocrystals can serve as templates for the formation of shape-controlled intermetallic nanocrystals using solution-mediated reactions with transition metal salts. In addition to accessing nanocrystal morphologies that have not yet been achieved for multi-metal intermetallic systems, this template-based strategy also appears to yield crystal structures that can be difficult to access by traditional solid-state synthetic methods. To demonstrate this approach and to generate guidelines for the formation of shape-controlled intermetallic nanocrystals, we focus initially on FeSn$_2$, 


which is an antiferromagnet that is sometimes used as a component in exchange-biased films.\textsuperscript{12} We then extend the strategy to intermetallic PdSn, which is a known catalyst.\textsuperscript{13} Finally, we show that the same approach also generates nanocrystals of CoSn\textsubscript{3}, and NiSn\textsubscript{3}. CoSn\textsubscript{3} is a low-temperature intermetallic phase that was only recently discovered,\textsuperscript{14} and it can be difficult to synthesize using traditional high-temperature solid-state methods. NiSn\textsubscript{3} does not appear on the Ni-Sn phase diagram.\textsuperscript{15}

\section*{2.2 Experimental Section}

\subsection*{2.2.1 Chemicals}

All chemicals were purchased from Alfa Aesar and were used as received without further processing or purification: FeCl\textsubscript{3}·6H\textsubscript{2}O (97.0-102.0%), SnCl\textsubscript{2} (anhydrous, 99% min.), CoCl\textsubscript{2}·6H\textsubscript{2}O (98.0-102.0%), NiCl\textsubscript{2}·6H\textsubscript{2}O (99.95%), and Pd(acac)\textsubscript{2} (Pd 34.63%). The reducing agent, surface stabilizer, and solvent were NaBH\textsubscript{4} (98%), poly(vinyl pyrrolidone) (PVP, MW = 40 000, 630 000, or 1 300 000), and tetraethylene glycol (TEG, 99+%), respectively. 1,2-dichlorobenzene (98+) was also used in some cases, as described below.

\subsection*{2.2.2 Synthesis of Intermetallic Nanostructures}

Intermetallic \textit{M}-Sn (\textit{M} = Fe, Co, Ni, Pd) nanocrystals were synthesized by sequential NaBH\textsubscript{4} reduction of the metal salts in tetraethylene glycol (TEG), followed by
heating to 170 – 205 °C under Ar in the presence of PVP (MW = 40 000) and/or other polymers such as poly(2-ethyl-2-oxazoline) (PEO; MW = 50,000). In a typical synthesis of FeSn₂ nanocrystals, 0.7 g of PVP and 0.3 g of PEO were dissolved in 45 mL of TEG at room temperature. The solution was heated to 170 °C, then SnCl₂ (0.130 g in 4 mL of TEG) was added. A freshly prepared solution of NaBH₄ (0.264 g in 8 mL of TEG) was then added dropwise while stirring. After 12 – 15 min at 170 °C, FeCl₃·6H₂O (0.090 g in 4 mL of TEG) was added. The resulting solution was heated to 170 – 205 °C for 1 – 2 h, resulting in a black colloidal solution. The FeSn₂ nanocrystals were isolated by centrifugation and washed with ethanol.

The same approach was used for PdSn, except that SnCl₂ (0.13 g in 4 mL of TEG) and Pd(acac)₂ (0.10 g in 4 mL of 1,2-dichlorobenzene) were used, and the final solution was heated to 170 – 190 °C for 30 min before isolating the black colloidal PdSn solution. For CoSn₃, SnCl₂ (0.13 g in 4 mL of TEG) and CoCl₂·6H₂O (0.05 g in 4 mL of TEG) were used, and the final solution was heated to 180 – 195 °C for 1.5 h, resulting in a black colloidal CoSn₃ solution. For NiSn₃, SnCl₂ (0.13 g in 4 mL of TEG) and NiCl₂·6H₂O (0.05 g in 4 mL of TEG) were used, and the final solution was heated to 150 °C for 1.5 h.

2.2.3 Synthesis of β-Sn Nanocrystal Shapes

Unless otherwise noted, 0.7 g of PVP (MW = 40 000) and 0.3 g of PEO (MW = 50 000) were dissolved in 45 mL of TEG at room temperature. The solution was heated to various temperatures (described below), then SnCl₂ (0.13 g in 4 mL of TEG) was
added. A freshly prepared solution of NaBH₄ (0.264 g in 8 mL of TEG) was then added dropwise while stirring. After 12 – 15 min, the resulting solution was removed from the heat, and the black-colored β-Sn nanocrystals were isolated by centrifugation and washed with ethanol. For the synthesis of predominantly large (> 30 nm) cube-shaped β-Sn nanocrystals, the temperature was 170 °C. To generate a mixture of large (> 30 nm) and small (< 15 nm) cube-shaped β-Sn nanocrystals, the temperature was 140 °C. To generate predominantly large (> 20 nm) spherical β-Sn nanocrystals, PVP with a molecular weight of 630,000 was used, and the temperature was 170 °C. For smaller (< 10 nm) β-Sn nanocrystal spheres, 0.4 g of PVP (MW = 630 000) was used without any PEO present, SnCl₂ was added at 80 °C, and the final solution temperature was 140 °C.

To access β-Sn nanorods, 0.4 g of PVP (MW = 630 000) was dissolved in 45 mL of TEG at room temperature. SnCl₂ (0.08 g in 4 mL of TEG) was then added, along with a freshly prepared solution of NaBH₄ (0.264 g in 8 mL of TEG) while stirring. The temperature was gradually increased to 120 °C over 40 min. Concurrently, β-Sn seed nanocrystals were prepared by sequentially adding 0.15 g of PVP, 0.025 g of SnCl₂, and 0.13 g of NaBH₄ to 8 mL of TEG. This solution of β-Sn seed nanocrystals was added to the original β-Sn nanocrystal solution at 120 °C before increasing the temperature to 160 °C for 1 h, then another solution of β-Sn seed nanocrystals was added. The temperature was increased to 190 °C, then removed from the heat. The predominantly rod-shaped β-Sn nanocrystals were isolated by centrifugation and washed with ethanol.
2.2.4 Characterization

Powder X-ray diffraction (XRD) data were collected on either a Bruker GADDS three-circle X-ray diffractometer using Cu Kα radiation or on a Bruker D-8 Advance powder diffractometer. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns, and energy dispersive X-ray analysis (EDS) were collected using a JEOL JEM-2010 TEM. Samples for TEM analysis were prepared by dropping an ethanol solution containing the β-Sn or M-Sn colloids onto the surface of a carbon-coated copper or nickel grid. Elemental analysis was performed using a Perkin Elmer DRCII inductively-coupled plasma mass spectrometer (ICP-MS).

2.3 Results and Discussion

2.3.1 Generation of Hollow Cube-Derived FeSn₂ Nanostructures

TEM images of representative FeSn₂ nanocrystals are shown in Figure 2-1 and 2-2. SAED (Figure 2-1a), XRD (Figure 2-1b), and EDS (Figure 2-3) data confirm that the composition and structure match that of CuAl₂-type FeSn₂. Interestingly, the nanocrystals adopt a variety of shapes that consist predominantly of hollow squares, U-shaped structures, and nanorods that are typically associated as dimers (Figure 2-2). Most of the FeSn₂ shapes consist of single-domain crystals (Figure 2-1c). Because the nanocrystals are predominantly cube-shaped and roughly uniform in size (although not rigorously monodisperse), they have a tendency to align into one-dimensional
superstructures (Figure 2-2a-e). The FeSn$_2$ nanocrystals are each generally capped with a 1-2 nm SnO$_x$ shell, as determined by TEM and XPS.

Figure 2-1 (a) TEM micrograph and SAED pattern (inset) of FeSn$_2$ nanocrystal shapes; (b) powder XRD pattern (top: experimental; bottom: simulated); HRTEM image of a single-domain FeSn$_2$ nanocrystals.
Figure 2-2 TEM micrographs of (a-e) assemblies of cube-derived FeSn$_2$ nanocrystals and (f) representative nanocrystal shapes (each ~50 nm), including hollow squares, U-shaped structures, and nanorod dimmers. Scale bars in (a-d) are 15 nm.
A closer look at the reaction provides important insights into how the intermetallic FeSn₂ nanocrystal shapes are formed and how their shape and size can be influenced by adjusting the reaction conditions. During the reaction, Sn nanocrystals are formed first by NaBH₄ reduction of Sn²⁺, then Fe³⁺ is added to the Sn nanocrystals under...
reducing conditions (excess NaBH₄) to form FeSn₂. A representative TEM image of the Sn nanoparticle seeds is shown in Figure 2-4a; SAED (Figure 2-4a, inset) and XRD (Figure 2-5) data confirm the formation of β-Sn. Careful control over the synthetic conditions can lead to predominantly (~90%) single-domain cube-shaped nanocrystals (Figure 2-4a) of β-Sn, although some spherical particles are usually observed.

Figure 2-4 TEM micrographs for Sn nanocrystals seeds (SAED pattern shown in the inset) and (d) crystal structure of β-Sn (purple represents surface atoms; gray represents interior atoms), showing the atom density on the side and top/bottom surfaces.
These cube-shaped $\beta$-Sn nanocrystals serve as reactive templates for chemical transformation into FeSn$_2$ with retention of the cubic morphology. Importantly, the $\beta$-Sn nanocrystals can be isolated, re-dispersed in TEG without any excess Sn salts, and then reacted with Fe$^{3+}$ under reducing conditions (NaBH$_4$) to form FeSn$_2$. This confirms that the $\beta$-Sn nanocrystals serve as seeds for transformation into FeSn$_2$. Chemical analysis (ICP) of the FeSn$_2$ solution after removing the FeSn$_2$ nanocrystals by centrifugation confirms that only trace amounts of Sn are present in the supernatant, which indicates that all of the Sn in the $\beta$-Sn nanocrystal seeds is incorporated into the FeSn$_2$ product. Thus, the reaction is not likely to be a galvanic replacement reaction, which would eject Sn$^{2+}$ back into the supernatant as predicted by the reaction necessary to generate FeSn$_2$ by this route: 7 Sn$^{0}$ + 2 Fe$^{3+}$ \rightarrow 2 FeSn$_2$ + 3 Sn$^{2+}$.

Figure 2-5 Representative powder XRD patterns for Sn (left), CoSn$_2$ (middle), and Ni$_3$Sn$_4$ (right). CoSn$_2$ and Ni$_3$Sn$_4$ were synthesized as described in the text ($\beta$-Sn nanoparticles reacted with Co$^{2+}$ and Ni$^{2+}$ with no excess NaBH$_4$, supporting a diffusion-based mechanism).
Rather, it is more likely to be a diffusion-based process where Fe diffuses into Sn. This assignment is also supported by the fact that CoSn₂ and Ni₃Sn₄ can be generated using the same route (Figure 2-5): β-Sn nanocrystals are synthesized by NaBH₄ reduction of Sn²⁺ in TEG, then isolated, re-dispersed in fresh TEG with no NaBH₄, and reacted with Co²⁺ to form CoSn₂ after heating to ~ 200 °C. Ni₃Sn₄ can be formed similarly by reacting Sn nanocrystals with Ni²⁺ in TEG with no NaBH₄ present. While FeSn₂ could in principle be formed via a galvanic displacement reaction between Sn nanoparticles and Fe³⁺ based on the reduction potentials of the Fe³⁺/Fe⁰ (-0.037 eV) and Sn²⁺/Sn⁰ (-0.1375 eV) redox couples, CoSn₂ and Ni₃Sn₄ could not, since the reduction potentials of the Co²⁺/Co⁰ (-0.28 eV) and Ni²⁺/Ni⁰ (-0.257 eV) couples are more negative than that of Sn²⁺/Sn⁰.

The shape-conserving reactivity and the formation of hollowed-out nanostructures can be rationalized by considering the crystal structure, morphology, and diffusion characteristics of the β-Sn nanoparticle templates (Figure 2-4d). The lattice fringes of the single-crystal β-Sn nanocubes (Figure 2-4b,c) indicate that the <100> crystallographic faces are exposed, consistent with previous reports of β-Sn nanowires.¹⁶ The structure of β-Sn is highly anisotropic: the top and bottom faces have a low density of surface atoms, while the four side faces have a much higher atomic density (Figure 2-4d). β-Sn is known to have different diffusion rates along the a and c axes as well, with the rate of diffusion along each axis being dependent upon the metal that is diffusing into the β-Sn crystal.¹⁷ Furthermore, because of the higher atomic density of Sn atoms on the four side faces relative to the top and bottom faces (Figure 2-4d), the top and bottom faces are
likely to be more reactive in solution than the sides, with the polymer being better able to adsorb to and stabilize the side faces, helping to inhibit their reactivity.

On the basis of all of these considerations, it is surmised that Fe absorption and diffusion into $\beta$-Sn is more likely to occur via the top and bottom faces. Consistent with this, the $\beta$-Sn cubes tend to transform into hollow cube-derived nanostructures (Figure 2-1 and 2-2), hollowing out from the center. The schematic shown in Figure 2-6 rationalizes the formation of each of the observed shapes based on this reaction pathway, which considers both preferential stabilization of the four side faces and the known anisotropic diffusion characteristics of $\beta$-Sn. In a few cases, reaction intermediates can be isolated and observed by TEM (Figure 2-6), providing some support for the proposed formation pathway. We can roughly control the degree of reactivity to create predominantly hollow structures vs. nanorods. However, we are unable at this point to control, to a large extent, which morphologies are favored during the reaction. This implies that it is dependent on subtle reaction conditions and possibly on variations in the size and shape of the Sn precursors, for which there are no reports of highly monodisperse shape-controlled nanocrystals in the literature. Consistent with this, all morphologies are accessible in statistically similar yields. Additional work to identify the reaction conditions necessary to preferentially access each of the morphologies is in progress.
This reactivity provides further evidence of the mechanism that is likely to be responsible for the formation of hollow cube-derived FeSn₂ nanostructures. Chemical analysis, discussed earlier, argues against galvanic replacement, since Sn is not removed during the deposition of Fe. Also, standard reduction potentials are inconsistent with a galvanic replacement mechanism, since control experiments (discussed earlier) confirm that CoSn₂ and Ni₃Sn₄ can form under conditions identical to those used for FeSn₂. Furthermore, excess Sn would be required for FeSn₂ to form via a galvanic replacement reaction, since some Sn would have to be sacrificially oxidized as Fe³⁺ reduces. The fact that Fe and Sn are present in a stoichiometric (1:2) ratio both before the reaction and in
the final product also argues against a galvanic replacement mechanism, since such a reaction would yield a product composition that differs from the nominal reaction stoichiometry. Another possible mechanism involves the formation of oxide particles or an oxide layer, e.g. SnO₂ or Fe₂O₃, during the reaction. All of the Sn nanocrystals and many of the FeSn₂ nanocrystals are capped with a 1-2 nm SnOₓ shell, as determined by TEM and XPS. However, it is likely that the oxide coating forms as a result of oxidation of the Sn metal nanocrystals rather than as a result of a reaction between the transition metal and Sn. Similar SnOₓ shells have been observed on many Sn-containing nanocrystals synthesized using related polyol-based techniques that do not rigorously exclude air,¹⁸,¹⁹ and the oxide shells tend to remain inert despite subsequent chemistry that modifies the compositions and structures of the metal cores.¹⁹

Thus, considering all of the available data that argues against galvanic displacement, the mechanism is most likely to be a Kirkendall process, where Fe metal deposits onto the Sn nanoparticles and the different diffusion rates of the different species in an anisotropic manner cause a depletion of material in the center of the nanostructure.⁶ This is also consistent with the known diffusion characteristics of Sn and Fe, where Sn would be expected to diffuse faster than Fe.¹⁷ Kirkendall effects have previously been implicated in the synthesis of hollow spherical structures,⁶,²⁰-²¹ but not the complex cube-derived structures shown here. Our results with the FeSn₂ system imply that anisotropic Kirkendall effects can lead to quite elaborate nanostructures with a range of shapes.
2.3.2 Size- and Shape-Dependent Reactivity

Since the chemical transformation of $\beta$-Sn into FeSn$_2$ conserves the cubic shape of the $\beta$-Sn nanocrystal seeds, it is reasonable to expect that FeSn$_2$ nanocrystals with other shapes and sizes could be accessed by controlling the morphology of the $\beta$-Sn template. As a first step toward this goal, we have been able to vary the synthetic conditions to yield samples of the $\beta$-Sn nanocrystal precursors with predominantly large ($> 30$ nm) cubes, mixtures of large ($> 30$ nm) and small ($< 15$ nm) cubes, and nanorods with diameters of $10 – 20$ nm and aspect ratios of 2-4 (formed in ~ 60% yield), as well as large ($> 20$ nm) and small ($< 10$ nm) spheres. The FeSn$_2$ nanocrystals derived from predominantly large ($> 30$ nm) cubes were shown in Figure 2-1 and Figure 2-2, and this type of $\beta$-Sn precursor reproducibly yields hollowed-out cube-derived structures as discussed earlier. In contrast, the mixture of both large and small cube-shaped $\beta$-Sn nanocrystals generates FeSn$_2$ nanocrystals with a bimodal size distribution similar to that observed for the $\beta$-Sn seeds that are used as precursors (Figure 2-7 and 2-8). In this bimodal sample, the large (~ 30 nm) $\beta$-Sn cubes transform to partially-hollow FeSn$_2$ cube-derived nanostructures as expected. However, the small ($< 15$ nm) $\beta$-Sn cubes transform to dense FeSn$_2$ cubes with no evidence of material depletion in the interior of the particles. (Based on careful SAED and EDS studies, both the small dense cubes and large etched cubes appear to be FeSn$_2$.) In both cases, the shape of the $\beta$-Sn precursors is conserved in the FeSn$_2$ product, but there is no formation of hollow structures for the smaller $\beta$-Sn cubes, implying a size-dependent reactivity regarding the hollowing-out process. Consistent with this, single-crystal $\beta$-Sn nanorods (Figure 2-7b,c) convert to
single-crystal FeSn$_2$ nanorods (Figure 2-7d) with retention of the aspect ratio of the precursors. Since the nanorod diameters (e.g. the <100> faces) are < 15 nm, no hollow structures are expected based on the size-dependent observations discussed above, and none are observed.

Figure 2-7 (a) TEM micrograph of bimodal FeSn$_2$ nanocrystals (>30 nm and <15 nm) synthesized by reacting similarly bimodal β-Sn nanocrystals with Fe$^{3+}$ under reducing conditions. The larger (>30 nm) FeSn$_2$ nanocubes are partially hollow, while the smaller (<15 nm) nanocrystals are dense. TEM micrographs of (b,c) β-Sn nanocrystals that are predominately rod-patterns for β-Sn nanorod and FeSn2 nanorods are shown in (e) and (f), respectively.
Building on these observations of size-dependent reactivity, there also appears to be a shape-dependent reactivity associated with the Sn $\rightarrow$ FeSn$_2$ transformation. For example, $\beta$-Sn nanocrystal spheres of $>20$ nm diameter (Figure 2-9) form FeSn$_2$ nanocrystals with predominantly dense (not hollow) cube shapes when reacted with Fe$^{3+}$ under reducing conditions (Figure 2-9b). Small ($<10$ nm) $\beta$-Sn spheres (Figure 2-9c, inset) also transform into cube-shaped FeSn$_2$ nanocrystals (Figure 2-9c) during the chemical transformation, but with no evidence of hollow particles. Apparently, $\beta$-Sn spheres transform into FeSn$_2$ cubes, while $\beta$-Sn cubes retain their cube-like structure.
Cubes are the dominant products in both cases. However, large (> 20 nm) $\beta$-Sn spheres tend to convert to dense (not hollow) FeSn$_2$ cubes, while $\beta$-Sn cubes of similar size convert to hollow or partially-hollow FeSn$_2$ cubes. This means that FeSn$_2$ cubes can be generated from either spheres or cubes of $\beta$-Sn, but hollow FeSn$_2$ nanostructures can only be obtained from single-crystal $\beta$-Sn nanocube templates. The proposed pathway for the formation of hollow FeSn$_2$ cube-derived nanostructures requires single-crystal $\beta$-Sn nanocubes as precursors, and the shape-dependent reactivity we observe is consistent with this. Similar shape-dependent reactivity has been observed in a few other systems that undergo chemical transformations.$^{22}$ The FeSn$_2$ system appears to have both size- and shape-dependent reactivity, which is summarized schematically in Figure 2-9d.
Figure 2-9 TEM micrographs and SAED patterns (insets) of (a) β-Sn nanospheres (mostly >20 nm), (b) FeSn₂ nanocubes formed from the β-Sn nanospheres in (a), and (c) FeSn₂ nanocubes (~10 nm) formed from the β-Sn nanospheres (<10 nm) shown in the inset. A schematic summary (qualitative, not shown to scale) of the various β-Sn to FeSn₂ transformations in shown in (d).
2.3.3 Extension to Other Systems

This reaction strategy can also be applied to the synthesis of shape-controlled nanocrystals in other Sn-containing intermetallic systems. For example, hollow cube-derived nanocrystals of intermetallic PdSn can be formed by reacting cube-shaped β-Sn nanoparticles with Pd$^{2+}$ under reducing conditions similar to those used to synthesize the hollow FeSn$_2$ nanostructures. Figure 2-10a shows a TEM image of intermetallic PdSn nanocrystals with predominantly hollow square and nanorod structures (Figure 2-10b,c), and these are generally single-domain crystals (Figure 2-11), as observed for FeSn$_2$ under similar conditions. SAED (Figure 2-10a) and XRD (Figure 2-10d) data confirm the FeB-type structure of PdSn, and EDS confirms a 1:1 Pd:Sn ratio (Figure 2-3).

![Figure 2-10](image-url)

Figure 2-10 (a-c) TEM micrographs of cube-derived PdSn nanostructures and (d) the corresponding XRD pattern (top: experimental; bottom: pattern from PDF card #4-0803). Scale bars are 20 nm in (b) and (c).
Similarly, β-Sn reacts with Co$^{2+}$ under reducing conditions to form binary intermetallic Co-Sn nanocrystals with a mixture of spherical and cubic morphologies (Figure 2-12) that matches the morphologies of the mixed cubic/spherical β-Sn precursors that were used as reactive templates (Figure 2-8). However, based on XRD (Figure 2-12b), SAED (Figure 2-12a, inset), and EDS analysis (not shown), the Co-Sn intermetallic phase that forms is α-CoSn$_3$, which is a recently-discovered compound that

Figure 2-11 HRTEM micrograph for the PdSn nanocrystal shown in Figure 7b, showing a single-domain PdSn nanocrystal (inset: same low-resolution TEM micrograph shown in Figure 7b).
does not appear on the originally published Co-Sn phase diagram.\textsuperscript{14} $\alpha$-CoSn\textsubscript{3} is only stable up to 275 °C, and to date, it has only been synthesized using peritectic reactions or tin flux methods.\textsuperscript{14} When we react $\beta$-Sn nanocrystals with a stoichiometric amount of Co\textsuperscript{2+} under reducing conditions, $\alpha$-CoSn\textsubscript{3} is reproducibly the first phase that forms in this system, although, as mentioned earlier, CoSn\textsubscript{2} can also be formed when appropriate stoichiometries are used. This result shows that in addition to forming shape-controlled intermetallic nanocrystals, this chemical conversion strategy can be used to routinely generate nanocrystals of solids that can be somewhat challenging to make using traditional solid-state synthesis methods.
Figure 2-12 (a) TEM micrograph, SAED pattern (inset), and (b) XRD pattern (top: experimental; bottom: PDF card#48-1813) for $\alpha$-CoSn$_3$ nanocrystals. (c) TEM micrograph, SAED pattern (inset), and XRD pattern (top: experimental; bottom: modified from PDF card#37-1197 [PtSn$_3$], as described in the text) for NiSn$_3$. 
Cube-shaped nanocrystals of intermetallic NiSn$_3$ can also be formed by reacting β-Sn nanocrystals with Ni$^{2+}$ under reducing conditions in a 1:3 stiochiometric ratio (Figure 2-12a). Like α-CoSn$_3$, NiSn$_3$ does not appear on the published Ni-Sn phase diagram.$^{15}$ However, to our knowledge, NiSn$_3$ has not been previously reported as an isolatable solid. However, the XRD pattern for NiSn$_3$ (Figure 2-12d) matches closely with that reported for PtSn$_3$ (PDF card # 37-1197), which was reported to be a metastable high-pressure phase that also does not appear on the equilibrium Pt-Sn phase diagram.$^{23}$ NiSn$_3$ indexes to a cubic unit cell with $a = 8.75$ Å, which is contracted relative to the literature report for PtSn$_3$ ($a = 9.002$ Å),$^{23}$ as expected for the replacement of Pt with Ni. The simulated XRD pattern for NiSn$_3$, shown in Figure 8d, was generated by retaining the intensities reported for PtSn$_3$ and shifting the peaks to match those of the 8.75 Å unit cell of NiSn$_3$. The crystal structure of PtSn$_3$ has not been solved,$^{23}$ and because our NiSn$_3$ sample is nanocrystalline with very broad XRD peaks, our data are not of high enough quality to propose or refine a structure, or to eliminate the possibility of oxygen incorporation. However, the agreement between the simulated and experimental data strongly implies that the structure of NiSn$_3$ is closely related to that reported for PtSn$_3$. Importantly, this result shows that our chemical conversion strategy succeeds in stabilizing compounds that, to our knowledge, have not previously been reported using other methods. Thus, in addition to providing the ability to generate shape-controlled nanocrystals, this approach represents a potentially powerful tool for solid-state synthesis and materials discovery. Work is in progress to more fully characterize the CoSn$_3$ and NiSn$_3$ nanocrystals.
2.4 Conclusions

In this chapter, we demonstrated that $\beta$-Sn nanocrystals can be used as reactive templates for the formation of intermetallic FeSn$_2$, PdSn, CoSn$_3$, and NiSn$_3$ nanocrystals via a simple solution-mediated chemical conversion strategy. This builds on other recently-reported chemical conversion strategies for accessing interesting nanomaterials, and represents one of only a few examples of single crystal-to-single crystal transformations in nanocrystals. The successful formation of intermetallic line compounds with narrow composition ranges highlights the degree of composition control that is achievable using this strategy, and shows that ideas that are well established for intermetallic phase formation in ultra-thin films and diffusion couples$^{24}$ are also applicable to the formation of bulk-scale nanocrystalline intermetallic compounds. As shown for the FeSn$_2$ system, a variety of complex cube-derived nanostructures are accessible by consideration of the size- and shape-dependent reactivity of the $\beta$-Sn precursors, as well as the anisotropic diffusion characteristics of $\beta$-Sn. For cases where $\beta$-Sn nanocrystal cubes are used as precursors, the shape is conserved in the derivative intermetallic nanocrystals, and this represents a rare single crystal-to-single crystal conversion that is likely facilitated by the similar structures of $\beta$-Sn and FeSn$_2$ (Figure 2-13).
While not yet exhaustive, these results provide a set of empirical guidelines for controlling the shapes of intermetallic nanocrystals that contain elements of notably different reduction potentials, reduction kinetics, and reactivity. This is especially useful because the techniques that have been developed in the past few years for perfecting the synthesis of shape-controlled metal\textsuperscript{11} and semiconductor\textsuperscript{22} nanocrystals do not generally appear to work well with these multi-metal intermetallic systems for the reasons noted above. By combining these new guidelines for shape-controlled synthesis with our earlier studies on the synthesis and reactivity of intermetallic nanocrystals,\textsuperscript{19,26-27} it is reasonable to anticipate that complex binary and ternary intermetallic nanocrystals in a variety of technologically-useful systems may be accessible as nanoscale rods, wires, cubes, spheres, triangles, platelets, and other morphologies that are available for the elemental systems that this chemical conversion strategy utilizes as reactive templates.

Figure 2-13 Crystal structures of $\beta$-Sn and CuAl$_2$-type FeSn$_2$ (green = Fe, purple = Sn), highlighting conserved structural features (zigzag chains of Sn atoms) that likely help to facilitate the single crystal-to-single crystal transformation.
In addition to its utility for generating intermetallic nanocrystals with a variety of shapes, this chemical conversion strategy has also proven to be useful for generating intermetallic compounds that can be challenging to prepare using traditional solid-state synthesis techniques. As such, it could serve as an interesting alternative to other non-equilibrium strategies for the synthesis of new, metastable, and low-temperature phases. Importantly, the temperature range in which this strategy is most successful (100 – 250 °C) is one that is difficult to access for intermetallics using other solid-state methods, so it is reasonable to anticipate that this technique may open the door to the discovery of new compounds as nanocrystals. The ability to combine unique synthetic capabilities with shape-controlled nanocrystal synthesis using simple solution chemistry techniques has the potential to greatly expand the complexity of solid-state materials that are accessible as nanostructures. This, in turn, will be important for accessing many technologically-relevant nanomaterials, including anisotropic magnets, highly-faceted nanoparticle catalysts, and nanostructures with interesting size- and dimension-dependent optical, electronic, and structural properties.

2.5 References


(b) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science*


A.K.; Leonard, B.M.; Cable, R.E.; Bauer, J.C.; Han, Y.-F.; Means, J.; Teizer, W.;

Chapter 3

A Library of Single-Crystal Metal-Tin Nanorods: Using Diffusion as a Tool for Controlling the Morphology of Intermetallic Nanocrystals

3.1 Introduction

Intermetallic compounds of the late transition metals form over a range of compositions and adopt many different crystal structures. This compositional and structural diversity makes intermetallics important and versatile materials for a variety of applications, including superconductors, magnetics, shape memory alloys, hydrogen storage materials, catalysts, and electrodes. However, because of this chemical diversity, synthesizing nanocrystalline intermetallic compounds with controlled shapes and sizes can be difficult. The methods typically used to rigorously control nanocrystal morphology use ligands, surfactants, or polymers that tend to bind preferentially to one or more surfaces, thereby limiting growth in certain directions and leading to nanocrystals with well-defined shapes. Finding the appropriate combination of surfactants to facilitate shape-controlled growth in nanocrystalline intermetallic systems is not

impossible, but remains rare and can be difficult to generalize to other systems.

Here we describe a general template-based strategy for synthesizing a library of morphology-controlled $M$-Sn ($M = $ Co, Ni, Cu, Ag, Au, Pt, Ru) intermetallic nanorods. This work builds significantly on results reported by several groups in the past few years involving the use of nanocrystal templates to generate derivative nanocrystals via a diffusion mechanism. For example, researchers have been able to synthesize Ag$_2$Se nanowires by reacting Se nanowires with a solution of AgNO$_3$, as well as a variety of hollow metal sulfides, phosphides, and oxides using reactions that employ a nanoscale Kirkendall effect. Some intermetallic nanocrystals with predominantly spherical and cubic shapes can also be generated using these methods. However, unlike previous reports, here we establish general and predictive guidelines for accessing single-crystal nanorods in a large number of chemically distinct intermetallic systems. We also demonstrate the ability to selectively generate hollow vs. dense nanorods, including within the same system. The formation of one-dimensional nanostructures of these compounds using a unified and materials-general method is significant, because the target systems represent a diverse range of useful materials that have known dimension- and size-dependent properties, including superconducting AuSn, catalytically active PtSn, and Ni$_3$Sn$_4$ and Cu$_6$Sn$_5$ with Li insertion capabilities for battery applications.
3.2 Experimental Section

3.2.1 Chemicals

The following metal reagents were used: SnCl\textsubscript{2} (anhydrous, 99% min.), CoCl\textsubscript{2}·6H\textsubscript{2}O (98.0-102%), NiCl\textsubscript{2}·6H\textsubscript{2}O (99.95%), Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (98.0-102%), RuCl\textsubscript{3}·6H\textsubscript{2}O (99.9%), HAuCl\textsubscript{4}·3H\textsubscript{2}O (Au 49.5% min), K\textsubscript{2}PtCl\textsubscript{6} (Pt 40.11%), AgNO\textsubscript{3} (99.9+%). The reducing agent, surface stabilizer, and solvent were NaBH\textsubscript{4} (98%), poly(vinyl pyrrolidone) (PVP, MW =630 000), tetraethylene glycol (TEG, 99+%), and ethylene glycol (EG, 99+) respectively. All chemicals were purchased from Alfa Aesar and used as received.

3.2.2 Synthesis of $\beta$-Sn Nanorods

Sn nanorods, used as templates, were synthesized in manner similar to that of our previous report.\textsuperscript{13} First, 0.4 g of PVP (MW = 630 000) was dissolved in 45 mL of TEG at room temperature. SnCl\textsubscript{2} (0.08 g in 4 mL of TEG) was added, along with a freshly prepared solution of NaBH\textsubscript{4} (0.264 g in 8 mL of TEG) while stirring. The temperature was gradually increased to 100 °C over 40 min. Concurrently, $\beta$-Sn seed nanocrystals were prepared by sequentially adding 0.25 g of PVP, 0.05 g of SnCl\textsubscript{2}, and 0.16 g of NaBH\textsubscript{4} to 20 mL of TEG at room temperature. This solution of $\beta$-Sn seed nanocrystals was added to the original $\beta$-Sn nanocrystal solution at 100 °C, then heated to 160 °C for 1 h. The temperature was then increased to 190 °C, and the solution was removed from the
heat. The predominately rod-shaped β-Sn nanocrystals were isolated by centrifugation and washed with ethanol.

### 3.2.3 Synthesis of Intermetallic Nanorods

To synthesize intermetallic $M$-Sn ($M = \text{Co, Ni, Au, Cu, Ag, Ru, Pt}$) nanocrystals at different reaction temperatures, the temperature of the solution of β-Sn seed nanocrystals was adjusted for the desired reaction temperature after synthesizing β-Sn nanorods. After reaching the desired reaction temperature, the appropriate metals salts were added to the solution of β-Sn seed nanocrystals: CoCl$_2\cdot$6H$_2$O (0.29 mmol, 0.07 g in 5 mL of TEG at 150 °C or above as described in the text), NiCl$_2\cdot$6H$_2$O (0.336 mmol, 0.08 g in 5 mL of TEG at 150 °C), HAuCl$_4\cdot$3H$_2$O (0.25 mmol, 0.098 g in 5 mL of TEG at 150 °C and 0.35 mmol, 0.137 g in 5 mL of TEG at room temperature and 0 °C), Cu(NO$_3$)$_2\cdot$3H$_2$O (0.175 mmol, 0.042 g in 5 mL of TEG at 150 °C and 0.25 mmol, 0.07 g in 5 mL of TEG at room temperature and 0 °C), AgNO$_3$ (0.2 mmol, 0.0339 g in 5 mL of TEG at 150 °C and 0.2 mmol, 0.0339 g in 5 mL of TEG at room temperature and 0 °C). For RuSn$_2$ and PtSn, the temperature of the β-Sn nanorod solution was held at 190 °C, then sequentially RuCl$_3\cdot$6H$_2$O (0.3 mmol, 0.06 g in 5 mL of EG, ethylene glycol) and K$_2$PtCl$_6$ (0.35 mmol, 0.17 g in 10 mL of EG) were added to the solution of β-Sn nanorods. The temperature was then increased to 200 °C and 290 °C, respectively. After reaching the desired temperature, the temperature was held for 30 min.
3.2.4 Characterization

X-ray diffraction (XRD) data were collected on a Bruker GADDS three-circle X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns, and energy-dispersive X-ray analysis (EDS) were collected using a JEOL JEM-2010 TEM. Samples were prepared by sonicating the nanocrystalline intermetallic powders in ethanol and dropping a small volume onto a carbon-coated nickel or copper grid.

3.3 Results and Discussion

3.3.1 Syntheses of a Library of Intermetallic Nanorods

Single-crystal nanorods of β-Sn (~72 % yield with additional spheres present) were synthesized using a multi-step seed-mediated strategy involving the reaction of SnCl₂ with NaBH₄ in tetraethylene glycol (TEG) in the presence of poly(vinylpyrrolidone) (PVP). These β-Sn nanocrystals (Figure 3-1), while not perfectly uniform in size or shape purity, are among the best reported in the literature for β-Sn in this size range and are of sufficient quality to draw meaningful conclusions from the studies that follow. When reacted with optimized amounts of appropriate metal salt solutions and excess NaBH₄ in TEG at temperatures of 150 °C or higher, the β-Sn nanorods cleanly convert to nanocrystalline M-Sn (M = Co, Ni, Cu, Ag, Au, Pt, Ru) intermetallic compounds, based on the XRD data shown in Figure 3-2 and in Figure 3-3. Interestingly, RuSn₂ is an elusive compound in bulk systems, described in the literature
as a metastable phase that does not appear on the equilibrium Ru-Sn phase diagram and one that is difficult to access synthetically and stabilize.\textsuperscript{[16]} RuSn\textsubscript{2} appears to form reproducibly using this template-based synthetic strategy.

Figure 3-1 Large-area TEM micrograph of $\beta$-Sn nanorods used as seeds.
Figure 3-2 Powder XRD patterns for nanocrystalline intermetallics formed by reacting β-Sn nanocrystals with appropriate metal salt solutions under reducing conditions. (a) PtSn, AuSn, Ag₄Sn, and Cu₆Sn₅, (b) CoSn₃, and (c) RuSn₂. Top: experimental. Bottom: patterns from PDF card # 25-0614 (PtSn); 8-0463 (AuSn); 29-1151 (Ag₄Sn); 45-1488 (Cu₆Sn₅); 48-1813 (CoSn₃); 51-0741 (RuSn₂).
Despite the fact that the conversion reactions cleanly yield $M$-Sn intermetallics, the transmission electron microscopy (TEM) images in Figure 3-4 show clear differences in the morphologies of the intermetallic nanocrystal products. When reacted with CoCl$_2$·6H$_2$O at 150 °C, the $\beta$-Sn nanorod templates form predominantly dense CoSn$_3$ nanorods. When reacted with NiCl$_2$·6H$_2$O at 150 °C, however, Ni$_3$Sn$_4$ forms a mixture of dense (minor product) and hollow (major product) nanorods. Similar reactions of $\beta$-Sn nanorods with Cu(NO$_3$)$_2$·3H$_2$O, AgNO$_3$, and HAuCl$_4$·3H$_2$O at 150 °C form Cu$_6$Sn$_5$, Ag$_4$Sn, and AuSn intermetallics, respectively, with dense spherical morphologies rather than nanorod shapes. Finally, reactions of $\beta$-Sn nanorods with RuCl$_3$·xH$_2$O at 200 °C and K$_2$PtCl$_6$ at 290 °C (the minimum temperatures necessary to form the desired Ru and Pt intermetallic products) produce hollow nanorods of RuSn$_2$ and PtSn, respectively, with no dense nanorods observed in panels of g and h in Figure 3-4 and larger area of TEM

Figure 3-3 Powder XRD patterns for $\beta$-Sn (left) and Ni$_3$Sn$_4$ (right). All other XRD data is shown in Figure 3-2 in the text.
image of hollow nanorods of RuSn$_2$ in Figure 3-5. For the systems that yield intermetallic nanorods, the yield of nanorods is always between 65-70%, which agrees well with the percentage of nanorods in the $\beta$-Sn precursor samples (~72%) and indicates that a large majority of the nanorods are converted with shape retention. Selected area electron diffraction (SAED) patterns, included in Figure 3-4 confirm the formation of intermetallic nanocrystals in all of the $M$-Sn systems, since these compounds are line phases that have narrow composition windows and composition-dependent crystal structures that differ from their constituent elements. The intermetallic nanorods produced from these reactions are generally single crystals, as shown for hollow nanorods of Ni$_3$Sn$_4$ (Figure 3-6a) and PtSn (Figure 3-7) and dense nanorods of CoSn$_3$ (Figure 3-6b).
Figure 3-4 TEM micrographs and SAED patterns of nanocrystalline (a) β-Sn, (b) CoSn₃, (c) Ni₃Sn₄, (d) AuSn, (e) Cu₆Sn₅, (f) Ag₄Sn, (g) RuSn₂ (200 °C), and (h) PtSn (290 °C). All reactions were carried out at 150 °C unless otherwise noted. Scale bars are 20 nm:
Figure 3-5 Larger-area TEM micrograph of RuSn$_2$ (200 °C).
Figure 3-6 High resolution TEM micrographs of (a) hollow single-crystal Ni$_3$Sn$_4$ nanorods and (b) dense single-crystal CoSn$_3$ nanorods. Scale bars are 5 nm.
3.3.2 Study of reaction temperatures and diffusion rates

Building on this observation, the Cu-Sn system was studied in detail. When reacted with CuCl₂·3H₂O at 150 °C, β-Sn nanorods convert to Cu₆Sn₅. However, the nanorod morphology is destroyed and the products are exclusively spherical nanocrystals (Figure 3-4e), which represent the equilibrium nanocrystals shapes that form via direct synthesis without the use of shape-controlled templates. When the reaction is carried out
at room temperature, spherical Cu$_6$Sn$_5$ nanocrystals are also formed (Figure 3-8a). However, when cooled to 0 °C, the nanorod shape is retained, generating single-crystal intermetallic Cu$_6$Sn$_5$ nanorods (panels b and e in Figure 3-8). Likewise, when β-Sn nanorods are reacted with HAuCl$_4$·3H$_2$O and AgNO$_3$ at 0 °C, single-crystal AuSn (panels d and f in Figure 3-8) and Ag$_4$Sn (Figure 3-8g) nanorods, respectively, are formed. This is in contrast to the AuSn and Ag$_4$Sn nanospheres that form at 150 °C (panels d and f in Figure 3-4) and room temperature (Figure 3-8c). Thus, for the systems that initially appeared unable to retain the morphology defined by the β-Sn nanorod templates, using a significantly lower reaction temperature facilitated morphological retention and yielded single-crystal nanorods. These results demonstrate that single-crystal intermetallic nanorods are accessible in all of the $M$-Sn systems studied using a single unified process, and imply that conditions could be identified to expand the library of intermetallic nanorods to include many other systems.
The results presented above can be combined to yield a self-consistent and predictive set of guidelines for rationally generating morphology-controllable intermetallic nanocrystals, and also for understanding the conditions under which intermetallic nanocrystals can be synthesized using diffusion-based template approaches. As one would predict, temperature plays a primary role in the formation of intermetallic nanocrystals, as well as the ability to retain the morphology of the β-Sn nanocrystal.
templates. The process that converts $\beta$-Sn nanorods to $M$-Sn nanorods is a diffusion-based process, and diffusion is a temperature-dependent phenomenon.\textsuperscript{17-18} For example, the morphology of CoSn$_3$ synthesized at 150 °C shows dense nanorods, while CoSn$_3$ produced at 180 °C consists of a mixture of the hollow nanorods and spheres, showing the intermediate stage between the fragmentation of nanorods into spheres (Figure 3-9). The melting point of an element can serve as a rough estimate of its rate of diffusion relative to that of other elements.\textsuperscript{18} This is useful for establishing qualitative and empirical guidelines for differences in reactivity among several comparable systems, especially considering the inherent complexity of nanoscale diffusion phenomena. Accordingly, the melting points of the transition elements used in this study define three diffusion categories (melting points, in °C,\textsuperscript{19} are in parentheses): (a) fast diffusers – Ag (961), Au (1064), Cu (1084); (b) moderate diffusers – Ni (1455), Co (1495); and (c) slow diffusers – Pt (1768), Ru (2334). The fast diffusers, which are known to have diffusion rates a few orders of magnitude greater than self diffusion (e.g. Sn in Sn),\textsuperscript{20} diffuse so fast that they destroy the template, precluding shape retention. Cooling the reaction sufficiently low to slow down diffusion in these systems facilitates shape retention, yielding single-crystal nanorods. The moderate diffusers are able to retain shape at moderate temperatures ($\sim$ 150 °C), with some remaining dense and others becoming hollow. Finally, the slow diffusers do not completely diffuse into the $\beta$-Sn nanocrystal templates until higher temperatures (> 200 °C), precluding the formation of intermetallic compounds at lower temperatures. Since their diffusion into the $\beta$-Sn nanocrystal
templates is slow relative to the rate of outward Sn diffusion, voids are created in the center of the nanorods, generating hollow nanorods via a nanoscale Kirkendall effect.\textsuperscript{9-13}

In addition to providing guidelines relevant to morphology control, these results also provide insight into understanding the lowest temperatures that intermetallic compounds can form using low-temperature solution chemistry routes. For example, the low-melting fast diffusers (Ag, Au, Cu) can form $M$-Sn intermetallics at or below room temperature. The high-melting slow diffusers (Pt, Ru) do not react with Sn at room temperature, and require significantly higher temperatures ($> 200 \degree\text{C}$) to form

Figure 3-9: TEM micrographs of (a) hollow single-crystal CoSn$_3$ nanorods and (b) a larger-view image showing the beginning of fragmentation into smaller spherical nanoparticles. The corresponding SAED pattern is shown in (c). Scale bars are 20 nm.
intermetallics. The intermediate melting and diffusing elements (Fe, Ni, Co) do not form intermetallics at room temperature, but react with Sn at moderate temperatures (~ 150 °C) to form intermetallics. This understanding, when coupled with the growing library of intermetallic compounds that are accessible as nanocrystals using similar routes, could aid our synthetic efforts and further expand our ability to generate nanocrystalline intermetallics on-demand in a variety of other systems.

3.4 Conclusions

In summary, we have shown that a library of single-crystal $M$-Sn intermetallic nanorods can be synthesized by exploiting the diffusion characteristics of the reacting metals. This information (relative diffusion rates estimated from melting points), which is well established in bulk and thin film systems, can be used as a predictive guideline in nanocrystal systems for establishing optimal reaction temperatures that (a) maintain the morphologies of the Sn nanocrystal templates (e.g. preferentially access spheres vs. nanorods), (b) generate dense vs. hollow nanorods via a nanoscale Kirkendall effect, and (c) allow one to estimate the relative minimum temperatures necessary for forming intermetallic compounds using low-temperature solution routes. This understanding, and its ability to be applied as a unified synthetic strategy in a practical and general manner, is important for advancing the morphology-controlled synthesis of a large number of technologically-relevant intermetallic and other multi-element nanocrystals using robust diffusion-based strategies.
3.5 References


Chapter 4

Room-Temperature Chemical Synthesis of Shape-Controlled Indium Nanoparticles

4.1 Introduction

The synthesis of shape-controlled metal nanocrystals is motivated by their wide range of properties that are useful for applications that include optics, electronics, magnetism, and catalysis. As a target for shape-controlled nanocrystal synthesis, indium metal is attractive because it is superconducting, is active for surface plasmon resonance (SPR), and is used as a component in low-melting solders and solid-state lubricants. Furthermore, the use of preformed shape-controlled nanoparticles as reactive templates is of potential importance to synthesize a variety of useful nanostructure materials. Previously, we have shown that single-metal nanocrystals can serve as reactive templates for the formation of more complex nanostructured compounds, including intermetallics, metal phosphides, and ternary metal oxides. For In based nanostructured materials, heterogeneous catalyst (e.g., in organic synthesis), III-V semiconductors (e.g., for light emitting diodes), optical materials (e.g., ITO as transparent conductive oxide), and In

based intermetallics and alloys can be potentially among the technologically relevant materials.\textsuperscript{7} Nanocrystalline In with predominantly spherical shapes has been synthesized using a variety of physical and chemical methods. Representative physical methods include laser ablation,\textsuperscript{8} evaporation,\textsuperscript{2} ultrasonication,\textsuperscript{5} and dispersing molten In into paraffin oil.\textsuperscript{9} Chemical methods have typically required the use of strong reducing agents such as sodium metal,\textsuperscript{3} zinc powder,\textsuperscript{10} and alkalides and electrides.\textsuperscript{11} Decomposition of low-valent organometallic complexes has also been used to synthesize In nanoparticles\textsuperscript{12} and nanowires.\textsuperscript{13} Except for thermal decomposition method, many chemical and physical approaches have resulted in uncontrolled products in terms of particle sizes and shapes.

While many chemical and physical approaches have been performed under harsh reaction conditions (e.g., high reaction temperatures and strong reducing agents), a majority of chemical approaches used for synthesizing shape-controlled metal nanoparticles such as Ag an Au have been conducted under mild reaction conditions.

While In\textsuperscript{3+} should be reducible to In\textsuperscript{0} by BH\textsubscript{4}\textsuperscript{−} based on standard reduction potentials ($E_{\text{In}^{3+}/\text{In}}^{\circ} = -0.338$ eV vs SHE, $E_{\text{BH}_3/\text{BH}_4^-}^{\circ} = -0.481$ eV vs SHE), there have been no reports describing the synthesis of In nanocrystals using borohydride reduction, polyol reactions, or related mild solution methods that are among the most common strategies for generating shape-controlled nanocrystals.\textsuperscript{14} Here we describe a simple kinetically controlled borohydride reduction process for synthesizing shape-controlled In nanocrystals at room temperature.
4.2 Experimental Section

4.2.1 Chemicals

Isopropyl alcohol (IPA, ACS GR, min 99.5% IPA, max 0.2% H2O), Methanol (99.9%), were purchased from EMD Chemicals via VWR. Ethanol (99.5%) was purchased from Pharmco. Deionized water (NANO pure, 18.2 MΩ) was used for water as reaction solvent. NaBH4 (98%), poly(vinyl pyrrolidone) (PVP, MW = 630,000), tetraethylene glycol (TEG, 99+%), In(ClO4)3·8H2O (99.9 %), In(NO3)3·xH2O (99.99%), InBr3 (99.99%), and InCl3 (99.99%) were purchased from Alfa Aesar. NaBH4, 2.0M solution in triethylene glycol dimethyl ether as reducing agent was purchased from Sigma-Aldrich. All chemicals were used as received without further processing or purification.

4.2.2 Synthesis of In Nanowire, Octahedra, and Truncated Octahedra

In nanowires were synthesized by the dropwise addition of a solution of NaBH4 in tetraethylene glycol (TEG) to a solution of InCl3 and poly(vinyl pyrrolidone) (PVP, MW = 630,000) in isopropyl alcohol (IPA). In a typical synthesis, InCl3 (10 mg) and PVP (0.10 g) were dissolved in 10 mL of IPA. After purging with Ar, 10 drops of NaBH4/TEG at a rate of 1 drop every 2s, then waiting 50 s before adding 5 additional drops at the same rate were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol. It is important to note that if
an IPA solution of NaBH₄ is used, In nanocrystals do not form, presumably because of a faster reaction of NaBH₄ with the alcohol than with In³⁺. Using TEG as the solvent for NaBH₄ maintains its reactivity long enough to reduce In³⁺ to In⁰ after it is added to IPA.

In octahedra were synthesized by the dropwise addition of a solution of NaBH₄ in tetraethylene glycol (TEG) to a solution of InCl₃ and poly(vinyl pyrrolidone) (PVP, MW = 630,000) in isopropyl alcohol (IPA). In a typical synthesis, InCl₃ (10 mg) and PVP (0.10 g) were dissolved in 10 mL of IPA. After purging with Ar, 15 drops of NaBH₄/TEG at a rate of 1 drop/s were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

In truncated octahedra were synthesized by the dropwise addition of a solution of NaBH₄ in tetraethylene glycol (TEG) to a solution of InCl₃ and poly(vinyl pyrrolidone) (PVP, MW = 630,000) in isopropyl alcohol (IPA). In a typical synthesis, InCl₃ (10 mg) and PVP (0.10 g) were dissolved in 10 mL of IPA. After purging with Ar, 10 drops of NaBH₄/TEG at a rate of 1 drop/s were added, followed by an 8-s pause and the addition of the remaining 5 drops at a rate of 1 drops/s to the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

4.2.3. Synthesis of In Spheres, Decahedra, Triangles, Nanowires, and Star-Like Shapes

In spheres were synthesized by the dropwise addition of a 2.0 M solution of NaBH₄ in triethylene glycol dimethyl ether (Triglyme) to a solution of and poly(vinyl
pyrrolidone) (PVP, MW = 630,000) in ethylene glycol (EG). In a typical synthesis, In(ClO₄)₃·8H₂O (10 mg) and PVP (0.10 g) were dissolved in 10 mL of EG. After purging with Ar, 15 drops of NaBH₄/TEG at a rate of 1 drop/10s were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

In decahedra were synthesized by the dropwise addition of a 2.0 M solution of NaBH₄ in triethylene glycol dimethyl ether (Triglyme) to a solution of In(ClO₄)₃·8H₂O and poly(vinyl pyrrolidone) (PVP, MW = 630,000) in ethylene glycol (EG). In a typical synthesis, In(ClO₄)₃·8H₂O (40 mg) and PVP (0.10 g) were dissolved in 10 mL of EG. After purging with Ar, 15 drops of NaBH₄/TEG at a rate of 1 drop/20s were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

In triangles were synthesized by the dropwise addition of a solution of NaBH₄ in tetraethylene glycol (TEG) to a solution of InCl₃, poly(vinyl pyrrolidone) (PVP, MW = 630,000), and 5 mg of NaCl in ethylene glycol (EG). In a typical synthesis, InCl₃ (10 mg) and PVP (0.10 g) were dissolved in 10 mL of EG. After purging with Ar, 15 drops of NaBH₄/TEG at a rate of 1 drop/s were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

In nanowires were synthesized by the dropwise addition of a solution of NaBH₄ in tetraethylene glycol (TEG) to a solution of InCl₃ and poly(vinyl pyrrolidone) (PVP, MW
= 630,000) in ethylene glycol (EG). In a typical synthesis, InCl$_3$ (10 mg) and PVP (0.10 g) were dissolved in 10 mL of EG. After purging with Ar, 15 drops of NaBH$_4$/TEG at a rate of 1 drop/40s were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

Star-like shape of In was synthesized by the dropwise addition of a solution of NaBH$_4$ in tetraethylene glycol (TEG) to a solution of InCl$_3$ and poly(vinyl pyrrolidone) (PVP, MW = 630,000) in water. In a typical synthesis, InCl$_3$ (10 mg) and PVP (0.10 g) were dissolved in 10 mL of water. After purging with Ar, 15 drops of NaBH$_4$/TEG at a rate of 1 drop/30s were added into the reaction. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol.

4.2.4 Characterization

Powder X-ray diffraction (XRD) data were collected on Bruker Advance D8 X-ray diffractometer using Cu Ka radiation. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were collected using a JEOL JEM-2010 LaB$_6$ microscope operating at 200kV. Samples for TEM analysis were prepared by dropping an ethanol solution containing the In nanoparticles onto the surface of a carbon coated copper or nickel grid. UV-vis data were collected using an Ocean Optics DH-2000-BAL with quartz cuvettes. Temperature dependent magnetization measurements at 8.5 Oe and 100 Oe applied fields were performed using a Quantum Design Superconducting Quantum Interference
Device (SQUID) magnetometer. Field emission scanning electron microscope (FESEM) images were taken by a JEOL 6700F operating at an accelerating voltage of 10 kV. FESEM samples were prepared by drying a drop of an ethanol suspension of particles onto a carbon-coated Cu grid, then mounting onto an Al specimen holder by carbon tape and coating with Ir.

4.3 Results and Discussion

4.3.1 Chemical Synthesis of In Nanowires, Octahedra, and Truncated Octahedra

The rate of dropwise addition of the NaBH$_4$/TEG solution to the InCl$_3$/IPA solution, and therefore the reduction kinetics, influenced the shape of the In nanocrystals. For example, Figure 4-1a shows transmission electron microscope (TEM) images of In nanowires (50-70 nm diameter, 3-4 µm long, 95% yield) synthesized by initially adding 10 drops of NaBH$_4$/TEG at a rate of 1 drop every 2 s, then waiting 50 s before adding 5 additional drops at the same rate. The selected area electron diffraction (SAED) pattern in Figure 4-2 confirms that the nanowires are comprised of In metal. The powder X-ray diffraction (XRD) pattern for this same sample (Figure 4-2) shows evidence of preferred orientation, with the 011, 002, and 022 peaks exhibiting relative intensities much higher than predicted for an isotropic sample. Figure 4-2 also shows the XRD pattern for irregularly-shaped In nanocrystals synthesized without controlling the reduction rate (Figure 4-3), which shows no preferred orientation.
Figure 4-1 TEM micrograph of indium (a) nanowires, (b) octahedra, and (c) truncated octahedra synthesized by borohydride reduction of In$^{3+}$. 

---

**Figure 4-1 TEM micrograph of indium (a) nanowires, (b) octahedra, and (c) truncated octahedra synthesized by borohydride reduction of In$^{3+}$.**
Figure 4-2 (Left) Powder XRD patterns for In nanoparticles and simulated XRD pattern for In metal; (right) higher-angle XRD data for all samples; (inset) representative SAED pattern for In nanowires.
When the reduction rate is increased, other nanocrystal morphologies can be accessed. For example, upon adding 15 drops of NaBH₄/TEG solution at a rate of 1 drop/s, 80 ± 7 nm In octahedra are formed in 85% yield (Figure 4-1b). When 10 drops of NaBH₄ solution are added at a rate of 1 drop/s, followed by an 8-second pause and the addition of the remaining 5 drops at a rate of 1 drop/s, 95 ± 5 nm truncated octahedra are formed in 80% yield (Figure 4-1c). Preliminary evidence suggests that other shapes, including triangles and decahedra, can also be accessed.
4.3.2 Mechanism of In Nanowire Formation

Shape control in this system appears to be driven by reduction kinetics, rather than by the influence of different types or concentrations of surface stabilizers or additives that are typically used for synthesizing non-spherical nanocrystals.\(^\text{14}\) Other shape-controlled metal nanocrystals have been proposed to form by a similar mechanism.\(^\text{15}\) The initial slow reduction step generates octahedral In nanoparticles, which act as seeds for the growth of nanowires. Preliminary data are consistent with this hypothesis, showing nanowires growing off of octahedra (Figure 4-4). This is also consistent with the XRD data showing preferred orientation, which correlates well with the observed morphologies and crystal growth directions (see Figure 4-5, 4-6, 4-7, 4-8, and 4-9). As shown in Figure 4-5, high-resolution TEM images of an indium octahedron are bounded by the 011 and 101 planes (highlighted in yellow), which help to explain the significant preferred orientation observed in the XRD data (enhanced intensity for 011 and 022 reflections). Furthermore, the In crystal structure in Figure 4-8, created by rotating to show the angles of intersection between the 011 and 101 planes, show that the angles formed by the octahedron and the angles formed by the intersection of the 011 and 101 planes are highly consistent, and imply that the octahedra are bounded by these planes. Again, this is consistent with the XRD data in Figure 4-2, which shows significant preferred orientation for the 011 and 022 reflections for the octahedra. Together with all evident data, In nanowires show enhanced intensity for the 002 and 020 reflections, since 002 and 020 will be parallel to the X-ray beam for nanowires that grow along 100, 010, 001 and are oriented due to their anisotropic shape. For the faster
reduction processes, a larger number of seeds are generated initially, limiting growth to zero-dimensional nanocrystals. Slower reduction (after the formation of seeds) leads to the growth of nanowires with tips that maintain the pointed geometry defined by the octahedral seeds (Figure 4-4d).

Figure 4-4 TEM images from intermediate stages of the reaction: (a) In nanowires growing off of octahedra seeds; (b,c) nanowires becoming thicker as the reaction progresses. (d) Enlarged TEM image showing the nanowire tips, which maintain the points defined by the octahedral seeds.
Figure 4-5 High-resolution TEM micrograph of an indium octahedron, showing planar spacings that match well with the 011 and 101 planes of indium metal ($d = 2.7 \text{ Å}$).
Figure 4-6 TEM micrograph of several indium octahedra (same image as shown in the inset to Figure 4-6), highlighting the angles formed by the edges of the octahedra. These angles compare favorably with those expected from the junction of the $011$ and $101$ planes (see Figure 4-7).
Figure 4-7 various representations of the crystal structure of indium: (a) In, showing the unit cell; (b) expanded version of the In crystal structure, with the 011 (purple) and 101 (blue) planes highlighted (Note: the structure has been rotated 90° counterclockwise relative to its traditional orientation); (c) same orientation and coloring scheme as in (b), showing only the atoms in the 011 and 101 planes; (d) same orientation and coloring scheme as in (c), rotated and showing the 002 plane (red plane) relative to 011 and 101.

Figure 4-8 Left: The In crystal structure in Figure 4-6c rotated to show the angle of intersection between the 011 and 101 planes. Right: TEM micrograph from Figure 4-5 showing an indium octahedron, highlighting the angles formed by the edges of the octahedra.
4.3.3 Study of Reduction Kinetics

As described previously, reduction kinetics can be controlled by adjusting the rate of dropwise addition of the NaBH₄/TEG solution to the InCl₃/IPA solution to yield various shapes of In nanoparticles. However, controlling reduction rates by adjusting the rate of dropwise addition of the NaBH₄/TEG solution are limited to a certain range. Thus, only a few shapes of In nanoparticles can be accessed by this approach. To expand the range of reduction rates, it is necessary to understand the fundamental chemistry behind this reduction reaction of sodium borohydride with alcohol type solvents. We attempted to expand the reduction rates by changing reaction solvents, metal precursors, and adding an additive (e.g., NaCl). Among these variables, the reaction solvents can be a critical parameter to expand the range of reduction rates. The reaction of sodium borohydride with an alcohol type solvent is a hydrolysis reaction that produces hydrogen gas. A closer look at this hydrolysis reaction provides important insights into how the

Figure 4-9 Proposed growth mechanism for the indium nanowires based on the preliminary data presented thus far: (a) octahedral seeds are formed from the initial reduction step; (b) slow reduction rates lead to growth of nanowires off of the tips of the octahedra in the [100], [010], and [001] directions; (c,d) the nanowires continue to grow in these directions, retaining the pointed tip defined by the octahedral seeds (see Figure 4-4).
hydrolysis reaction can be controlled. This hydrolysis reaction is associated with deprotonation of the solvent while the reaction occurs, simultaneously releasing hydrogen gas. In this regard, the acidity of reaction solvents can be a key parameter for controlling the hydrolysis reaction. The reaction solvent having high pKa value enables this hydrolysis to occur with slow reduction rates, while the hydrolysis reaction with the reaction solvent possessing low pKa value can generate fast reduction rates. Basically, the increase and/or the decrease of reactivity of sodium borohydride can be achieved by reaction with various alcohol type solvents, and a wide range of reduction kinetics can be generated. Based on this hypothesis, a variety of reaction solvents have been tested for obtaining a wide range of reduction kinetics. For the case of ethylene glycol as reaction solvent, ethylene glycol can provide the fastest reduction kinetics, since EG is among the solvents having the lowest pKa values, while, as shown in the previous chapter, IPA has a relatively high pKa value,¹⁸ which was used for synthesizing In nanowires, octahedra, and truncated octahedra.

The syntheses of In decahedra and spheres were performed by carefully varying the rate of dropwise addition of sodium borohydride solution in ethylene glycol. Decahedra and spheres are relatively stable products compared to other shapes.¹⁹ Therefore, the fastest reduction kinetics are likely to lead to the formation of spherical and decahedral In nanoparticles. Upon adding 15 drops of 2.0 M NaBH₄ in Triglyme solution at a rate of 1 drop/10s, 70 nm In nanospheres are formed with a relatively broad size distribution (Figure 4-10). When 15 drops of 2.0 M NaBH₄ solution are added at a rate of 1 drop/20s, 100 nm decahedra In nanoparticles are formed in 80 % yield (Figure 4-11). For the synthesis of spherical and decahedral In nanoparticles, sodium borohydride
2.0 M solution in Triglyme was used for reduction of In\(^{3+}\) instead of tetraethylene glycol as a solvent, since Triglyme is an inert solvent with excellent chemical stability, which can presumably maximize the reactivity of sodium borohydride in alcohol solvent.

Furthermore, instead of using InCl\(_3\), In(ClO\(_4\))\(_3\) \(\cdot\) 8H\(_2\)O was also used for syntheses of In nanospheres and decahedra. Preliminary data suggest that the reduction kinetics can be varied by metal precursors as well. The fastest reduction kinetics are achieved by In(ClO\(_4\))\(_3\) \(\cdot\) 8H\(_2\)O, then InCl\(_3\) that is very similar with InBr\(_3\), and In(NO\(_3\))\(_3\) \(\cdot\) xH\(_2\)O that is difficult to be reduced by sodium borohydride solution. This different reduction capability in metal precursors can be associated with chemical reactivity of metal precursors.\(^{20}\)
Figure 4-10 TEM micrograph of spherical In nanoparticles.
Figure 4-11 TEM micrographs of decahedral In nanoparticles
For the synthesis of triangular In nanoparticles, NaCl was added to the reaction as an additive with the use of InCl₃ as metal precursor. The reaction of sodium borohydride with InCl₃ produces NaCl, and the addition of sodium chloride to the reaction can influence its equilibrium, which can be pushed forward or backward depending on the amounts of sodium chloride, eventually influencing the reduction kinetics. For comparison, experiments were performed without NaCl and different amounts of NaCl under otherwise identical reaction conditions. When 5 mg of NaCl was added to the reaction, the percentage of triangle-shaped In nanoparticles with 110 nm particle size are 50% as shown in Figure 4-12, while without addition of NaCl, In triangles are formed in 20-25% yield (not shown). With 11 mg of NaCl, the final product consists of irregular-shaped In nanoparticles with few triangle nanoparticles, due largely to too slow reduction rate to achieve this shape. Again, this result suggests that additions can also influence the reduction kinetics, which is very consistent with the hypothesis.
Consistent with the hypothesis, In nanowires (70-80 nm diameter, 3-4 \( \mu \)m long, 75 % yield) are again accessed in ethylene glycol as reaction solvent with a much slower
rate of addition of sodium borohydride (15 drops of sodium borohydride at a rate of 1 drop/40s) than in IPA (10 drops of NaBH$_4$/TEG at a rate of 1 drop every 2s, then waiting to 50 s before adding 5 additional drops at the same rate). (Figure 4-13). This result can be useful for the synthesis of In based alloys and intermetallics. Some intermetallics and alloys can be only accessed at higher temperature than room temperatures.$^{21}$ Thus the exploration of synthetic conditions of the synthesis of In nanowires in ethylene glycol can be beneficial for direct use of preformed In nanowires as reactive templates for the syntheses of In based alloys and intermetallics without isolation and re-dispersion of In nanoparticles into high boiling point solvent.
Figure 4-13 TEM micrographs of In nanowires synthesized in ethylene glycol.
Interestingly, In nanoparticles are generated even in water. With careful control of the rate of addition of sodium borohydride, star-like shapes of In nanoparticles in water are formed with 70-80 nm diameter and 450-500 nm long, with 90% yield. (Figure 4-14). Again without control of the rate of addition of sodium borohydride, only irregular-shaped In nanoparticles are formed. However, only water can facilitate the formation of star-like shape of In nanoparticles at room temperature, which is also consistent with the hypothesis. When 15 drops of sodium borohydride solution are added at a rate of 1 drop/30s, the star-like shape of In nanoparticles are formed (Figure 4-14).

To understand growth mechanism of the star-like shaped In nanoparticles, TEM samples were intermittently taken during the growth progress as a function of time. The reaction intermediates observed by TEM show a couple of stages before the formation of star-like shape of In nanoparticles (Figure 4-14a, b, and c). At the initial stage (t = 150s), the small In nanospheres are formed, and subsequently, nanowire-like shape is formed via self-assembly mechanism, following formation of a bundle by stacking a couple of nanowires. These bundles of nanowires seem to start to form the branches from the backbone of a bundle of nanowires (t = 240s). At the last stage (t = 300s), complete formation of branch with backbone consisting of a couple of nanowires is observed. On the basis of TEM observations, we illustrate a schematic drawing in Figure 4-14d. The corresponding SAED pattern (inset) indicates that these star-like shaped In nanoparticles show some degree of amorphous feature relative to other shapes, probably contributed from smaller In nanospheres as well as the possible presence of amorphous indium oxide. Further detail study of the reaction pathway is in progress.
Considering all three parameters such as reaction solvent, additive, and addition rate of sodium borohydride solution, we were able to synthesize spheres, decahedra, triangles, star-like shape, and nanowires of In. Spherical In nanoparticles were synthesized by the addition of sodium borohydride with the rate of 1 drop/s that is an identical rate of addition of sodium borohydride used for obtaining In octahedra. However, In octahedra are formed in isopropyl alcohol with sodium borohydride in
tetraethylene glycol, while the spherical In nanoparticles are formed in ethylene glycol with minor modification of reaction conditions, including use of Triglyme for sodium borohydride and \( \text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O} \). Again these results imply that different reduction kinetics can be accessed by varying reaction solvents, metal precursors, use of an additive, and use of Triglyme as a solvent for sodium borohydride. Table 4-1 summarize all reaction parameters for obtaining various shapes of In nanoparticles.

<table>
<thead>
<tr>
<th>Spheres</th>
<th>Decahedra</th>
<th>Triangles</th>
<th>Star-like shape</th>
<th>Wires</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursors</td>
<td>( \text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O} )</td>
<td>( \text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O} )</td>
<td>\text{InCl}_3</td>
<td>\text{InCl}_3</td>
</tr>
<tr>
<td>Solvents</td>
<td>Ethylene glycol</td>
<td>Ethylene glycol</td>
<td>Ethylene glycol</td>
<td>Water</td>
</tr>
<tr>
<td>Yield</td>
<td>100 %</td>
<td>80 %</td>
<td>50 %</td>
<td>95 %</td>
</tr>
<tr>
<td>Reduction rates</td>
<td>15 drops at a rate of 1 drop/10s</td>
<td>15 drops at a rate of 1 drop/20s</td>
<td>15 drops at a rate of 1 drop/s</td>
<td>15 drops at a rate of 1 drop/30s</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>2.0 M NaBH(_4) in Triglyme</td>
<td>2.0 M NaBH(_4) in Triglyme</td>
<td>0.37 M NaBH(_4) in TEG</td>
<td>0.37 M NaBH(_4) in TEG</td>
</tr>
<tr>
<td>NaCl</td>
<td>No</td>
<td>No</td>
<td>Yes (5 mg)</td>
<td>No</td>
</tr>
</tbody>
</table>

### 4.3.4 Optical Properties and Superconductivity of In Nanoparticles

In nanoparticles are known to exhibit an SPR peak at UV-visible wavelengths. The In octahedra show an SPR peak centered around 400 nm (Figure 4-15), which is within the range of reported wavelengths for the In SPR band.\(^3,^8,^9\) Also, bulk In metal is superconducting with \( T_c = 3.4 \text{ K} \),\(^2\) and all of the In nanoparticles are superconducting as
well. Temperature dependent magnetization data, $M(T)$, for each sample measured with 8.5 and 100 Oe applied fields are shown in Figure 4-16a and b, respectively. The data were normalized to the magnetic moment at $T = 1.8$ K. A sample of bulk In powder is included for comparison. All samples show diamagnetic behavior below 3.4 K, indicating the existence of the superconducting transition, even for the essentially zero-dimensional octahedra. Unlike the sharp transition observed in bulk In at 8.5 Oe (Figure 4b), a gradual drop in magnetization is seen in all of the In nanoparticle samples, similar to that observed for Sn and Pb nanowires.\textsuperscript{22} Interestingly, while measurements at 100 Oe significantly decrease $T_c$ in bulk In as expected because of its low critical field, $T_c$ remains almost unchanged for all of the In nanoparticle samples. This suggests that the In nanoparticles have a much higher critical field than bulk In, similar to recently reported results on In nanopowder synthesized via thermal evaporation of bulk In.\textsuperscript{2}

---

Figure 4-15 Representative UV-visible absorption spectrum of In nanoparticles (octahedra).
4.4 Conclusions

Shape-controlled In nanoparticles have been synthesized using a room-temperature NaBH$_4$ reduction strategy. In nanowires, octahedra, and truncated octahedra
can be accessed simply by changing the rate of dropwise addition of NaBH₄/TEG into a solution of InCl₃/PVP/IPA. For the cases of spherical, triangular, decahedra, and star-like shape In nanoparticles, the reaction conditions was slightly modified for obtaining optimal reduction rates by using different metal precursors, sodium borohydride in Triglyme, and addictive (NaCl) with carefully adjusting reduction rates. These nanoparticles exhibit the expected SPR properties, as well as superconductivity with a higher critical field than bulk In. It is anticipated that the shape-controlled In nanoparticles could also serve as templates for conversion into other In-based nanomaterials, including InP and In-based intermetallics.

4.5 References


Chapter 5
Chemical Synthesis of Shape- and Size-Controlled Ge Nanocrystals at Room Temperature

5.1 Introduction

Much effort into the synthesis of semiconductor nanocrystals, or quantum dots, has been made because of their unique optical, photophysical, and electronic properties that afford a large number of technological applications, including light-emitting diodes (LEDs), photodiodes, photovoltaic solar cells, gas sensors, and fluorescent labeling.¹ For example, CdSe, CdS, ZnS, and PbSe semiconductors have been intensively studied for decades, due to the various types of controllable synthetic approaches.²

Among the routes for synthesizing semiconductor nanocrystals, solution chemical methods provide much potential for producing well-controlled sizes, shapes, and even surface modifications with high chemical yields. Even though much progress has been made in the syntheses of many types of semiconductor systems via solution chemical methods,¹,² these solution chemical routes have not been applied to the production of group IV nanocrystals. Particularly, the synthesis of Ge nanocrystals has been challenging. Ge nanocrystals have several intriguing features, including a strong visible photoluminescence, larger Bohr radius than that of Si (indicating possible existence of quantum confinement for even larger particle sizes), and nontoxicity relative to other common semiconductor analogues (e.g., CdSe, PbS), affording biological applications without further chemical steps.³ These interesting characteristics have fueled the
development of chemical approaches for the synthesis of Ge nanocrystals. For example, many alternative solution-based approaches have been developed, including solution phase reduction of Ge(II) and Ge(IV) precursors by strong reducing agents (NaK alloy, sodium or lithium naphthalenide, sodium or lithium naphthalenide, sodium or lithium naphthalenide, supercritical thermolysis, thermal decomposition of organogermanes, GeI₂, and Ge(II) alkoxide precursors, and metathesis of Ge Zintl salts with GeCl₄. Although these synthetic routes have been somewhat successful synthesizing Ge nanocrystals with some degree of control, there still remain many obstacles to be overcome. Most reactions have been performed under harsh conditions. For instance, high reaction temperatures and high pressures are necessary to promote crystallization and/or thermally decompose the precursors, in which the solvents also can decompose, yielding undesirable byproducts that make the purification process difficult for obtaining the desired products. Strong reducing agents have been required, which can lead to poorly controlled shapes and sizes of nanocrystals. Some systems have been performed with a specialized experimental set-up to reach high pressures and high temperatures for the decomposition of precursors and for crystallization. Furthermore, under these harsh reaction conditions, there have been difficulties in finding appropriate precursors and reaction solvents.

Therefore, it is necessary to develop versatile synthetic approaches that can be carried out under mild reaction conditions, which can lead to more controllable products in terms of well-defined size and shape. Additionally, using mild reaction conditions would eliminate issues of the solvent decomposition, a delicate experiment set-up, and finding appropriate precursors and solvents. We have developed a mild chemical approach with kinetically controlled sodium borohydride reduction route to synthesize
various shaped In nanoparticles at room temperature. This chemical synthetic approach appears to be a general, robust, and facile chemical solution route relative to other solution based chemical approaches, especially useful for the metal systems that can be difficult to reduce by mild reducing agents. Herein, we present the synthesis of size- and shape-controlled germanium nanocrystals via kinetically controlled sodium borohydride reduction process at room temperature in the presence of poly (vinyl pyrrolidone)(PVP).

5.2 Experimental Section

5.2.1 Chemicals

Isopropyl alcohol (IPA, ACS GR, min 99.5% IPA, max 0.2% H2O) and methanol (99.9%) were purchased from EMD Chemicals via VWR. Ethanol (99.5%) was purchased from Pharmco. NaBH₄, 2.0M solution in triethylene glycol dimethyl ether as reducing agent, was purchased from Sigma-Aldrich. Poly(vinyl pyrrolidone) (PVP, MW = 630,000), GeCl₄ (99.99%), GeI₂ (99.99%), and GeI₄ (99.99%) were purchased from Alfa Aesar. All chemicals were used as received without further processing or purification.

5.2.2 Synthesis of Spherical and Cube-Like Germanium Nanocrystals

Spherical Ge nanocrystals were synthesized by the injection of a solution of NaBH₄ in triethylene glycol dimethyl ether (Triglyme) to a solution of GeCl₄ in the
presence of poly(vinyl pyrrolidone) (PVP, MW = 630,000) in ethylene glycol (EG). In a typical synthesis, GeCl₄ (267 μL) and PVP (0.05 g) were dissolved in 10 mL of EG. After purging with Ar, 6 mL of NaBH₄/Triglyme solution was added with a two-channel syringe pump (KD Scientific 200) at a rate of 1.5 mL/min for 2 mL and the addition of the remaining 4 mL of sodium borohydride solution at a rate of 0.15 mL/min to the reaction solution at ambient temperature. After 30 min of stirring, the precipitate was separated by centrifugation and washed with ethanol. The isolated product was easily dispersible in water and ethanol. It is worth pointing out that the desired product can be isolated from the precipitate. Because the precipitate is composed of a mixture of organic byproducts such as molecular species and/or oligomeric species with germanium nanocrystals, which is commonly observed in similar chemical approaches in the literature,⁴⁻⁷ the separation and purification processes were performed by exploiting the solubility differences of these mixtures; the desired germanium nanocrystals appear more soluble in ethanol than the byproducts.

In order to obtain cube-shaped germanium nanocrystals, the reduction kinetics were controlled via the injection rate of sodium borohydride solutions. 6 mL of NaBH₄/Triglyme solution was added with a two-channel syringe pump (KD Scientific 200) at a rate of 2.5 mL/min for 2 mL and the addition of the remaining 4 mL of sodium borohydride solution at a rate of 0.15 mL/min to the reaction solution at ambient temperature.

Germanium nanocrystals with the bimodal size distribution were synthesized with a higher concentration of germanium tetrachloride. Instead of using 267 μL of germanium tetrachloride (GeCl₄), 300 μL of germanium tetrachloride (GeCl₄) was
employed to yield bimodal size distribution of germanium nanocrystals with the same injection rate of sodium borohydride solution used for obtaining 6 nm in average diameter of germanium nanocrystals. In a typical synthesis, GeCl₄ (300 μL) and PVP (0.05 g) were dissolved in 10 mL of EG. After purging with Ar, 6 mL of NaBH₄/Triglyme solution was added with a two-channel syringe pump (KD Scientific 200) at a rate of 1.5 mL/min for 2 mL and the addition of the remaining 4 mL of sodium borohydride solution at a rate of 0.15 mL/min to the reaction solution at ambient temperature. The larger particles show a mean diameter of 10 nm and the smaller particles a mean diameter of 4 nm.

With ethanol as the reaction solvent instead of ethylene glycol, we have synthesized large Ge nanoparticles that are approximately 50 nm average diameter, which can not be produced in ethylene glycol. In a typical synthesis, GeCl₄ (267 μL) and PVP (0.05 g) were dissolved in 10 mL of EG. After purging with Ar, 6 mL of NaBH₄/Triglyme solution was added with a two-channel syringe pump (KD Scientific 200) at a rate of 1 mL/min for 2 mL and the addition of the remaining 4 mL of sodium borohydride solution at a rate of 0.25 mL/min to the reaction solution at ambient temperature.

5.2.3 Characterization

Powder X-ray diffraction (XRD) data were collected on Bruker Advance D8 X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were collected using a JEOL JEM-2010
LaB₆ microscope operating at 200kV. Samples for TEM analysis were prepared by dropping an ethanol solution containing the Ge nanoparticles onto the surface of a carbon coated copper or nickel grid. UV-vis data were collected using an Ocean Optics DH-2000-BAL with quartz cuvettes. Photoluminescence emission spectra were collected by a Photo Technology Instrument (PTI) using an 814 photomultiplier detection system with quartz cuvettes. The emission was monitored following excitation from a PTI N₂ dye laser (model GL-302). Two channel syringe pump (KD Scientific-200) was used to inject sodium borohydride solution to the reactions.

5.3 Results and Discussion

A representative TEM image of germanium nanocrystals synthesized by room temperature sodium borohydride reduction of precursor in the presence of PVP is shown in Figure 5-1. As shown in the low-resolution TEM image, the germanium nanocrystals have a average diameter of 6 nm, with high monodispersity, and are relatively free of organic contaminations that are often observed in the synthesis of germanium nanocrystals.⁴⁻⁷ The high resolution TEM image of a single Ge nanocrystal in Figure 5-1c shows the crystallinity of germanium nanocrystals. Most of the Ge nanocrystals are single domain crystals. The lattice fringes (2.00 Å) shown in Figure 5-1c correspond to \{220\} planes of diamond cubic structure of germanium. The selected area electron diffraction (SAED) pattern shows diffraction rings that clearly correspond to the \{111\}, \{220\}, \{311\}, \{331\}, and \{440\} diffraction planes. SAED pattern and lattice fringes exhibit signature of the diamond cubic structure of germanium.
Figure 5-2 shows powder X-ray diffraction patterns of the as-prepared germanium nanocrystals, as well as the sample annealed at 600 °C for 1h in argon. As shown in Figure 5-2a, the as-synthesized germanium nanocrystals have a characteristic of an amorphous phase of germanium. It is known that germanium has a strong covalent character. Thus, higher temperatures are, in general, necessary to crystallize the
amorphous phase of germanium. Therefore, the sample was annealed at 600 °C for 1h, and clearly shows diamond cubic structure of germanium. Several distinctive peaks match exactly with the simulated pattern of germanium. The energy dispersive x-ray spectroscopy (EDS) also confirms the presence of germanium in Figure 5-3. On the basis of all data available, it is evident that the composition and structure clearly confirm the diamond cubic structure of germanium.

As commonly observed in other chemical approaches,\textsuperscript{4-7} the final product contains a mixture of germanium nanocrystals with presumably organic byproducts that can be molecular and/or oligomeric species. Thus, the purification and separation process have been conducted with utilization of solubility differences in this mixture; the desired germanium nanocrystals appear more soluble in ethanol than the byproducts. Using other chemical approaches, it has been difficult to obtain germanium nanocrystals from these undesired byproducts. For example, the chemical approach performed with high temperature decomposition of tetraethylgermane (TEG) in organic solvents can produce germanium nanocrystals embedded in an organic matrix.\textsuperscript{7} Several dissolution steps can be required for separation of the desired germanium nanocrystals from the byproducts.

To verify the surface of germanium nanocrystals, FT-IR spectrum was collected (not shown). For comparison, two samples were characterized (one with only PVP and the other with germanium nanocrystals stabilized by PVP). Like other chemical reduction methods,\textsuperscript{4} the final product shows hydrogen terminated germanium nanocrystals. It is reported that hydrogen terminated germanium nanocrystals exhibit stretching vibration mode around 2100 cm\textsuperscript{-1}. Germanium nanocrystals capped with PVP show a stretching vibration mode around 2057 cm\textsuperscript{-1}. Even though FT-IR measurements
exclusively can not illustrate evidence of PVP binding to nanocrystals surface, FT-IR spectra show a presence of a hydrocarbon layer on the surface of nanocrystals.

Figure 5-2: Powder XRD patterns for (a) the as-prepared Ge nanocrystals and (b) Ge nanocrystals annealed at 600 °C for 1h.
As previously reported,\textsuperscript{11} of the reaction conditions examined, the reduction kinetics can be the critical parameter to obtain well-defined shapes and sizes of nanocrystals. Careful control of reduction kinetics leads to well-dispersed and highly monodisperse germanium nanocrystals with moderate chemical yields. Controlling reduction kinetics can be achieved by not only varying injection rates of sodium borohydride solution but also regulation of the reactivity of sodium borohydride by changing the reaction solvents. In general, too fast reduction kinetics result in low chemical yields that make the characterization of germanium nanocrystals difficult due to low chemical yields, while with slow reduction kinetics, the germanium nanocrystals become unstable by longer reaction times, presumably due largely to the oxidation

Figure 5-3: Energy-dispersive X-ray spectrum (EDS) of the as-prepared Ge nanocrystals.
process since hydrogen terminated germanium can only be stable for less than an hour. The slow reduction rates produce a relatively broad size distribution of germanium nanocrystals. Therefore, optimized reduction rates are required for generating germanium nanocrystals with a desirable monodispersity, shape, and size. An optimized reduction rate depends on the reaction solvents since the reactivity of sodium borohydride varies with reaction solvents. Through systematic studies, an optimized reduction rate can be generated.

Another parameter mostly likely associated with the reduction rates can be associated with metal precursors. Surprisingly, even though germanium precursors should be easily reducible with sodium borohydride, based on their reduction potentials, the reduction of germanium precursors (i.e., germanium tetrachloride) was performed with an excess amount of sodium borohydride than the reduction of In$^{3+}$, although the reduction potentials of germanium precursors have relatively more positive potentials than indium precursors.\(^{12}\) Interestingly, the other germanium precursors, including germanium iodides (II) and (IV) can not be reduced by sodium borohydride process at room temperature.

Of the critical reaction parameters, the concentration of precursors can be one of the key variables. It has been reported that the higher concentration of germanium precursors can lead to a larger mean particle size.\(^{5d}\) In our case, with higher concentration of germanium tetrachloride, the bimodal size distribution of germanium nanocrystals are formed (Figure 5-4). This result indicates that the initial concentration of precursors can influence the particle size of final products. Figure 5-4 shows TEM micrographs of the bimodal size distribution of germanium nanocrystals (the average
diameter of larger nanoparticles is 10 nm and the mean diameter of smaller particles is 3 nm).

To produce germanium nanocrystals with larger particle sizes, the reactions were performed in ethanol as the reaction solvent, rather than in ethylene glycol. As mentioned before, the reduction kinetics can be controlled by reaction solvents and can be a critical component in controlling sizes of nanocrystals. As a result, a different range of reduction rates can be generated by the reaction of sodium borohydride with ethanol. The reduction rates achieved in ethanol can be slower than in ethylene glycol, since ethanol has higher pKa value than ethylene glycol. This result is very consistent with that observed in a previous report. Even though we can not provide theoretically a range of
reduction rates, on the basis of systematic studies, we can readily generate an empirical range of the reduction rates. The reaction performed in ethanol, rather than in ethylene glycol, clearly leads to larger particles than in ethylene glycol with higher chemical yields, yet the size distribution is broader than in ethylene glycol (Figure 5-6). Again, this confirms that the reduction rates can influence chemical yield, size distribution, particle size, and shape (discussed later).

Interestingly, the reduction rates appear to be a crucial parameter in controlling particle shape as well, along with size distribution, particle size, and chemical yields. Cube and/or cube-like shapes of germanium nanocrystals are generated by carefully
controlled reduction kinetics. With the slightly faster injection rates of sodium borohydride than those used for synthesizing spherical germanium nanocrystals, cubic shape germanium nanocrystals are formed (Figure 5-6). In a few cases, the reaction intermediates were observed by TEM, which provides an important insight into how to form the cubic shape of germanium nanocrystals. On the basis of TEM observations, at the initial stage, small nanospheres and/or nanocubes can be formed, then can be gradually self- assembled into cube-like shapes, and subsequently can be fused to form dense cube and/or cube-like-shapes of germanium nanocrystals (Figure 5-6b). The schematic drawing in Figure 5-6d illustrates the most likely pathway of the formation of the cubic shape of germanium nanocrystals. It is noteworthy pointing out that this is the first example to demonstrate a kinetically controlled in-situ self assembly process to generate anisotropic nanocrystals. Thus, it is easily anticipated that we could create other shapes of germanium nanocrystals via a kinetically controlled in-situ self assembly route. Preliminary data illustrate that other shapes can be accessed by controlled reduction kinetics (not shown).
Figure 5-7 shows the thermal analysis of the TGA/DSC data of germanium nanocrystals. The data were acquired with a 10 °C/min heating rate under flowing argon. As expected, there are exothermic and endothermic peaks. An exothermic peak that corresponds to the phase transition from amorphous to crystalline Ge appears at around 561 °C, which is roughly consistent with temperature of crystallization observed by XRD. Two endothermic peaks are observed at 794 and at 938 °C. The endothermic peak around 794 °C can be associated with sintering of the germanium nanocrystals and the latter can be involved with melting of nanoparticles, which is consistent with a previous report.4a
Germanium is known to be an indirect band gap semiconductor that emits light weakly. However, in the nanoscale regime, the germanium nanocrystals can produce strong photoluminescence.\textsuperscript{5c,10b} Figure 5-8 shows representative examples of the UV-visible absorbance and photoluminescence spectra of germanium nanocrystals. As shown in Figure 5-8a, the maximum absorbance appears around 280 nm with a relatively broad feature, presumably due largely to the broad particle size distribution of the sample. The PL spectrum of Ge nanocrystals excited with 286 nm light shown in Figure 5-8b also exhibit a broad peak at 326 nm, and the PL emission spectrum indicates that the sample
consists of a broad size distribution. Detailed studies of the optical properties are in progress.

Figure 5-8: (a) Room temperature UV-visible absorbance and (b) photoluminescence (excitation wavelength of 286 nm and emission wavelength of 326 nm).
5.4 Conclusions

We demonstrated that the shape, size, size distribution, and chemical yield can be controlled by reduction kinetics. 6 nm Ge nanocrystals with a uniform size distribution are formed with at a rate of 1.5 mL/min for 2 mL and the addition of the remaining 4 mL of sodium borohydride solution at a rate of 0.15 mL/min to the reaction solution at ambient temperature. However when the injection rate of sodium borohydride solution was slightly increased to 2.5 mL/min for 2 mL of sodium borohydride solution and addition of the remaining 4 mL of sodium borohydride solution at a rate of 0.15 mL/min to the reaction solution, cubic shape of germanium nanocrystals are formed. This represents the first example of a kinetically controlled in-situ self assembly process to create anisotropic Ge nanocrystals. To produce larger nanocrystals, the reactions were conducted in ethanol since the reduction rates also can be adjusted by reaction solvents. In this case, slower reduction rates achieved by utilization of ethanol as a reaction solvent lead to 50 nm germanium nanocrystals with broad size distribution and with an increase of chemical yield. The concentration of the germanium precursor also has an influence on particle size; higher concentrations of germanium precursors result in Ge nanocrystals with a bimodal size distribution. Detailed studies of the optical properties of these samples are in progress. While not yet exhaustive, these results can support the idea that controlling reduction kinetics are necessary to be considered for controlling particle size, shape, distribution, and chemical yield. This chemically controlled reduction process can be especially useful and unique because the approaches that have been developed in past
decades for the synthesis of shape- and size-controlled semiconductors do not generally seem to work with the group IV semiconductor nanocrystals.

5.5. References


Chapter 6

General Conclusions

This dissertation has described the development of the chemical conversion strategy to access a variety of chemically distinct intermetallic systems, as well as a new chemical approach to synthesize shape-and size-controlled metal nanoparticles. The chemical conversion methodology we developed allows us to rationally design nanomaterials through use of size-and shape-controlled nanoparticles. This represents significant progress for size-and shape-controlled intermetallic syntheses, since many chemical and physical routes have not been applicable to intermetallic systems. In addition, this chemical conversion strategy provides important perspectives for accessing the compounds that can be difficult to synthesize by other chemical routes. Synthesis of a library of intermetallic nanorods provide important insights into what reaction parameters can be critical for the maintaining Sn nanorod shape; the reaction temperatures that link to diffusion rates of elements play a vital role in maintaining $\beta$-Sn morphology. The prerequisite for this chemical conversion strategy for accessible shape- and size-controlled final products is to generate metal nanoparticle templates with size- and shape-control. The development of new chemical approaches can be useful and necessary for obtaining precisely size-and shape-controlled metal nanoparticles for further use as reactive templates. The kinetically controlled reduction process we developed herein appears to be robust and general strategy for accessing metal nanoparticles.
In the course of the first part of this research, two chemical approaches have been developed for the synthesis of intermetallic and metal nanocrystals: chemical conversion approach and chemical approach for accessing single metal nanoparticles. The chemical conversion strategy has been developed for the synthesis of shape-and size-controlled β-Sn based-intermetallic compounds. Size-and shape-controlled β-Sn nanocrystals have been synthesized. Particularly, β-Sn nanocrystals are notoriously difficult to synthesize. Thus, synthetic approaches we attempted with organic capping ligands such as oleic acid, oleylamine, trioctylphosphine (TOP), and trioctylphosphine oxide (TOPO) were not successful for the formation of intermetallic compounds in nonpolar solvents. Single crystal nanorods of β-Sn were synthesized using a multistep seed-mediated strategy. Since a general seed-mediated strategy did not work for the Sn nanocrystals, we modified the synthetic approach to obtain a moderate quality of Sn nanorods. Even though Sn nanorods are not perfectly uniform in size and shape, Sn nanorods synthesized using a multistep seed mediated strategy are among the best samples reported in the literature.\footnote{1} With controlled reaction temperature, amounts of PVP, and using a different molecular weight of PVP, we successfully synthesized cubes (small and large), spheres (small and large), and nanorods (using a multistep seed mediated strategy). With various Sn nanocrystals, a variety of shapes (spheres, dense cubes, hollow squares, U-shaped structures, nanorods, and nanorod dimers) of Sn based intermetallic compounds are generated via chemical conversion strategy.

One of the most interesting results from this research is the mechanism that accounts for the formation of cube-derived nanostructures (hollow squares, U-shaped structures, and nanorod dimers). The mechanism appears to be a Kirkendall process,
which is supported by several perspectives such as β-Sn structure, chemical analysis, and control experiments via consideration of reduction potentials. Kirkendall effect has been previously reported in the synthesis of hollow spherical nanoparticles, but not the anisotropic nanostructures described here. Since size-and shape-controlled β-Sn nanocrystals were able to be synthesized, detailed studies of size-and shape-dependent reactivity by consideration of Kirkendall effect were examined. Nanorods, small cubes, large spheres, and small spheres chemically transformed into dense nanorods, dense cubes, large dense cubes, and small dense cubes, respectively, while cubes (> 30 nm) of β-Sn chemically transformed into hollowed-out cube-derived nanostructures.

The generalization of the chemical conversion strategy to β-Sn containing intermetallic systems was successfully achieved for the formation of PdSn, α-CoSn₃, and NiSn₃ compounds. α-CoSn₃ is a low temperature intermetallic phase that was only recently discovered and it can be difficult to synthesize using traditional high temperature solid state methods. Interestingly, the XRD pattern of NiSn₃ closely matches with that reported for PtSn₃, which was reported as metastable high pressure phase. These results imply that the chemical conversion strategy can be a useful route for the synthesis of new, metastable, and low-temperature phases.

In the second part of conversion chemistry, we attempted to synthesize a large number of intermetallic nanorods by utilization of rod-shaped β-Sn. Among the intermetallic compounds we synthesized via chemical conversion strategy, RuSn₂ is formed, which interestingly is also a compound described as a metastable phase in the literature. During the syntheses of a library of intermetallic nanorods, we realized that Fe, Co, Ni, Pt, and Ru containing intermetallic compounds retain their template
morphology, but, Ag, Cu, and Au containing intermetallic compounds do not have any rod-shape in their final products. This result was rationalized by temperature dependent diffusion rates of these elements; the diffusion rates of Ag, Cu, and Au are faster than Fe, Co, Ni, Pt, and Ru, because they have relatively lower melting points than Fe, Co, Ni, Pt, and Ru. In other words, the reaction temperatures play a key role in maintaining rod-shaped \(\beta\)-Sn since diffusion rates depend on reaction temperatures. Through this research, we also realized that three compounds, containing Au, Ag, and Cu, can be synthesized at room temperature, since these elements involved in the formation of intermetallic compounds with Sn seeds have faster diffusion rates than other elements, such as Fe, Co, Ni, Pt, and Ru.

In the third part of the research, we have developed a kinetically controlled sodium borohydride reduction process to synthesize shape-controlled In nanoparticles. We have synthesized octahedra, truncated octahedra, nanowires (in IPA and in ethylene glycol), decahedra, spheres, triangles, and star-like shapes. Several reaction parameters have been considered as key variables to adjust the reduction rates, including reaction solvent, additives, and solvents for sodium borohydride (Triglyme vs TEG). The range of reduction rates by varying the reaction solvents is the critical parameter to obtain various shapes of In nanoparticles. This chemical process has proven to be useful since many chemical and physical approaches have been performed under harsh reaction conditions, which can lead to roughly controlled final products. We have also rationalized that nanowires grow off from octahedra seeds, and then gradually nanowires become thicker as the reaction progress. Enlarged TEM images show the nanowire tip that maintains the points defined by the octahedral seeds. In octahedra show SPR peak
that appears around 400 nm and interesting superconductivity. For comparison, we included bulk In metal. The measurements of the temperature dependent magnetization at 8.5 Oe and 100 Oe applied field indicate that all samples show diamagnetic behavior below 3.4 K. Instead of showing the sharp transition observed in bulk In at 8.5 Oe, a gradual drop was observed in all In nanoparticles. At 100 Oe applied field, \( T_c \) in bulk In metal significantly was decreased, while In nanoparticles show \( T_c \) unchanged, which imply that In nanoparticle have a much higher critical field than bulk In.

In the last part of research we have conducted, we have shown that this kinetically controlled reduction process can be applied to the Ge system. Ge nanoparticles have been synthesized with sodium borohydride reduction process at room temperature in the presence of PVP. The resultant nanoparticles have 6 nm mean diameter with high monodispersity. As expected, the Ge nanocrystals are soluble in polar solvents, which implies that nanoparticles can be directly used for biological applications. Interestingly, cubic shape of the germanium nanocrystals can be synthesized via kinetically controlled in-situ self assembly process of germanium nanospheres. To obtain large Ge nanocrystals, we performed the reaction with different concentrations of germanium tetrachloride. The final product shows bimodal size distribution (larger particle is 10 nm and smaller particle is 3 nm). Even larger Ge nanocrystals have been synthesized in ethanol as the reaction solvent. Due to different reduction kinetics, we generated 50 nm Ge nanocrystals in ethanol. For investigation of optical properties of germanium nanocrystals, PL spectra were measured. The detail studies of optical properties are in progress.
The synthetic work presented in this dissertation has several important implications. The precise control over size-and shape-controlled intermetallics and metal nanoparticles can be achieved using chemical conversion strategy and kinetically controlled reduction process. Such accomplishments would provide access to a wide range of nanomaterials for technological applications and would also facilitate size-, shape-, and structure-dependent studies of many important physical phenomena. Eventually, combining these chemical approaches may lead to the formation of crucial nanomaterials viable for integration into new technologies and devices.

References


VITA

Nam Hawn Chou

Education

The Pennsylvania State University, Ph.D. August 2009

Yonsei University, M.A. June 2004

Hannam University, B.A. February 2002

Selected Awards

Braucher Fellowship, The Pennsylvania State University, 2008-2009

Rohm & Haas Travel Award 2008-2009

Selected Publications