Structural Diversity Of Nanocrystal Self-Assembly And Their Unique Optical Properties

Yaoting Wu
University of Pennsylvania, alex012288@gmail.com

Follow this and additional works at: https://repository.upenn.edu/edissertations
Part of the Inorganic Chemistry Commons

Recommended Citation
https://repository.upenn.edu/edissertations/2889

This paper is posted at ScholarlyCommons. https://repository.upenn.edu/edissertations/2889
For more information, please contact repository@pobox.upenn.edu.
Structural Diversity Of Nanocrystal Self-Assembly And Their Unique Optical Properties

Abstract
The colloidal nanocrystals (NCs) are nanometer-sized inorganic particles with distinctive properties from their extremely small size, high surface-to-volume ratio, and diverse morphologies. By tuning the assembly conditions, the NC will form diverse superstructures with specific crystalline lattices and precise chemical compositions. The interparticle coupling and collective physical phenomena that emerge makes these superstructures promising as novel optical and electrical materials. Understanding the driving force of assembly, crystal structure and defects of the superlattice, and their relationship with properties are still incomplete. In this work, we perform cation exchange, asymmetric modification, and oxidative etching to create distinctive NC building blocks for self-assembly. We characterize the diverse crystal structures comprised of these building blocks and investigate the driving factors behind the structure formation. We perform ligand exchange to enhance the coupling of neighboring building blocks and investigate the enhanced carrier transfer in the NC superlattices with the help of ultrafast spectroscopy. In the meantime, In-situ grazing incidence small-angle X-ray scattering (GISAXS) technique allows us to understand the kinetics of ligand exchange in the performed NC superlattice membranes for the first time. The ligand exchange will precisely control the inter-particle spacing and extent of coupling in the NC superlattice. NC superlattices have predominantly been producing as extend 2D thin films. In this work, we explore the use of emulsion confinement and non-solvent destabilization-driven self-assembly technique to prepare discrete 3-D superstructures (superparticles, superballs, etc.) with distinctive morphologies and crystalline structure. Their strong mechanical strength allows multi-step post-treatments including ligand exchange, thermal annealing, which further enhance the atomic fusion and orientational coupling, and generate promising optical and electrical properties.

Degree Type
Dissertation

Degree Name
Doctor of Philosophy (PhD)

Graduate Group
Chemistry

First Advisor
Christopher B. Murray

Second Advisor
Eric J. Schelter

Subject Categories
Inorganic Chemistry

This dissertation is available at ScholarlyCommons: https://repository.upenn.edu/edissertations/2889
STRUCTURAL DIVERSITY OF NANOCRYSTAL SELF-ASSEMBLY AND THEIR UNIQUE OPTICAL PROPERTIES

Yaoting Wu

A DISSERTATION

In

Chemistry

Presented to the Faculties of the University of Pennsylvania

in

Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

2018

Supervisor of Dissertation

____________________
Dr. Christopher B. Murray
Richard Perry University Professor of Chemistry and Materials Science and Engineering

Graduate Group Chairperson

____________________
Dr. Gary A. Molander
Hirshman-Makineni Professor of Chemistry

Dissertation Committee

Dr. Eric J. Schelter, Professor of Chemistry (CHAIR)

Dr. Cherie R. Kagan, Stephen J. Angello Professor of Electrical Systems and Engineering, Materials Science and Engineering, and Chemistry

Dr. Donald H. Berry, Professor of Chemistry
STRUCTURAL DIVERSITY OF NANOCRYSTAL SELF-ASSEMBLY AND THEIR
UNIQUE OPTICAL AND ELECTRICAL PROPERTIES

COPYRIGHT

2018

Yaoting Wu

This work is licensed under the
Creative Commons Attribution-
NonCommercial-ShareAlike 3.0
License

To view a copy of this license, visit

https://creativecommons.org/licenses/by-nc-sa/3.0/us/
ACKNOWLEDGMENTS

I would like to extend my thanks to many people. This work cannot be possible without efforts from them. First of all, I want to thank my advisor, Professor Chris Murray for his contributions of time and funding to continuously support my Ph.D. research. He creates a favorable environment for high-quality scientific research and gives me and the rest of the group freedom to explore our interest in science. I also want to thank the members of Murray group for their support to my study with their expertise, advise and collaboration. Especially, I want to thank Davit Jishkariani, Blaise Fleury and Mingliang Zhang, who are outstanding scientists. It is my honor to learn from their expertise, collaborate with them in work and turn scientific ideas into reality together. I want to thank Ben Diroll and Ashley Gaulding for their transfer of knowledge in synthesis and characterization. I also want to thank Sen Zhang, Vicky Doan-Nguyen, Haoran Yang and Hongseok Yun for sharing their knowledge of catalyst, magnetism, and thermoelectricity. I am thankful to Chris Murray and all my lab-mates for their efforts to run the lab and improve our capabilities. I have my pleasure to work and discuss with all of them.

Regarding people out of our research group, I want to thank my committee members, Professor Eric Schelter, Professor Cherie Kagan and Professor Donald Berry for their advice, comments, and encouragement during my Ph.D. Especially, I appreciate Professor Cherie Kagan and her students, Nicholas Greybush, Wenxiang Chen and Tianshuo Zhao for their support to my research.

I also want to thank my collaborators out of Penn. I appreciate the invaluable contribution of Professor Jason Baxter and his student Siming Li to our collaboration project of carrier
transfer in nanocrystal superlattice. I appreciate Joseph Strzalka and Zhang Jiang from Argonne National Lab to help me plan and perform the in-situ GISAXS characterizations. I appreciate the knowledge and advice from Professor Alfons van Blaaderen and his student Da Wang in heterodimer and superstructure projects. Last but not least, I want to thank my family and especially my wife Sichao Li for all their love, support, and encouragement.
ABSTRACT

STRUCTURAL DIVERSITY OF NANOCRYSTAL SELF-ASSEMBLY AND THEIR UNIQUE OPTICAL AND ELECTRICAL PROPERTIES

Yaoting Wu

Dr. Christopher B. Murray

The colloidal nanocrystals (NCs) are nanometer-sized inorganic particles with distinctive properties from their extremely small size, high surface-to-volume ratio, and diverse morphologies. By tuning the assembly conditions, the NC will form diverse superstructures with specific crystalline lattices and precise chemical compositions. The interparticle coupling and collective physical phenomena that emerge makes these superstructures promising as novel optical and electrical materials. Understanding the driving force of assembly, crystal structure and defects of the superlattice, and their relationship with properties are still incomplete. In this work, we perform cation exchange, asymmetric modification, and oxidative etching to create distinctive NC building blocks for self-assembly. We characterize the diverse crystal structures comprised of these building blocks and investigate the driving factors behind the structure formation. We perform ligand exchange to enhance the coupling of neighboring building blocks and investigate the enhanced carrier transfer in the NC superlattices with the help of ultrafast spectroscopy. In the meantime, In-situ grazing incidence small-angle X-ray scattering (GISAXS) technique allows us to understand the kinetics of ligand exchange in the performed NC superlattice membranes for the first time. The ligand exchange will precisely control the inter-particle
spacing and extent of coupling in the NC superlattice. NC superlattices have predominantly been producing as extend 2D thin films. In this work, we explore the use of emulsion confinement and non-solvent destabilization-driven self-assembly technique to prepare discrete 3-D superstructures (superparticles, superballs, etc.) with distinctive morphologies and crystalline structure. Their strong mechanical strength allows multi-step post-treatments including ligand exchange, thermal annealing, which further enhance the atomic fusion and orientational coupling, and generate promising optical and electrical properties.
TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ III

1 INTRODUCTION .............................................................................................................. 1

1.1 Nanocrystal and Nanocrystal Assembly ........................................................................ 1

1.2 Physical Properties of Nanocrystal Assembly ............................................................... 6

1.3 Summary of Thesis Contents ....................................................................................... 8

2 PREPARATION AND STRUCTURAL CHARACTERIZATION OF NANOCRYSTAL
SUPERLATTICE .................................................................................................................... 9

2.1 Synthesis of Nanocrystals ............................................................................................ 9

2.1.1 Classical Nanocrystal Synthesis Methods ............................................................... 10

2.1.2 Cation Exchange Reaction with Nanocrystals ....................................................... 11

2.2 Nanocrystal Self-Assembly ....................................................................................... 13

2.2.1 Evaporation and Destabilization Driven Self-assembly ........................................ 14

2.2.2 Thermodynamic Interactions in Nanocrystal Self-assembly .................................. 16

2.3 Experimental Details of Nanocrystal Synthesis ........................................................... 20

2.3.1 Synthesis of PbE Nanocrystals (E=S, Se, Te) .......................................................... 20

2.3.2 Synthesis of Gold Nanocrystals ............................................................................. 21

2.3.3 Synthesis of Platinum Nanocubes ......................................................................... 22

2.3.4 Synthesis of Au-Fe_{3}O_{4} and Pt-Fe_{3}O_{4} Heterodimers ...................................... 22

2.3.5 Cation Exchange in PbE Nanocrystals .................................................................. 23

3 STRUCTURAL DIVERSITY OF NANOCRYSTAL SUPERLATTICE ....................... 25

3.1 Motivations for Nanocrystal Self-Assembly ............................................................... 25

3.2 Self-assembly of Cation Exchanged Nanocrystals ..................................................... 26

3.2.1 Cation Exchange Reactions on PbE Nanocrystals ............................................... 26

3.2.2 Binary Nanocrystal Superlattices (BNSLs) from Cation Exchanged Nanocrystals ... 30

3.3 Self-Assembly of Amphiphilic Janus Heterodimers ................................................... 34

3.4 Structural Diversity of NC Superlattice Film Self-Assembled from PbSe nanocrystal ... 43

3.5 Conclusions .................................................................................................................. 52

4 ENHANCED CHARGE TRANSFER IN BINARY NANOCRYSTAL SUPERLATTICE
BY LIQUID-AIR INTERFACE LIGAND EXCHANGE ...................................................... 53
4.1 Motivations for Ligand Exchange on Liquid-Air Interface ........................................53
4.2 GISAXS Background and Theory ........................................................................56
4.3 *In-Situ* GISAXS Characterization of Ligand Exchange with Binary Nanocrystal Superlattice 59
   4.3.1 *In-Situ* GISAXS Experiment Setup ..................................................................60
   4.3.2 Ligand Exchange Kinetics on Single Component NC Superlattice Film ...............63
   4.3.3 Structural Transformation of Superlattice in Ligand Exchange ............................71
   4.3.4 Ligand Exchange with Binary Nanocrystal Superlattice Film .............................73
4.4 Directional Carrier Transfer in Binary Nanocrystal Superlattice Characterized by Transient Absorption ..........................................................82
4.5 Conclusions ........................................................................................................86

5 3-D NANOCRYSTAL SUPERSTRUCTURES BY DESTABILIZATION-DRIVEN SELF-ASSEMBLY ..................................................................................87
   5.1 Motivations for 3-D Nanocrystal Superstructure by Destabilization-driven Self-Assembly ...87
   5.2 Preparation of 3-D Superstructures by Destabilization-Driven Self-Assembly .............89
   5.3 Stepwise Post-Treatment of 3-D NC Superstructures by Ligand Exchange and Thermal Anneal 92
   5.4 Conclusion .........................................................................................................98

6 3-D NANOCRYSTAL SUPERSTRUCTURES FROM EMULSION CONFINED SELF-ASSEMBLY ............................................................................99
   6.1 Motivations to Prepare 3-D NC Superstructures Through Emulsion Confinement ..........99
   6.2 Preparation of Superstructures by Emulsion Confined Self-Assembly ......................100
   6.3 Structural Diversity and Formation Mechanism ..................................................102
   6.4 Spike-Like Superstructure through Emulsion-Confined Self-Assembly ....................108
   6.5 Conclusion .........................................................................................................110
LIST OF FIGURES

Figure 1.1  (a) Picture of as-synthesized CdTe NC in the reactor. The insert is TEM image of corresponding CdTe NC. The scale bar represents 50 nm. (b) Zig-Zag shape PbSe nanowires formed by orientated assembly and attachment of PbSe NCs. The scale bar represents 50 nm. (c) Binary nanocrystal superlattice films formed with 5.6 nm and 7.4 nm PbTe NC. The scale bar represents 100 nm. (d) Supercrystal self-assembled from 5.0 nm Au NC. The scale bar represents 100 nm. .......................................................... 2

Figure 1.2  A scheme shows typical experimental approaches to prepare NC superlattices. Reprinted from Boles et al. .......................................................... 4

Figure 1.3  Upper left picture shows as-synthesized semiconductor NCs. The lower left sketch shows a model of single NC coated with hydrocarbon chain molecules. Up middle sketch shows the assembly of NCs into multiple layer films on a substrate. Two layers of ligand split the NCs. Solid-state ligand exchange follows step (i), and solution ligand exchange follows step (ii). Both generate strongly coupled films. Reprinted from Boles et al. .......................................................... 6

Figure 2.1  Michael Faraday's Gold Colloids sample. .......................................................... 9

Figure 2.2  La Mer plot which shows the process of nucleation and growth in synthesizing monodisperse NCs. $S$ and $S_c$ are supersaturation and critical supersaturation, respectively. Reprinted from Schladt et al. .......................................................... 10

Figure 2.3  TEM images of (a) initial CdSe NCs (their diameter is 4.2 nm), (b) Ag$_2$Se NCs synthesized from cation exchange reaction with CdSe NCs in (a), and (c) the CdSe NCs synthesized from the reverse cation exchange reaction with Ag$_2$Se NCs. Reprinted from Son et al. .......................................................... 12

Figure 2.4  Schematic diagram to show the cation exchange reaction with PbSe NC and Cd$^{2+}$ cations to form CdSe/PbSe core/shell NC. Reprinted from Lin et al. .......................................................... 13

Figure 2.5  Schematics of NC self-assembly at liquid-air interface. Reprinted from Dong et al. .......................................................... 15

Figure 2.6  The total potential, and the sum of the van der Waals attraction and the steric repulsion at two different coating layer thickness. (d=1.6 nm and 1.2 nm) Reprinted from Lalatone et al. .......................................................... 18

Figure 3.1  (a-c) TEM images of directly synthesized PbSe of three sizes and (d-f) corresponding CdSe NCs produced by cation exchange (g-i) Small-angle X-ray scattering pattern of PbSe and CdSe NCs in (a-f), respectively. (j-l) Wide-angle X-ray scattering
pattern of PbSe and CdSe NCs in (a), (b) and (c), respectively. The scale bars represent 20nm. (m) UV-Vis absorption spectrum of multiple sizes PbSe of direct synthesis and (n) CdSe NCs of cation exchange from PbSe.

**Figure 3.2** (a) Percentage of residual lead in multiple size CdS, CdSe and CdTe NCs by cation exchange at 180 °C for 30 min. (b) *In-situ* percentage of residual lead in large size CdS, CdSe and CdTe during cation exchange. The scale bar represents 2 nm. (c) A high-resolution TEM image of medium size CdTe NCs. The scale bar represents 2 nm. (d) A random mixture of PbSe and cation exchanged CdSe NC with 9:1 ratio.

**Figure 3.3** TEM and corresponding FFT images of MgZn$_2$ type BNSL superlattice films formed with 4.7 nm PbSe, CdSe and 6.5 nm PbSe, CdSe. (a) 5.5 nm PbSe and 7.3 nm PbSe (b) 5.5 nm PbSe and 7.3 nm CdSe (c) 5.5 nm CdSe and 7.3 nm PbSe (d) 5.5 nm CdSe and 7.3 nm CdSe. Inserts are corresponding FFT images of BNSL. The scale bars represent 50 nm.

**Figure 3.4** TEM and FFT images of NaZn$_3$ type BNSL superlattice films formed with 3.2 nm PbSe, CdSe and 6.5 nm PbSe, CdSe. (a) PbSe 3.3 nm and PbSe 7.3 nm (b) PbSe 3.3 nm and CdSe 7.3 nm (c) CdSe 3.3 nm and PbSe 7.3 nm (d) CdSe 3.3 nm and CdSe 7.3 nm. Inserts are corresponding FFT images of BNSL. The scale bars represent 50 nm.

**Figure 3.5** Schematics of the two-step ligand exchange process to coat the heterodimers using thiol-based ligand hydrophobic ligand and phosphonic acid based hydrophilic ligand. Reprinted from Jishkariani et al. 161

**Figure 3.6** EDX chemical mapping of a Janus heterodimer superlattice (a) HAADF-STEM image to show the superlattice from post-modification heterodimers (b) element of the platinum’s distribution (c) element of iron’s distribution, (d) element of surfer’s distribution, (e) overlapping of sulfur and platinum, and (f) overlapping of iron and platinum. The inserts show enlarged 100 nm × 100 nm areas. Scale bars in (a–f) are 200 nm. Scale bars in insets are 20 nm. Reprinted from Jishkariani et al. 161

**Figure 3.7** (a) Schematics to show the of liquid–air assembly of post-modification heterodimers and the transfer process by “stamping.” TEM images of self-assembly with (b) as-synthesized Pt-Fe$_3$O$_4$ heterodimers (c) Pt-Fe$_3$O$_4$ heterodimers. Only the Fe$_3$O$_4$ part is functioned with the phosphonic acid-based ligand. (d) Pt-Fe$_3$O$_4$ heterodimers. Both Pt and Fe$_3$O$_4$ part are functioned with thiol, and phosphonic acid-based ligands Scale bars in (b) and (c) are 400 nm, in (d) is 100 nm. (Digital FFT of an entire image are provided as insets in the top right corners of each image) Reprinted from Jishkariani et al. 161

**Figure 3.8** (a) Reconstruction of Pt-Fe$_3$O$_4$ heterodimer superlattices with HAADF-STEM tomographic images. The yellow represents Pt, and blue represents the Fe$_3$O$_4$. The insert is FFT images of the same area superlattice. (b) A zoom-in image of Pt-Fe$_3$O$_4$ heterodimer superlattices in the dashed window in (a). (c) XZ slice view of the Pt-Fe$_3$O$_4$ heterodimer
superlattice. (d) Four possible orientations of heterodimers. (e) Orientation quantification of Pt-Fe3O4 Janus heterodimers. Reprinted from Jishkariani et al. 161

**Figure 3.9** (a) TEM image of as-synthesis Au-Fe3O4 heterodimers (b) HAADF-TEM image of NC superlattice self-assembled with asymmetrical functioned Au-Fe3O4 (c) Low magnification HAADF-TEM image of NC superlattice self-assembled with asymmetrical functioned Au-Fe3O4 at a tilting angle of 70 deg. (d) High magnification HAADF-TEM image of NC superlattice self-assembled with asymmetrical functioned Au-Fe3O4 at a tilting angle of 74 deg.

**Figure 3.10** (a) TEM image of monolayer superlattice films self-assembled on liquid-air interface with 6.4 nm PbSe NC (b) The electron diffraction pattern indicating a (100) projection of NCs to the substrate (c) HR-TEM images of superlattice in (a) (d) TEM images of a monolayer and bilayer boundary of superlattice, and corresponding lattice constant of a unit cell in this projection.

**Figure 3.11** (a) GISAXS pattern and (b) TEM images of oxidized 7.1 nm PbSe NC superlattice. (c) HR-TEM images of bi-layer PbSe superlattice. The building blocked are grouped by Red, yellow, and blue arrows which are perpendicular to the (100) facet. Each group devotes to the diffraction spots of the same color in (d). The scale bar represents 5 nm. (d) SAED diffraction pattern and simulation of bilayer NC superlattice self-assembled with 7.1 nm PbSe NC. (e) The cartoon on top of HR-TEM images shows the building blocks’ orientation and the inter-particle relationship of one-layer PbSe NC. Each orange/black polyhedron represents one NC. (f) The cartoon on top of HR-TEM images show the building blocks’ orientation and inter-layer attachment of bi-layer NC superlattice. Each blue/red polyhedron represents one PbSe NC of the other layer.

**Figure 3.12** Se K-edge XAS spectrum of as-synthesized PbSe and oxidized PbSe.

**Figure 3.13** High-resolution TEM images of (a) as-synthesized and (b) Oxidized PbSe NC under the projection of [100] axis. (c) atomic models of PbSe NC tilting at a small degree from the projection of [100] axis. (d) High-resolution TEM images of as-synthesized and (e) Oxidized PbSe NC under the projection of [110] axis. (f) atomic models of PbSe NC tilting at a small degree from the projection of [110] axis. The scale bars represent 5 nm.

**Figure 4.1** (a) Low magnification and (b) high magnification SEM images of FePt NC superlattice after liquid-air and then solid-state ligand exchange with formic acid. (c) Low magnification and (d) high magnification SEM images of FePt NC superlattice film by solid-state ligand exchange only with formic acid. Reprinted from Dong et al. 78

**Figure 4.2** Schematics graph to show the GISAX principles behind the Au NC growth characterization. Reprinted from Gilles et al. 232
**Figure 4.3** (a) Side view of GISAXS solvent chamber. The superlattice on top of the Teflon well can be seen through the Kapton window. (b) Top view of Teflon well in GISAXS solvent chamber. The injection and withdraw needles are fixed on the diagonal corner of the Teflon well. (c) A broad view of the solvent chamber on XYZ stage in the GISAXS hood. The solvent change is located at GISAXS beam stage in one of the Advanced Photon Source beam station in Argonne National Lab (4) Cartoon of the set-up about how the scattering diagram is collected.

**Figure 4.4** Line-cut of the peak (11-1) in GISAXS diffraction pattern collected at 0 s, 30 s, 60 s, 90 s, 120 s, and 150 s. The sample is 7.1 nm PbSe superlattice treated with blank acetonitrile.

**Figure 4.5** (a) GISAXS pattern of 6.7 nm CdSe NC superlattice film at 0s and (d) 150s of ligand exchange reaction with MPA. (b) TEM images of corresponding CdSe superlattice film at 0s (black frame) and 150s (red frame) of ligand exchange. The insert is small angle electron diffraction pattern of local area superlattice. The scale bars represent 50 nm (c) The time slices of (11-1) scattering peak of CdSe superlattice during ligand exchange. (e) The q_y coordination of (11-1) scattering peak against the time during ligand exchange. (f) FT-IR spectra of the superlattice in (a) and (d).

**Figure 4.6** GISAXS diffraction pattern taken at (a) 0 s and (b) 150 s. The sample is 4.9 nm CdSe superlattice, ligand exchange with MPA.

**Figure 4.7** The q_y coordination of (11-1) GISAXS peak against time. The sample is (a) 4.9 nm CdSe SL with 0.02 M MPA. (b) 6.7 nm CdSe with 0.02 M MPA and 0.02 M EDT (c) 7.1 nm PbSe with 0.02 M MPA and 0.02 M EDT. (d) 7.1 nm PbSe with 0.02 M TBAC, TBAB and TBAI.

**Figure 4.8** FT-IR spectra of original 6.4 nm PbSe NC superlattice and the ones ligand exchange with TBAI, TBAB, TBAC, MPA and EDT for 150 s.

**Figure 4.9** GISAXS pattern and TEM images of 7.1 nm PbSe superlattice at 150s, ligand exchange with (a, b) TBAC, (c, d) TBAB, (e, f) TBAI. Each scale bar represents 200 nm.

**Figure 4.10** (a, b) Photographs of a typical film on top of diethylene glycol (a) before and (b) after ligand exchange with MPA. The scale bar represents 10 mm. (c) FT-IR spectra of BNSL film self-assembled with 4.5 nm and 6.0 nm PbSe NCs before and after ligand exchange with MPA. Reprinted from Wu et al. 79

**Figure 4.11** TEM and Fourier Transform images of BNSL films self-assembled with 4.5 nm and 6.0 nm PbSe NCs (a) before and (b) after ligand exchange with 0.1 M 3-MPA in acetonitrile. Scale bars represent 100 nm. (c) Structural model of MgZn_2-type BNSL. (d, e) Corresponding GISAXS diagram of BNSL films in (a) and (b). (f) Line-cut along the dashed line on GISAXS patterns in (d) and (e). Reprinted from Wu et al. 79
Figure 4.12 GISAXS diffraction pattern of MgZn$_2$-type BNSL films self-assembled with different size PbSe NCs at (a) 0 s and (b) 150 s of ligand exchange with MPA. The red and green rectangular in (a) mark the diffraction peaks from which we can get the (c) in-plane and (d) out-of-plane kinetics curves of ligand exchange. (e) Models of a MgZn$_2$-type unit cell and corresponding lattice constant at 0 s and (f) 150s. .......................................................... 78

Figure 4.13 (a-c) TEM and Fourier Transform images and (d-f) GISAXS patterns of BNSL films self-assembled with: (a,d) 4.5 and 6.0 nm NCs and ligand-exchanged with TBAI, (b,e) 3.2 and 4.5 nm NCs before ligand exchange, (c,f) 3.2 and 4.5 nm NCs ligand-exchanged with MPA. Scale bars represent 50 nm. Reprinted from Wu et al. 79 ............... 80

Figure 4.14 TEM images of BNSL film (self-assembled with 4.5nm and 6.0 nm PbSe NCs) after ligand exchange with (a) 0.1M NH$_4$SCN in acetonitrile and (b) 0.1 M Formic acid in acetonitrile. Scale bars represent 50 nm. Reprinted from Wu et al. 79 ......................... 81

Figure 4.15 (a) 2D plot of NIR-TA spectra of oleic acid (OAc)-capped 4.5 nm PbSe superlattice film. (b) NIR-TA spectra of Oleic acid-capped 4.5 nm PbSe superlattice film at several pump-probe delay times and the linear absorption spectrum. (c) Dynamics of the 1S bleach of 4.5 nm PbSe NCs under three conditions: dispersed in tetrachloroethylene, SL film before ligand exchange, and same film following a ligand exchange. Samples were pumped at 3.2 eV with 12-18 µJ/cm$^2$. (d) Fluence-dependent dynamics of a superlattice film of MPA-capped 4.5 nm NCs (points) with global fitting by an Auger recombination process (lines). The fluence was 6.1 µJ/cm$^2$ for N$_0$ = 1.9x10$^{18}$ cm$^{-3}$. Reprinted from Wu et al. 79 ......................... 83

Figure 4.16 2D plot of NIR-TA spectra as a function of both probe energy and the pump-probe delay time of MPA-capped NC films for (a) 3.2 nm NC SL, (b) 4.5 nm NC SL, and (c) BNSL film. (d) Cartoon showing the transfer of photoexcited carriers from 3.2 nm PbSe NC to 4.5 nm PbSe NC. (e) 1S bleach dynamics of 3.2 nm NCs in single-component SL and BNSL probed at 1.18 eV and 1.14 eV. (f) 1S bleach dynamics of 4.5 nm NCs in single-component SL and BNSL, probed at 0.87 eV. Reprinted from Wu et al. 79 ......................... 85

Figure 5.1 SEM images of supercrystals formed from various Au–Pd core-shell (a) cubes, (b) truncated cubes, (c) cuboctahedra, (d, e) truncated octahedra, and (f–h) octahedra by the droplet evaporation method. Reprinted from Chiu et al. 272 ......................................................... 88

Figure 5.2 (a) Cartoon of the experimental setup for destabilization-driven self-assembly. (b) SEM image of the NC supercrystal self-assembled by 5 nm Au NCs (c). The superstructures have polyhedron morphology. And their size is in the range of 0.5 to 10 µL. (d) High-resolution SEM image to show the fcc lattice of supercrystal. (e) SEM image of a single supercrystal in (b). .................................................................................................................. 89
Figure 5.3  (a) Bright field and (b) dark field TEM images of superlattice thin film which is sliced from superstructures. The superstructure is prepared by a mixture of PbSe and Au NC at 1:1 ratio. Bright spots in (b) show scattering from Au NCs. 91

Figure 5.4  (a) Picture of magnetic nanorods prepared in a glass vial. (b) SEM images of the rod self-assembled with iron oxide NCs. Insert is TEM image taken on the tip of the nanorod. (c) Mesoporous carbon framework prepared from the rod-like superstructure. The dark substance in the center of carbon framework is unreacted iron. 92

Figure 5.5  TEM image (up) and electron diffraction pattern (down) of an NC supercrystal assembled from PbSe NCs (a) without extra treatment (b) ligand exchange with MPA (c) thermal annealing at 150°C in an inert environment. (d) ligand exchange with MPA, followed by ligand exchange with MPA at 150°C in an inert atmosphere. 94

Figure 5.6  TEM image (up) and electron diffraction pattern(down) of (a)CdSe NC film by spin coating (b)CdSe supercrystal with ligand exchange and thermal anneal at 150 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, (f) 400 °C (g) 450 °C (h) 500 °C for 30 minutes. 97

Figure 6.1  (a) Cartoon about the formation of droplets through the mesoporous membrane. (b) Images of the emulsions which are pumped out of the member and dispersed into the continuous phase. The insert is microporous SiN film. 101

Figure 6.2  Pictures of droplet out of the (a) mesoporous film (b)-(g) plastic needles as a function of time. The pictures are taken by DLS camera in high-speed mode. 102

Figure 6.3  (a) size and distribution of superstructures which can be prepared by the emulsion confined self-assembly from the microporous film. (b) Size of the superstructure as a function of solvent concentration. (c) Size of the superstructure as a function of flow rate. (d) The rate of bubbles out of the film as a function of flow rate (pumping rate). 103

Figure 6.4  SEM images and cartoon to show the morphology of superlattice from emulsion confined self-assembled. The morphology changes as a function of dispersed phase concentration. 106

Figure 6.5  (a) SEM image of a typical hollow core superball. (b) The inner structure of a superball sliced by the FIB (c) SEM image of the thin film which is sliced from (b) and transferred to a copper bar. (d) The GISAXS diffraction pattern of superstructures. (e) and (f) TEM images of the sliced thin film in (c). 107

Figure 6.6  (a) Scheme of the needle-like superstructure synthesis. (b) SEM images of the needle-like superstructure. (c) TEM images of the needle-like superstructure. Reprinted from Wang et al.. 132 108
Figure 6.7 (a)-(c) SEM images of magnetics of different aspect ratio. (d) the cartoon to show the formation of magnetic spikes. (e) length and (f) aspect ratio distribution analysis of magnetic spikes in (a), (b) and (c) ...
1 INTRODUCTION

1.1 Nanocrystal and Nanocrystal Assembly
Self-assembly is defined as a spontaneous process in which the pre-existing components form an organized structure through non-covalent interactions.\(^1,^2\) NCs are ideal building blocks for self-assembly owning to the easy preparation, uniformity, well tunability over their size, shape,\(^3,^4\) and distinctive optical,\(^5\) electrical,\(^6\) and catalytic\(^7\) properties. Self-assembly of NCs enables advanced properties based on long-range-order superstructures and fixed chemical components.\(^8\)\(^-\)\(^12\) Examples of typical NCs and the self-assembly are presented in Figure 1.1. This thesis strives to investigate the structural diversity of two dimensional and three-dimensional superlattice structures from IV-VI semiconductor NCs and their unique optical and electrical properties.

NCs can self-assemble into crystalline superlattice by evaporation\(^13\) or destabilization driven methods.\(^14\) The schematic diagram in Figure 1.2 shows a general process of NC self-assembly. Evaporation-introduced self-assembly can happen in one,\(^15\) two\(^16\) or three dimensional\(^17\) limited environments to form thin films or clusters. One classical method\(^13\) is to drop-cast NC solution onto a solid substrate. The substrate is sealed in a container with a tiny window to allow slow evaporation of solvent, which takes minutes to days. By the end of solvent evaporation, a solid superlattice film forms on the substrate. The slow evaporation methodology can be implemented under a variety of conditions, for example, on a dip-coating substrate,\(^15\) at the liquid-air interface in Langmuir-Blodgett (LB) trough,\(^18\) and inside emulsion droplets dispersed in aqueous phase.\(^19,^20\) By taking advantage of \textit{in-situ} X-ray technique, the spontaneous process of self-assembly and the formation of
superlattice can be further investigated.\textsuperscript{21,22} Chap. 2 and 3 explore slow evaporation introduced self-assembly on the liquid-air interface, their structural diversity, and the driving force behind them.

**Figure 1.1** (a) Picture of as-synthesized CdTe NC in the reactor. The insert is TEM image of corresponding CdTe NC. The scale bar represents 50 nm. (b) Zig-Zag shape PbSe nanowires formed by orientated assembly and attachment of PbSe NCs. The scale bar represents 50 nm. (c) Binary nanocrystal superlattice films formed with 5.6 nm and 7.4 nm PbTe NC. The scale bar represents 100 nm. (d) Supercrystal self-assembled from 5.0 nm Au NC. The scale bar represents 100 nm.
Destabilization driven self-assembly happens via direct addition\textsuperscript{23,24} or diffusion\textsuperscript{14,25,26} of non-solvent into the solvent of NCs. As the proportion of non-solvent increase, the parallel long hydrocarbon chain ligands contract and form bundles\textsuperscript{27} to reduce contact with the poor solvent, while NCs also aggregate into clusters.\textsuperscript{28} A swift mixture of solvent and non-solvent always generates amorphous clusters,\textsuperscript{3,29-31} which are used to separate NCs from the synthesis solution for purification purpose. A slow diffusion of non-solvent will drive NCs to aggregate in an energy-favorable way. To reduce the free energy of the entire system, the NCs of similar size tend to attach and form a closed-packing superlattice. Through this self-selection process, the NCs within the same cluster own higher monodispersity.\textsuperscript{14,25} Hence, the destabilization-driven self-assembly is often used for NCs’ size selection. The structure, post-treatment, and properties of polyhedrons generated by destabilization driven self-assembly will be discussed in Chap.5.
Figure 1.2 A scheme shows typical experimental approaches to prepare NC superlattices. Reprinted from Boles et al.\textsuperscript{2}

Decades of the investigation show that a variety of crystal structures can be prepared using NC building blocks. In the process of self-assembly, the size, shape, and morphology of NCs,\textsuperscript{32-34} the coating ligands,\textsuperscript{35-40} temperature,\textsuperscript{41-43} solvent,\textsuperscript{21,44,45} and kinetics of assembly\textsuperscript{46,47} are all important factors to consider. In general, perfect sphere models are used to replace polyhedron shape NCs in analysis and simulation of stacking\textsuperscript{43} and attachment\textsuperscript{48,49} of NCs in the superlattice. Recently, further investigations are put forward that the ligands on the surface of NC place an important role in driving the orientation
preferred attachment and determining the crystal structure of superlattice.\textsuperscript{50-53} Our investigations based on PbSe NCs superlattice reveal that ligand distribution on the polyhedral faceted surface, specifically, on \{111\} and \{100\} facets, guide the preferred or orientated attachment in the NC superlattice, and deliver a variety of crystal structures by tuning the ligand-ligand and ligand-substrate interactions. Experimental result and discussion can be found in Chap. 3.

Under ambient conditions, long hydrocarbon chain small molecules,\textsuperscript{16,54} DNA,\textsuperscript{55,56} or polymers\textsuperscript{57-59} are favorable for the formation of the long-range-order in NC superlattices with few defects. The application of external electrical\textsuperscript{60,61} and magnetic fields\textsuperscript{62,63} gives further tunability over the crystal structure and morphology of the assembled superstructure. The highly-ordered crystal structure and fixed chemical components in the resulting crystal structure enable promising optical\textsuperscript{64-66} and electrical\textsuperscript{67-69} properties as a new generation of optoelectrical materials. In spite of this progress, several challenges remain to overcome. For example, the long hydrocarbon chain molecules used in the standard synthesis function as an insulating layer to isolate NCs and suppress or eliminate the local or long-range carrier transfer within the superlattice.\textsuperscript{70-74} Solid or liquid state ligand exchange is widely applied to remove the insulating layers, reduce the inter-particle spacing and enhance the coupling between neighboring NCs.\textsuperscript{40,75-77} (A schematic diagram of the ligand exchange process is shown in Figure 1.3) However, neither of the two perfectly maintains the order of NC superlattice after ligand exchange. Thus, development of improved ligand exchange methods is required to efficiently remove the ligand while generating fewer defects in the NC superlattice.\textsuperscript{78,79} In Chap. 3, we introduced the
application of in-situ ligand exchange technique in binary nanocrystal superlattice (BNSL) film, and report the directional carrier transfer within these films after ligand exchange.

**Figure 1.3** Upper left picture shows as-synthesized semiconductor NCs. The lower left sketch shows a model of single NC coated with hydrocarbon chain molecules. Up middle sketch shows the assembly of NCs into multiple layer films on a substrate. Two layers of ligand split the NCs. Solid-state ligand exchange follows step (i), and solution ligand exchange follows step (ii). Both generate strongly coupled films. Reprinted from Boles *et. al.*

### 1.2 Physical Properties of Nanocrystal Assembly

NC self-assemblies show a series of unique optical, electrical, and catalytic properties, owing to their diverse crystal structures, well tunable chemical compositions, and long-range-order crystalline structure. The superlattice assembled from different size/composition of semiconductor NCs obtains a mixture of bandgaps and tunable bandgap alignments. Thus, the enhanced coupling enables directional charge and energy transport within the superlattice and make it promising for efficient photovoltaic conversion. The coupling between plasmonic and semiconductor NCs
leads to enhancement of photoluminescence, which correlates with the inter-particle spacing.\textsuperscript{87-89} For example, 10.4 times photoluminescence enhancement is reported at a 20 spacer between Au nanorods and semiconductor NCs.\textsuperscript{90} In a BNSL film where the inter-particle spacing is only several nanometers, an energy transfer from CdSe to Au NCs is also reported.\textsuperscript{91} In Chap. 4, we discuss the directional charge and energy transfer within the type-I heterojunction of BNSL self-assembled with PbSe NCs, which is characterized by ultrafast spectroscopy.

A group of NCs, for example, lead chalcogenide NC, Platinum nanocubes or some anisotropic NCs can self-assemble into superlattice with the coherent orientational order.\textsuperscript{73,92} By removing the coating molecules, neighbor NCs attach through atomic bonds, which eliminates the tuning barriers and enables carriers delocalization within the superlattice. Evers \textit{et al.} report the charge carrier mobility of 260±15 \text{cm}^2\text{V}^{-1}\text{s}^{-1} in 2-D percolative PbSe NC networks.\textsuperscript{93} The value is not too far from bulk PbSe materials. The challenge remains to further reduce the translational and orientational defect of the superlattice in ligand exchange to further improve the carrier transfer within the superlattice.

By taking advantage of the large heterojunction area, fixed chemical composition and synergistic effect of two building blocks, the BNSL gives new designs of the efficient catalyst.\textsuperscript{82,94} Yijing Kang \textit{et al.} reports that the BNSL from Pt and Pd NCs show high catalytical activity in oxygen reduction reaction, owing to the shape effect of Pt NCs and the synergistic effects of Pt-Pd combinations in a crystalline structure.\textsuperscript{82}
1.3 Summary of Thesis Contents
This thesis contains six chapters. Chap. 2 introduces classic synthesis methodologies of NCs with the scope of II-VI semiconductors, metal NCs, magnetic NCs and the process of self-assembly to prepare superlattice films. It also gives a review of commonly used characterization technique including electron microscopy, optical spectroscopy, and X-ray scattering. Chap. 3 discusses the structural diversity of superlattices from NC self-assembly, as well as the driving factors behind it. Chap. 4 reports the investigation of the ligand exchange kinetics in superlattice film, which is characterized by in-situ GISAXS technique. Followed by ligand exchange, we investigate the charge and energy transfer within the superlattice using ultrafast spectroscopy. Chap. 5 discusses the formation of 3-D superstructures from destabilization driven self-assembly, and Chap. 6 discusses the emulsion-confined self-assembly technique. It describes the driving force, formation mechanism, and post-treatment on 3-D superstructures and their potential applications.
2 PREPARATION AND STRUCTURAL CHARACTERIZATION OF NANOCRYSTAL SUPERLATTICE

2.1 Synthesis of Nanocrystals
The synthesis of NCs can date back to mid-19th century; Faraday synthesized the colloidal gold NCs by reducing gold chloride. Figure 2.1 shows a representative picture of the colloidal gold NC solution. Since then, the development of synthesis methodology generated a library of NCs of the different chemical composition.\textsuperscript{95} To get long-range-order structure and homogeneous chemical properties, self-assembly of NC superlattice has strict requirements over NC building blocks with high consistency in size, shape and surface chemistry. Classic rapid injection and thermal decomposition methods are applicable to a large portfolio of NCs with high quality and tunability. Besides that, cation exchanged method is a good compensation to produce NCs with complex crystal structural, which can be hardly obtained by direct synthesis.

\textbf{Figure 2.1} Michael Faraday's Gold Colloids sample.\textsuperscript{96}
2.1.1 Classical Nanocrystal Synthesis Methods
An early study of La Mer & Dinegar reveals the mechanism of forming monodisperse colloidal, which requires a rapid nucleation process to form high-quality seeds followed by the well-controlled growth on the core. Schematics diagram of the reaction mechanism is in Figure 2.2. The nucleation happens by a rapid mixture of precursors at high enough temperature, during which time the concentration of monomers ramps up very quickly. When the concentration exceeds a threshold, the nuclei form to relieve the supersaturation. The formation of nuclei reduces the monomer concentration to the level below the threshold. The residual monomers continue to grow the nuclei until depletion but no new nuclei forms at this stage.

Figure 2.2 La Mer plot which shows the process of nucleation and growth in synthesizing monodisperse NCs. S and $S_c$ are supersaturation and critical supersaturation, respectively. Reprinted from Schladt et al. 97
In 1993, Murray et al. reported the hot-injection synthesis of monodisperse NCs, which is supported by La Mer & Dinegar’s model. The hot-injection synthesis is widely applicable for a series of the semiconductor NCs. In a typical process to synthesize II-Vi NCs, metal-chalcogenide (metal-organic compound as a metal source and organophosphine chalcogenide as chalcogenide source) precursor are pre-mixed and swiftly injected into reaction flask with hot (~150-350°C ) coordinating solvent, which is usually long hydrocarbon phosphines, hydrocarbon phosphine oxides, hydrocarbon amines and so on. By swift injection of precursor mixtures, the metal chalcogenide (ME, M=Metal and E=S, Se, Te) monomers rapidly form and raise up above the saturation concentration. The monomers nucleate to form the nuclei for the rest of free monomers to grow on. The hot-injection based method applies to a series of II-VI, IV-VI, III-V, I-VI, II-V semiconductor NCs and some metal NCs.

Besides the hot-injection synthesis, high-temperature synthesis is also developed to prepare a range of metal oxides, metal and halide NCs. High-temperature synthesis happens by ramping up the reaction temperate to decompose pre-mixed precursor in the reaction flask. Although the procedure is different, the hot-injection reaction still can be explained with La Mer & Dinegar’s model, in which the rapid nucleation happens during the temperature increase.

2.1.2 Cation Exchange Reaction with Nanocrystals
Since the first report of ion exchange reaction on NCs, it catches growing attention as an alternative technique to compensate the direct synthesis. It also gives the probability to
prepare more complex nanostructure which may not be possible by direct synthesis. Either cation or anion in the atomic lattice can be replaced with guest ions during ion exchange, but cation exchange has more investigations and reports than anion exchange.\textsuperscript{115-117} In a typical cation exchange reaction, the anions maintain the framework of atomic lattice while the guest cations replace the original ones through vacancy-assist mechanism\textsuperscript{118,119} or “kick-out” mechanism,\textsuperscript{120,121} which will be discussed in Chap. 3.

Figure 2.3 TEM images of (a) initial CdSe NCs (their diameter is 4.2 nm), (b) Ag\textsubscript{2}Se NCs synthesized from cation exchange reaction with CdSe NCs in (a), and (c) the CdSe NCs synthesized from the reverse cation exchange reaction with Ag\textsubscript{2}Se NCs. Reprinted from Son et al.\textsuperscript{114}
Complete cation exchange maintains the size, shape, and morphology of the template but generates NCs of the distinct chemical composition. The first example of nanoscale cation exchange is given by Son et al. in 2004. (Figure 2.3) Partial or incomplete ion exchange generate more complex heterostructure, most of which can be hardly obtained from direct synthesis, but develop unique properties. For example, through cation exchange reaction of PbSe and Cd$^{2+}$, a thin layer of CdSe forms by replacing the original Pb$^{2+}$ in the atomic lattice. The PbSe/CdSe core/shell structure allows higher quantum yield by removing the trap states on the surface.$^{122-124}$ The schematic diagram to develop PbSe/CdSe core/shell NC by cation exchange can be found in Figure 2.4.$^{122}$

![Figure 2.4](image.png)

**Figure 2.4** Schematic diagram to show the cation exchange reaction with PbSe NC and Cd$^{2+}$ cations to form CdSe/PbSe core/shell NC. Reprinted from Lin et al.$^{122}$

### 2.2 Nanocrystal Self-Assembly

NC self-assembly describes a spontaneous process in which the NC building blocks aggregated into superstructures by either covalent or non-covalent interaction. In general, NCs are analogized as artificial atoms and self-assembly into closed-packed structures with
high packing fraction and minimum thermodynamic free energy.\textsuperscript{125,126} The analogy is realistic to explain the formation of close packing structures. But in recent decades, more non-close packed structures are reported.\textsuperscript{21,127,128} Many factors are proven to affect the structure of the superlattice in self-assembly, such as the morphology of NCs, the ligand density and distribution, the assembly rate and condition, the outer filed, and so on.

2.2.1 Evaporation and Destabilization Driven Self-assembly.
Solvent evaporation and destabilization are two most common methods for NC self-assembly. In a typical evaporation driven process, the solvent is allowed to evaporate at a slow rate to maintain a thermodynamic stable state.\textsuperscript{129} At the late stage of evaporation, the concentration of NC reaches a critical point in which the NC begins to aggregate. At this stage, \textit{In-situ} X-Ray investigation\textsuperscript{129} reveals that NCs form discrete islands on the liquid-air or solid-air interface, followed by the growth of these islands with the further evaporation of the solvent. The evaporation driven self-assembly can happen on a solid-air or liquid-air interface with 1-D, 2-D or 3-D limitations. The most widely investigated method is to dropcast a certain amount of liquid on a substrate in a sealed container. A small window opens to control the rate of evaporation. Sometimes, temperature control is also implemented. By the end of evaporation, if the concentration is low, NCs will form discrete domains with unique morphology,\textsuperscript{13} and if the concentration is high, NCs will form a homogeneous film with long-range-order.\textsuperscript{58} The self-assembly also happens on liquid-air interface\textsuperscript{16,78} to form a floating film that can be integrated but by lamination on to solid supports or over an open frame to create free-standing films or membranes. As is shown in
Figure 2.5, NC solution is drop-casted into a Teflon well which preloads immiscible liquid (water, ethylene glycol, etc.). A glass slide is used to cover the well to reduce the rate of evaporation. By the end of evaporation, a thin layer of solid film forms and is ready to be transferred to any substrate for any post-treatment. Recently, self-assembly of NC by emulsion confinement has caught people’s attention as it generates a new complex of materials with distinctive structure and properties. A series of 3-D homo- or hetero-superstructures have been reported. The superstructure forms by separate organically disperse NC solution into emulsions using shear force or sonication. The organic (oil) emulsions are often stabilized by surfactants and dispersed in water as the continuous phase. Through slow evaporation of the solvent, the NCs self-assemble into a variety of superstructures which depends on the size, shape, and interaction of NC building blocks.

Figure 2.5 Schematics of NC self-assembly at liquid-air interface. Reprinted from Dong et al.¹⁶
Diffusion-driven self-assembly happens by slow diffusion of non-solvent into the solution of the NC. In this process, NCs become unstable and tend to contact others to reduce the thermodynamic free energy. A rapid mixture of solution and non-solvent will generate amorphous aggregates. If the destabilization processes slowly enough, the particles tend to aggregate into an ordered superlattice. A typical set up of assembly is to put NC solution into a test tube, and the non-solvent is carefully loaded into the test tube to avoid mixing. Due to the molecular diffusion and gravity force, the non-solvent slowly mix with a solvent to generate NC superstructure, mostly in polyhedron shape.\textsuperscript{14,25} Our recent research reveals that self-assembly also happens by diffusion of solvent into the non-solvent phase. We prepare the NC solution droplet by pumping the NC solution into non-solvent through the microporous film. Due to limited solubility of solution (hexane, octane, etc.) in continuous non-solution phase (methanol, ethanol, etc.), the solvent slowly diffuses out of the emulsion while NC remains inside. Finally, NC self-assembly into spherical superstructures with high mono-dispersity. The mechanism and unique properties of the superstructure obtained from emulsion confined self-assembly will be discussed in detail in Chap. 6.

2.2.2 Thermodynamic Interactions in Nanocrystal Self-assembly
NC self-assembly is a spontaneous process to allow solution state mutual repulsive NCs to assemble into inter-attractive solid-state superlattice. The driving forces include the Van
der Waals forces,\textsuperscript{133-135} steric repulsion,\textsuperscript{136} electrostatic interaction,\textsuperscript{134,137,138} and dipole moments.\textsuperscript{139,140}

The Van der Waals attraction between the inorganic cores and the steric repulsion between ligands play important roles in driving the mesoscopic organization of superlattice. Inter-particle Van der Waals pair potential can be expressed as $U_{vdW}(r) = -\frac{A}{\pi^2 r^6}$, $A$ is Hamaker constant, which is defined as $A = \pi^2 \times C \times \rho_1 \times \rho_2$. It correlates with property of materials. $C$ is the coefficient in the particle–particle pair interaction. $\rho_1$ and $\rho_2$ represent the number density of two interacting materials.\textsuperscript{141} In nanometer scales, the strength of Van der Waals forces correlates with the size of NCs and the chemical composition. For example, in Wu \textit{et. al.}'s report of the high-temperature self-assembly,\textsuperscript{41} Pd NCs start to self-assemble at size larger than 5 nm, in which size the Van der Waals attraction overcomes the steric repulsions. Under the same conduction, Fe NCs start to assemble till they reach 11 nm, due to the smaller Hamaker constant of Fe and smaller Van der Waals attractions.

In solution state, the Van der Waals interaction is countered by the steric repulsions, which make NCs to be dispersible into the solvent. The steric repulsions are the sum of ligand-ligand potentials which correlates with the size of ligands and curvature of the NCs.\textsuperscript{2,142,143} In a self-assembled superlattice, the total steric interaction energy is reduced through close packing structure, deformation of ligand shell and the interdigitation of ligand which minimizes the void spacing. When ligand takes a relatively high-volume percentage, for example, NC with the small inorganic core, or large organic shell (polymer or dendrimer
coating), the deformation of organic coating enables the filling of void spacing, in which case the non-close packed structure (bcc, etc.) become energy favorable.\textsuperscript{38,57,127} Lalatonne \textit{et al.} calculated that the sum of inter-particle Van der Waals attraction and the steric repulsions with the change of inter-particle spacing, indicating that the total energy highly depends on the inter-particle distances.\textsuperscript{135} (Figure 2.6)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_6.png}
\caption{The total potential, and the sum of the van der Waals attraction and the steric repulsion at two different coating layer thickness. (d=1.6 nm and 1.2 nm) Reprinted from Lalatonne \textit{et al.}.\textsuperscript{135}}
\end{figure}
For NCs coating with charged ligands, the electrostatic repulsions also counter-balance the van der Waals attractions. The charged ligand originates from either direct synthesis (e.g., citrate-capped gold NC144 and cetrimonium bromide (CTAB)-capped gold nanorod145) or post-synthesis ligand exchange (e.g., ammonium thiocyanate-capped semiconductor NC146). The charged ligand binds to the surface of the NC, and free counter ion forms a core-shell double layer to stabilize the NC in high dielectric constant solution. Gold nanorod coating with CTAB has a more complex bilayer structure. The inner layer CTAB binds to the surface of gold nanorod with quaternary ammonium group (head group) and connects to the outer layer of CTAB through the hydrophobic tails. The charged head group of the outer layer helps gold nanorod to be dispersible in a polar liquid. The bilayer structure enables gold NC high stability and makes it hard for ligand exchange.147

In NC self-assembly, hydrophobic and hydrophilic interactions are also widely applied to guide the shape and crystalline structure of assembled superstructure.148-151 For example, by drop-casting NC/hexane solution to the surface of polar diethylene glycol in LB trough or Teflon well, the hydrophobic interaction allows NC to stay on top of the liquid phase and assemble into two-dimensional superlattice.152,153 In emulsion-confined self-assembly, hydrophobic interactions allow the NCs to stay inside oil droplets during the emulsification. Thus, 3-D superstructure forms by evaporation of the oil phase.154,155 In Chap. 3, we report our investigations about modifying the counterparts of NC heterodimers (Au-Fe₃O₄, Pt-Fe₃O₄) with hydrophilic and hydrophobic ligands. By drop casting the amphiphilic NC onto the liquid-air interface, hydrophilic attraction allows the heterodimers to touch the
polar liquid phase with Au/Pt head while the non-polar Fe₃O₄ parts touch the air. This design enables the preferential alignment of NCs in the self-assembled superlattice.

2.3 Experimental Details of Nanocrystal Synthesis

2.3.1 Synthesis of PbE Nanocrystals (E=S, Se, Te)

The PbE NCs are synthesized following classical hot-injection method.

To synthesize PbS NCs, 0.9 g PbO and 40.0 mL oleic acid are mixed in a flask and degassed at 120 °C for 1 hour. 10.0 mL bis(trimethylsilyl)sulfide (TMS) and octadecene mixtures (by dissolving 42.0 μL TMS in 2.0 mL octadecene) are swiftly injected into the flask under nitrogen atmosphere. The NCs are allowed to grow for the 30 s, then cooled by an ice bath. Then the NCs are washed with isopropanol for three times. The purified NC is dispersed in hexane and stored in glove box. The size of PbS NCs can be tunable by changing the proportional ratio of oleic acid and octadecene in the reaction. Less oleic acid delivers smaller PbS NCs. This recipe is revised on published recipes.¹⁵⁶

To synthesize PbSe NCs, 0.829 g PbO, 20.0 mL ODE and 3.0 mL oleic acid are mixed in a reaction flask, then degassed in vacuum at 120 °C for 1 hour. The solution is further heated to 150 °C in a nitrogen atmosphere. 1.0 M trioctylphosphine (TOP)-Se mixture is prepared by dissolving Se shots into TOP by stirring overnight. 60.0 μL diphenyl phosphine is added to 8 mL TOP-Se solution, and then swiftly injected into the reaction flask. The reaction is maintained at 150 °C for 5 min. By the end of the reaction, an ice bath is used to quench the reaction. The 4.5 nm NCs are purified with 2-propanol three
times and then stored in hexane. The size of PbSe NC is tunable by changing the growth time and injection temperature. The 3.2 nm PbSe NC are synthesized by injecting TOP-Se at 120 °C and reacting for 5 min. The 6.0 nm PbSe NC are synthesized by injecting TOP-Se at 180 °C and reacting for 10 min. This recipe is revised on published recipes.\textsuperscript{79,157}

To synthesize PbTe NCs: 1.138 g lead acetate trihydrate is mixed with 2.0 mL oleic acid and 20.0 mL squalene. The mixture is degassed at 100 °C for 2 hours. Then the mixture is heated to 185 °C under a nitrogen atmosphere. 4.0 mL TOP-Te mixture (0.75 M) is injected, and the PbTe NC is allowed to grow at 175 °C for 20 s to 150 s to reach the size from 6.4 nm to 10.0 nm. The NCs are purified with 2-propanol three times and then stored in hexane. This recipe is revised on published recipes.\textsuperscript{158}

\subsection*{2.3.2 Synthesis of Gold Nanocrystals}

The gold NC are synthesized following reported procedures.\textsuperscript{159,160} To synthesize the 5.2 nm gold NCs, 200.0 mg HAuCl\textsubscript{4}·3H\textsubscript{2}O are dissolved in 10.0 mL of tetralin and 10.0 mL of oleylamine with magnetic stirring. Then, a mixture containing 90.0 mg of borane tert-butylamine, 1 mL of tetralin and 1mL of oleylamine is injected into the HAuCl\textsubscript{4} solution. The solution turned deep red immediately, and the reaction is kept at room temperature for 2 h. Then, acetone (120.0 mL) is added to the reaction. The NCs are separated from the solution by centrifuging at 8000 rpm for more than 3 min. The collected gold NCs are dispersed in 20.0 mL of hexane, washed two more times by using 120.0 mL of ethanol and centrifuging. The purified particles are stored in hexane for further use.
To synthesize the 7.6 nm gold NCs, 100.0 mg HAuCl₄·3H₂O is dissolved in 20.0 mL of octadecene and 1 mL of oleylamine with magnetic stirring. Then, 30.0 mg of the 5.2 nm gold NCs suspended in hexane are injected into the solution as seeds for growth. The mixture is maintained at 60 °C for 2 h. After the reaction cools down, the sample is purified with ethanol for three times. The washed gold NCs are stored in hexane for further use. The synthesis of the 10.2 nm gold NCs followed the same recipe as described above but using 7.6 nm gold NCs as seeds instead.

2.3.3 Synthesis of Platinum Nanocubes
To synthesize 7.3 nm Platinum nanocube, 200.0 mg Platinum acetylacetonate is mixed with 2.0 mL oleic acid, 2.0 mL oleylamine, and 20.0 mL octadecene. The mixture is degassed at 120 °C for 30 min, during which time the platinum acetylacetonate is dissolved, and the solution turns clear. Then, the flask is refilled with nitrogen and the liquid is heated to 190 °C. 0.02 mL Iron pentacarbonyl is pre-mixed with 0.2 mL octadecene in the glove box. Then the reductant is injected into the reaction flask. The nanocubes grow for one hour. Then they are washed three times with ethanol. 0.02 mL of oleic acid is added to the NC solution after each purification to eliminate purification. This recipe is revised on published ones.¹⁶¹,¹⁶²

2.3.4 Synthesis of Au-Fe₃O₄ and Pt-Fe₃O₄ Heterodimers
Pt-Fe₃O₄ heterodimer is synthesized following reported recipes.¹⁶¹-¹⁶³ 0.45 mL oleylamine is mixed with 10.0 mL octadecene in a reaction flask. The mixture is degassed at 120 °C
for 30 min; then the reaction flask is refilled with nitrogen. 0.035 mL of Iron pentacarbonyl is mixed with 0.125 mL octadecene in the glovebox, then injected into the flask. After 5 min, 10.0 mg Platinum nanocubes are injected into the flask with 1.0 mL octadecene and 0.5 mL oleylamine. The reaction is heated to 310 °C at a controlled rate of 3 °C per min and then kept at this temperature for 30 min. Then, air is bubbled into the flask to oxidize the Fe, and the particles are washed with ethanol three times. Pt-Fe₃O₄ heterodimers are synthesized following reported recipes.¹⁶²

Au-Fe₃O₄ heterodimer is synthesized following reported recipes.¹⁶⁴ Specifically, 0.32g hexadecyl ammonium chloride is mixed with 1.0 mL oleylamine and 12.0 mL octadecene in a reaction flask. The mixture is heated to 120 °C under the nitrogen atmosphere. 24.0 mg of Au NC in hexane is injected into the flask. The reaction is degassed by 30 mins, then heated to 180 °C under the nitrogen atmosphere. 0.28 mL of Iron pentacarbonyl is swiftly injected. The reaction is kept running for 30 min, then cool to 60 °C. Air is bubbled into the flask for 30 min to oxidize the iron. Then the heterodimer is purified by ethanol for three times.

2.3.5 Cation Exchange in PbE Nanocrystals
Cation exchange reaction is performed by quick injection of toluene dissolved PbE NCs into Cd(oleate)₂ solution at 180 °C. In a typical procedure, 750 mg Cadmium oxide, 5.0 mL oleic acid and 25.0 mL 1-octadecene are mixed and degassed at 110 °C for 30 minutes. Then the reaction is heated to 250 °C under the flow of nitrogen to get a clear solution. The mixture is cooled to 110 °C and degassed for another 1 hour before it is heated again
to 180 °C under nitrogen. When the temperature is stable at 180 °C, 2.0 mL of 50.0 mg/mL PbE and toluene mixture are quickly injected into the solution. After 45 minutes, the reaction is cooled down by an ice bath, and then washed with isopropanol and acetone for three times. This recipe is a modification of a published procedure.\textsuperscript{165}

To perform multi-step cation exchange, Cadmium oleate precursor is prepared by dissolving 750 mg Cadmium oxide in 5.0 mL oleic acid and introducing 25.0 mL 1-octadecene into that mixture. 0.75 mL Cadmium oleate solution is mixed with 20.0 mL octadecene and degassed at 110 °C for 1 hour. Then a 1.0 mL PbS and toluene mixture (100.0 mg/mL) is injected and reacted for 45 minutes. The product is purified three times with isopropanol and dispersed in toluene. The reaction is repeated once more followed by the final reaction.
3 STRUCTURAL DIVERSITY OF NANOCRYSTAL SUPERLATTICE*

3.1 Motivations for Nanocrystal Self-Assembly
Over the last two decades, a wide range of accessible NC modification strategies for inorganic cores and organic ligands have been developed. These allow bottom-up NC self-assembly to produce a series of well-order superstructures with unique optical and electrical properties. In the process of self-assembly, the final structure and properties can be affected by many factors such as the Van der Waals attraction, steric repulsion, dipole moment, magnetic moment, amphiphilic interaction, and isotropic morphology. Many questions remain to be answered regarding the structural diversity of NC superlattices, and a combination of experiments and theory will be needed to reveal the interaction between structure and properties in these systems to allow them to be harnessed in the advanced material system.

This chapter includes three parts. The first part investigates the possibility to use cation exchanged NCs as new building blocks for self-assembly. We investigate the cation exchange mechanism to fully transform PbE to CdE NCs, and the structural diversity of BNSL films from cation exchanged NCs. The second part discusses the asymmetric

* Part of the content is adapted with permission from: Davit Jishkariani, Yaoting Wu, Da Wang, Yang Liu, Alfons van Blaaderen, and Christopher B. Murray. Preparation and Self-Assembly of Dendronized Janus Fe₃O₄–Pt and Fe₃O₄–Au Heterodimers. ACS Nano, 2017, 11 (8), pp 7958–7966. Copyright © 2017 American Chemical Society.
modification on heterodimers and studies the effect of hydrophilic/hydrophobic interaction to guide the preferred orientation of NCs in the superlattice. The third part discusses the effect of PbSe NC’s ligand distribution to the crystal structure of superlattice.

3.2 Self-assembly of Cation Exchanged Nanocrystals*

3.2.1 Cation Exchange Reactions on PbE Nanocrystals
Cation exchange reactions are put forward as a powerful technique to complement the classic solvothermal synthesis. In a typical cation exchange reaction, the anions remain stable in the sublattice framework while cations are replaced by guest ions from solution.\textsuperscript{115,121,166,167} Cation exchange tunes the chemical compositions of NCs without affecting the original size, shape, and morphology, which means cation changed NCs maintains the dimensional features of template but can take on new, distinctive properties correlated with the chemical compositions.\textsuperscript{115,167-170} Partial cation exchange enables the production of hetero-structured NCs which are not accessible by direct synthesis. For example, PbE to CdE NC cation exchange can generate core/shell structure at intermediate stages.\textsuperscript{120} the cation exchanged shell passivate the traps on the surface and enhance the photoluminescence of the NC.\textsuperscript{122-124,171-174}

Under typical solvothermal conditions, the cation exchange between PbE and Cd\textsuperscript{2+} produces PbE/CdE core-shell NCs.\textsuperscript{119} It is hard to obtain pure CdE NC from Pb/Cd cation exchange since the self-limiting features of the reaction stop the reaction at the core-shell

\* The author acknowledges Ben Diroll for his contribution to X-ray characterization.
However, it is valuable to get rid of all the Pb\(^{2+}\) possible as the residual cations can cause defects or generate trap states to reduce the optoelectronic quality (i.e., quantum yield, lifetime, etc.). \(^{176}\) Higher reaction temperature is reported to reduce the core size further, but unfortunately is seen to activate Ostwald Ripening in solution which in turn results in higher polydispersity of the NCs samples. \(^{122,165,177}\) Thus, it is important to better understand the thermodynamics of cation exchange, find the ideal conditions to achieve full exchange and preserve uniformity in both size and morphology.

High-temperature cation exchange reactions are conducted at 180°C using different sized PbSe NCs. TEM images (Figure 3.1(a)-(f)) show that cation exchanged nanocrystals retain the size and uniformity of PbSe template, which is further confirmed by overlapping of small-angle x-ray scattering (SAXS) pattern of samples before and after cation exchange, as is shown by (Figure 3.1(g)-(i)). UV-Vis absorption spectra (Figure 3.1(m) and (n)) show a shift of extinction band gaps from visible to infrared range, indicating the change of chemical composition. The structural transformation is characterized by wide-angle X-ray scattering (WAXS) patterns. (Figure 3.1(j)-(l)) The crystal structure transfer from PbSe’s rock salt \(\text{PbSe} (Fm\overline{3}m)\) to CdSe’s zinc blende \(\text{CdSe} (F\bar{4}3m)\). Disappearance of the peak \((200)\) indicates that almost all the PbSe has transform to CdSe.
Figure 3.1 (a-c) TEM images of directly synthesized PbSe of three sizes and (d-f) corresponding CdSe NCs produced by cation exchange (g-i) Small-angle X-ray scattering pattern of PbSe and CdSe NCs in (a-f), respectively. (j-l) Wide-angle X-ray scattering pattern of PbSe and CdSe NCs in (a), (b) and (c), respectively. The scale bars represent 20nm. (m) UV-Vis absorption spectrum of multiple sizes PbSe of direct synthesis and (n) CdSe NCs of cation exchange from PbSe.
Although WAXS gives a qualitative analysis about the extent of cation exchange, it is hard to determine the absolute percentage of residual Pb$^{2+}$ in the NC. Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used as a much more precise technique to characterize the residual Pb$^{2+}$ through cation exchange. As is shown in Figure 3.2 (a), for PbE NCs within the size range of 3-8 nm, more than 88% of Pb$^{2+}$ is replaced by Cd$^{2+}$. The residual Pb$^{2+}$ correlated with the particle size and counter anions. In general, large CdE NCs retain more Pb$^{2+}$ than small ones, which is consistent with the outside-in exchange mechanism, while the CdS has more Pb$^{2+}$ than CdSe and CdTe of similar sizes. HR-TEM imaging of post exchange examples shows that the Pb$^{2+}$ stays in the center and there is a sharp boundary seen in core-shell interface. (Figure 3.2(c))
Figure 3.2 (a) Percentage of residual lead in multiple size CdS, CdSe and CdTe NCs by cation exchange at 180 °C for 30 min. (b) In-situ percentage of residual lead in large size CdS, CdSe and CdTe during cation exchange. The scale bar represents 2 nm. (c) A high-resolution TEM image of medium size CdTe NCs. The scale bar represents 2 nm. (d) A random mixture of PbSe and cation exchanged CdSe NC with 9:1 ratio.

3.2.2 Binary Nanocrystal Superlattices (BNSLs) from Cation Exchanged Nanocrystals
The two-dimensional BNSL films have a delicate crystal structure and fixed chemical
component, which enables directional charge and energy transport between neighboring NCs in the long-range-order structure. Since the size and monodispersity are retained by cation exchange, the pristine and post-exchange NCs are ideal building blocks to form BNSL of different crystal structures and compositions. The size combination of small (~3.0 nm), medium (~5.0 nm) and large (~7.0 nm) NCs generates MgZn$_2$ and NaZn$_{13}$-type superlattice. Figure 3.3 shows MgZn$_2$-type BNSL films formed with 5.5 nm and 7.3 nm PbSe and CdSe NC. In the superlattice, the same size of PbSe and CdSe are interchangeable without changing the crystal structure. 3.1 nm and 6.5 nm NC combination give NaZn$_{13}$-type superlattice. Similarly, the cation exchanged CdS can replace the same size PbS NC in the BNSL superlattice. (Figure 3.4)
Figure 3.3 TEM and corresponding FFT images of MgZn$_2$ type BNSL superlattice films formed with 4.7 nm PbSe, CdSe and 6.5 nm PbSe, CdSe. (a) 5.5 nm PbSe and 7.3 nm PbSe (b) 5.5 nm PbSe and 7.3 nm CdSe (c) 5.5 nm CdSe and 7.3 nm PbSe (d) 5.5 nm CdSe and 7.3 nm CdSe. Inserts are corresponding FFT images of BNSL. The scale bars represent 50 nm.
Figure 3.4 TEM and FFT images of NaZn$_{13}$ type BNSL superlattice films formed with 3.2 nm PbSe, CdSe and 6.5 nm PbSe, CdSe. (a) PbSe 3.3 nm and PbSe 7.3 nm (b) PbSe 3.3 nm and CdSe 7.3 nm (c) CdSe 3.3 nm and PbSe 7.3 nm (d) CdSe 3.3 nm and CdSe 7.3 nm. Inserts are corresponding FFT images of BNSL. The scale bars represent 50 nm.
3.3 Self-Assembly of Amphiphilic Janus Heterodimers

In recent years, hydrophobic\(^{148,150,178}\) and hydrophilic\(^{149,179,180}\) interactions are extensively explored to guide the directional self-assembly of colloidal particles for distinctive properties. For example, the surface of colloidal particles can be decorated with both hydrophobic and hydrophilic patterns of different domains, to produce the Janus particle (Janus is the name of two-faced god in ancient Roman religion and myth). Chen et al. have reported that the amphiphilic decorated particles can self-assemble into complex Kagome structure, giving the possibility of enhanced magnetic anisotropy.\(^{181,182}\) Asymmetric modification of particles can be done by vapor deposition,\(^{183}\) electrostatic depositions,\(^{184}\) layer-by-layer depositions,\(^{185}\) and seeded-emulsion polymerization.\(^{186}\) However, most of the decoration process is implemented on the micrometer size colloidal. Fewer examples of asymmetric modification have been presented with the nanometer-size particles since their much smaller size and larger surface-to-volume ratio inhibit the precise control over modification on different parts on the surface.\(^{187}\)

The stabilizing layer on the surface of NCs, organic ligand plays a key role in controlling NC interactions including Van der Waals attractions and steric repulsions. In a recent project, we investigate the asymmetric modification process by taking advantage of different surface binding properties of phosphoric acid and thiol-based ligands.\(^{161}\)

---

* The author acknowledges Davit Jishkariani for his contribution to dendrimer synthesis and ligand exchange. The author acknowledges Da Wang for his contribution to elemental and structural characterization.
We investigate the asymmetric modification of Pt-Fe₃O₄ NCs. The size and relative ratio of Pt and Fe₃O₄ compositions are tunable in a wide range. For a more extensive study, we selected Janus particle samples in which the Pt is 7.3 ± 0.5 nm (face diagonal length of the inorganic part), and the Fe₃O₄ is 15.4 ± 2.2 nm (inorganic part). The asymmetric modification of the Pt-Fe₃O₄ heterodimers is possible because phosphoric acid-based ligand binds strongly with Fe₃O₄₁₈₈,₁₈₉ while thiol-based ligand binds strongly with Au.₁⁹₀-₁⁹₂ Dendrimer ligands, which are highly branched macromolecules, are chose for modification because of their high uniformity in size and properties. The phosphonic acid-based dendrimer ligand is designed to be hydrophobic, with long hydro-carbon tails, and the thiol-based dendrimer ligands are designed with ethylene glycol groups to make them hydrophilic. The details of synthesis can be found in our published papers.₁⁶¹ Structure of phosphonic acid-based dendrimer ligand (1), thiol-based ligand (2) and the schematics of ligand exchange are shown in Figure 3.5.

Figure 3.5 Schematics of the two-step ligand exchange process to coat the heterodimers using thiol-based ligand hydrophobic ligand and phosphonic acid based hydrophilic ligand. Reprinted from Jishkariani et al.₁⁶¹
The asymmetric modification is done by performing sequential ligand exchanges on Pt and Fe₃O₄ part: The Fe₃O₄ part of the heterodimer is coated with the phosphonic acid-based ligand through solution phase ligand exchange. Specifically, the phosphonic acid-based ligand is mixed with heterodimers in chloroform. The reaction mixture is stirred at 35 °C overnight; then the heterodimers are washed three times using methanol and chloroform. Following that, the Pt part is decorated with the thiol-based ligand with the same procedure. EDX mapping is used to characterize the distribution of ligands on heterodimers. The signal from elements of Platinum and Iron matches with the NCs imaging. As is shown in Figure 3.6, overlapping of the signal from sulfur and platinum reveals the selective coating of the thiol based-ligand on the platinum part of heterodimers.
Figure 3.6 EDX chemical mapping of a Janus heterodimer superlattice (a) HAADF-STEM image to show the superlattice from post-modification heterodimers (b) element of the platinum’s distribution (c) element of iron’s distribution, (d) element of surfer’s distribution, (e) overlapping od sulfur and platinum, and (f) overlapping of iron and platinum. The inserts show enlarged 100 nm × 100 nm areas. Scale bars in (a–f) are 200 nm. Scale bars in insets are 20 nm. Reprinted from Jishkariani et al. 161

The modified heterodimers are applicable for self-assembly at the liquid-air interface. Our experimental result reveals that the asymmetric ligand exchange tunes the translational and orientational order of heterodimers in the superlattice. We compare the structure of superlattice self-assembled with pristine heterodimer, only phosphonic acid-based ligand modified heterodimer and fully exchanged ones. Gradually, the translational order of superlattice become better through the extent of ligand exchange. Figure 3.7 shows a disordered assembly of pristine heterodimers. The disorder is due to the relatively high
poly-dispersity (14% on Fe₃O₄ and 7.3% on Pt) and irregular shape of building blocks. The short-range order of superlattice improves when using heterodimers coated with a phosphonic acid based ligand and is further improved by using fully coated ones. The insert FFT images of Figure 3.7 (a-c) reveals the rising degree of order.

Two explanations can be put forward for the improvement of lattice order by ligand exchange. First, the dendrimer ligand coating changes the effective size of heterodimers and improves their overall monodispersity. Second, the amphiphilic modification of heterodimers guides their orientation at the liquid-air interface. The morphology of heterodimers disrupts the superstructure ordering when the heterodimers align in the same orientation.

**Figure 3.7** (a) Schematics to show the of liquid–air assembly of post-modification heterodimers and the transfer process by “stamping.” TEM images of self-assembly with (b) as-synthesized Pt-Fe₃O₄ heterodimers (c) Pt-Fe₃O₄ heterodimers. Only the Fe₃O₄ part is functioned with the phosphonic acid-based ligand. (d) Pt-Fe₃O₄ heterodimers. Both Pt and Fe₃O₄ part are functioned with thiol, and phosphonic acid-based ligands Scale bars in (b) and (c) are 400 nm, in (d) is 100 nm. (Digital FFT of an entire image are provided as insets in the top right corners of each image) Reprinted from Jishkariani et al.. ¹⁶¹
To validate the hypothesis, we use HAADF-TEM tomography to characterize the structure of superlattice. Figure 3.8 (a)-(b) shows the reconstructed image of a local superlattice composed of 882 NCs. XZ slices of the superlattice shows all the heterodimers are on the same plane. (Figure 3.8 (c)) They can be grouped into four orientations based on the relative position of platinum to the iron oxide body. The four orientations can be seen in Figure 3.8 (d).

In a randomly orientated NC superlattice, four orientations should have the same ratio. Our tomography analysis reveals that a high proportion of heterodimers choose orientation 1 and 4, which means the platinum part prefers to be above or below the Fe₃O₄ part. And there is no distinctive difference of the proportional ratio between orientation 1 and 4. The orientational assembly of the NC superlattice can be either entropy driven or enthalpy driven. In an entropy driving self-assembly, the steric repulsions of heterodimer guide the NC to orient with Pt part up or down to fulfill the in-plane spacing filling of the superlattice. In an enthalpy driving self-assembly, the hydrophilic interaction between Pt and diethylene glycol make the heterodimers to point down at the liquid-air interface. Above experiments reveal an entropy driving process for asymmetric functioned heterodimers.
Figure 3.8 (a) Reconstruction of Pt-Fe$_3$O$_4$ heterodimer superlattices with HAADF-STEM tomographic images. The yellow represents Pt, and blue represents the Fe$_3$O$_4$. The insert is FFT images of the same area superlattice. (b) A zoom-in image of Pt-Fe$_3$O$_4$ heterodimer superlattices in the dashed window in (a). (c) XZ slice view of the Pt-Fe$_3$O$_4$ heterodimer superlattice. (d) Four possible orientations of heterodimers. (e) Orientation quantification of Pt-Fe$_3$O$_4$ Janus heterodimers. Reprinted from Jishkariani et al.\textsuperscript{161}
However, it doesn’t necessarily mean that the hydrophobic/hydrophilic interactions fail to guide the orientational preference of NC superlattice. To understand the strength of the interactions, we prepare the Au-Fe$_3$O$_4$ heterodimers in which the Au and Fe$_3$O$_4$ parts have comparable size and monodispersity. (As is shown in Figure 3.9 (a)) Compared to the Pt-Fe$_3$O$_4$ heterodimers, the new Au-Fe$_3$O$_4$ dimer has a larger Au part but a smaller Fe$_3$O$_4$ part. Similar ligand exchanges are done by coating the Fe$_3$O$_4$ part with phosphonic acid-based hydrophobic dendrimers and the Au part with thiol-based hydrophilic dendrimers, as is shown in Figure 3.5. The NC superlattice films are prepared by heterodimer self-assembly on diethylene glycol-air interface. HADDF-STEM images (Figure 3.9 (b)) show that the heterodimers self-assemble into well-order close packing NC superlattice. We use STEM tomography and reconstruction to investigate the preference of orientation of building blocks in a superlattice. Figure 3.9 (c) and (d) show the low and high magnification HAADF-TEM image at a tilting angle about 74 deg. Most of the heterodimers show a preference of orientation with Au part out of the carbon film. Quantitatively, 88% of the dimers aligns in this orientation. According to the analysis based on tomography, we can infer that the hydrophilic/hydrophobic interactions also play important roles to drive the preference of orientation of building blocks in a self-assembled NC superlattice, as long as the size proportion of heterodimers are well balanced.
Figure 3.9 (a) TEM image of as-synthesis Au-Fe3O4 heterodimers (b) HAADF-TEM image of NC superlattice self-assembled with asymmetrical functioned Au-Fe3O4 (c) Low magnification HAADF-TEM image of NC superlattice self-assembled with asymmetrical functioned Au-Fe3O4 at a tilting angle of 70 deg. (d) High magnification HAADF-TEM image of NC superlattice self-assembled with asymmetrical functioned Au-Fe3O4 at a tilting angle of 74 deg.
3.4 Structural Diversity of NC Superlattice Film Self-Assembled from PbSe nanocrystal

The hard sphere models of self-assembly have been used to explain the formation of close-packing NC superlattice under ambient conditions. Recently an increasing number of non-close packing structures of superlattice have been reported, indicating a complex dynamic process of self-assembly and the potential impact of enthalpic interactions. With a single batch of PbSe NCs, a variety of non-close packing crystal structures can be obtained under diverse assembly conditions. Some of the structures are reported for the first time. Following that, we investigate the driving factors behind the NC superlattice structural diversity.

In an entropy-driven process of self-assembly, a large proportion of spherical NCs self-assemble into fcc or hcp-type superlattice, which has small void spacing and low free energy. But this is not necessarily true for PbE (E=S, Se, Te) NCs, as both square and hexagonal structure superlattice from PbE as building blocks have been separately reported. But none of the reports explains the driving factors for a different structure. In this part, our experimental analysis on PbSe NC and superlattice reveals that the surface oxidation can be the reason behind structural transformation from square to hexagonal lattice.

The cubic monolayer lattice can be prepared by drop-casting a small amount of as-synthesized PbSe NC (10 µL, 2 mg/mL) solution on to the surface of diethylene glycol in a Teflon well (~2 cm² area). The NCs connect with 4 nearest neighbors with \{100\} facet
and align with their [100] axis vertical to the interface. Figure 3.10’s TEM and SAED image reveal the structure mentioned above.

The *in-situ* GISAXS experiment by Geuchies *et al.*\textsuperscript{50} report that it is the electrostatic interactions between {100} facet drives the structural transformation from a random-oriented hexagon lattice to the orientated square lattice. During the dynamic process, the stabilizing ligand - oleic acid detaches from the surface to initiate the attachment and fusion of neighbor NCs.
Figure 3.10 (a) TEM image of monolayer superlattice films self-assembled on liquid-air interface with 6.4 nm PbSe NC (b) The electron diffraction pattern indicating a (100) projection of NCs to the substrate (c) HR-TEM images of superlattice in (a) (d) TEM images of a monolayer and bilayer boundary of superlattice, and corresponding lattice constant of a unit cell in this projection.
Under air-free conditions, the long time (over 1 year) aged PbSe NCs continue to form a square lattice upon drop casting. In contrast, when the same stock solutions are exposed to air for a few days, the NCs self-assemble to form an fcc-type superlattice, according to the GISAXS and TEM characterization (Figure 3.11 (b)). This indicates that oxidation of the particle surface is an important factor driving the structural transformation.

The fcc-type NC superlattice gives a distinctive SAED pattern. The orientation of NC building blocks in the superlattice is extracted from HR-TEM images (Figure 3.11 (c)) and simulation of SAED patterns (Figure 3.11 (d)). Simulation of six-fold symmetry wide-angle SAED pattern shows it is composed of three (110) diffraction spots rotated by 60°. It means there are three preferred in-plane orientations, but all the orientations have 〈110〉 axis vertical to the substrate. The arc curve of (002) diffraction peaks shows similar intensity, which means the three in-plane orientations have a similar prevalence. The HR-TEM image in Figure 3.11 (c) shows that the three orientations are randomly represented in this local area. As is shown by the PbSe polyhedron (orange/black) models overlapped to the TEM image, within the same plane, one NC touches 6 nearest co-planar neighbors with its two 〈100〉 facets and four 〈111〉 facets. Between two planes of the superlattice (blue/red polyhedron and orange/black polyhedron), the NC contacts with the most nearby 6 NCs (3 on top and 3 below) through two 〈100〉 facets and four ridges between 〈100〉 and 〈111〉 facets.
Figure 3.11 (a) GISAXS pattern and (b) TEM images of oxidized 7.1 nm PbSe NC superlattice. (c) HR-TEM images of bi-layer PbSe superlattice. The building blocked are grouped by Red, yellow, and blue arrows which are perpendicular to the (100) facet. Each group devotes to the diffraction spots of the same color in (d). The scale bar represents 5 nm. (d) SAED diffraction pattern and simulation of bilayer NC superlattice self-assembled with 7.1 nm PbSe NC. (e) The cartoon on top of HR-TEM images shows the building blocks’ orientation and the inter-particle relationship of one-layer PbSe NC. Each orange/black polyhedron represents one NC. (f) The cartoon on top of HR-TEM images show the building blocks’ orientation and inter-layer attachment of bi-layer NC superlattice. Each blue/red polyhedron represents one PbSe NC of the other layer.

PbSe NCs are highly sensitive to oxidation, which is a complex process of multiple reactions happening to both the ligand shell and inorganic core. Gunawan et al. perform EELS measurements on air-exposed PbSe NCs. It shows the oxidation introduces conjugated double bonds in the oleic acid coating ligands. The conjugated double bonds cause ligands to extend out and interdigitate with ligands from neighbor NCs. Moreels et al. use NMR to characterize the change to the organic capping of PbSe NCs during oxidation and show that the oxidation causes the loss of oleic acid and Pb atoms, in the form of lead-oleates in solution. The oxidation reaction process proceeds through a series pathway onto the surface of PbSe. SeO₂, PbO, and PbSeO₃ are typical compounds generated by oxidation of bulk PbSe. The oxidation layer on the surface of PbSe is not structurally stable, and it gradually detaches from the surface, reducing the particles’ size and expands the particle size distribution. Optically, the air exposure leads to an irreversible blue shift of absorbance peaks, and quenches the higher-energy emission after only a few second of air-exposure, by introducing trap states through oxidation.
X-ray absorption spectroscopy (XAS) collect the information about the geometric and electronic structure of target atoms by exciting their core electrons with monochromatic X-ray. Here we use XAS to characterize the as-synthesized and air-exposed PbSe NCs. The Se K-edge XAS is sensitive to the change of oxidation and coordination states of Se atoms. As is shown in Figure 3.12 (a), the Se K-edge XAS data show a sharp, single absorption feature at 12660 eV, which originates from the 1s-4p transition. The absorption feature of pristine is supported by publications. The clear oscillations at the extended regions show the high uniformity of the atomic crystal structure. By air exposure, the absorption feature becomes board, indicating the formation of new oxidation state, which is generated by surface oxidation. It validates that the PbSe NC surfaces are oxidized by even brief air exposure.
According to Zherebetskyy et al.’s analysis of pristine PbSe NCs,\textsuperscript{214} \{111\} facet prefers to bind with oleate (OA-) while \{100\} facet binds to oleic acid at the favorable energy state. The binding energy per OA-/OAH to \{111\}/\{100\} facet is -0.52 eV and -0.16eV, respectively. The significant binding energy difference explains the detachment of ligand from \{100\} facet and the atomic diffusion during the self-assembly of as-synthesized NCs.

We compare the atomic lattice of pristine and air-exposed PbSe NCs under HR-TEM. As is shown in Figure 3.13 (a) and (d), the pristine PbSe NC show clear and sharp edge under
the projection of [111] and [110] axis. By air-exposure, the NCs show a zig-zag edge under the projection of [100] axis (Figure 3.13 (b)), and passivated corners under the projection of [110] axis (Figure 3.13 (e)), which is caused by the detachment of atoms.

Figure 3.13 High-resolution TEM images of (a) as-synthesized and (b) Oxidized PbSe NC under the projection of [100] axis. (c) atomic models of PbSe NC tilting at a small degree from the projection of [100] axis. (d) High-resolution TEM images of as-synthesized and (e) Oxidized PbSe NC under the projection of [110] axis. (f) atomic models of PbSe NC tilting at a small degree from the projection of [110] axis. The scale bars represent 5 nm.
Based on above analysis, oxidation reactions change the surface chemistry of PbSe NC by detaching the ligand and superficial atoms, especially on \{111\} facet which is Pb\(^{2+}\) rich. The oxidation makes \{111\} and \{100\} facets similar in ligand density. Thus, the oxidized-PbSe NCs tend to form an fcc-type superlattice and where proximal NC randomly choose contacts between \{111\} and \{100\} facets.

3.5 Conclusions
The crystal structure of superlattice has a strong correlation with their distinctive optical and electrical properties.\(^{21,79,81}\) In this chapter, we investigate the formation of superlattice film of diverse crystal structures by tuning the building blocks, coating ligands, and NC interactions. We reveal that the cation exchange is an efficient tool to tune the chemical composition and properties of NCs but maintains the size, shape, and uniformity. The cation exchange reaction creates new building blocks for self-assembly. Its products are interchangeable with their templates in the NC superlattice, which creates a broad portfolio of heterojunction alignment in the same crystal structure. By performing the asymmetric modification on heterodimers, we prepare the Janus-like structures with both hydrophilic and hydrophobic parts on single NC. By tuning the strength of interactions, we can get close-packed NC superlattice with a high degree of orientational coherence. We also investigate the diverse crystal structures of superlattice from pristine or oxygen-aged NCs. It reveals the significance of ligand redistribution to affect the NC interactions, which further determine the crystal structure of NC superlattice.
4 ENHANCED CHARGE TRANSFER IN BINARY NANOCRYSTAL SUPERLATTICE BY LIQUID-AIR INTERFACE LIGAND EXCHANGE*

4.1 Motivations for Ligand Exchange on Liquid-Air Interface

BNSL films form by self-assembly of two kinds of NCs into two- or three-dimensional long-range-order colloidal crystal structures. Such materials offer more precise control over their components and chemical composition in the crystal lattice than what can be achieved with a randomly mixed NC films. The interpenetration of two kinds of NCs gives a larger contact area than a traditional planar heterojunction. Thus, the enhanced coupling between neighboring NCs of different band gaps and band alignments is expected to result in efficient directional charge or energy transfer across the heterojunction interface. Additionally, for the bicontinuous type of NC superlattice, in which the two NC components of superlattice are inter-connected, each NC species provide pathways for long-range charge transport and extraction different charge carriers. The collective optical and electrical properties of the NC building blocks make BNSL films desirable for potential optoelectronic applications.

Strong inter-particle coupling is required to obtain high-efficient interfacial charge or energy transfer across a heterojunction. However, the coupling and charge/energy transfer is limited by the long, insulating long hydrocarbon chain ligands which come with the as-synthesized NCs. Ligand exchange is widely used as a post-treatment technique replace the as-synthesized ligand with small molecules, reduce the inter-particle spacing and enhance the strength of electronic coupling between neighboring NCs. Through the development of ligand exchange, a wide array of ligands has been put forward. These ligands can be grouped by the nanocrystal-ligand interactions, the dispersed state in ligand exchange or the number of binding sites. There are three types of ligand based on nanocrystal-ligand interactions: L-type, X-type, and Z-type ligands. L-type ligands donate a pair of electrons to the empty orbital of surficial metal cations. Typical L-type ligands include hydrocarbon amines, hydrocarbon phosphines, and hydrocarbon phosphine oxides. X-type ligands have unpaired electrons. It takes one electron from metal cations to form the covalent bond. Examples of X-type ligands are halide anions (Cl\textsuperscript{−}, Br\textsuperscript{−} or I\textsuperscript{−}) and carboxylate (RCOO\textsuperscript{−}). The Z-type ligands bind as electron acceptors and take electrons from the counter ion of nanocrystals. Z-type ligands examples are AlCl\textsubscript{3}, H\textsuperscript{+}. Ligand exchange reactions can happen in either solid or liquid state. When possible, solution-based exchange has been favored if the NCs can remain dispersible in a liquid state. It allows device fabrication by a solution based processes. For example, by ligand exchange with ammonium thiocyanate, the solution dispersed CdSe quantum dots can be fabricated into photodetectors with highly sensitive photoconductivity. Unfortunately, only a small proportion of molecules are feasible for liquid state ligand exchange. The existing
electrostatic repulsion prohibits ligand-exchanged NCs from self-assemble into long-range-structure. Solid state ligand exchange can in principle be applied to a much wider range of compact ligands.\textsuperscript{215,221} However, solid-state ligand exchange reduces the inter-particle spacing, which often causes severe cracks and disrupts the long-range order of the NC superlattice. Besides the two most common methods (solutions bases, and solid state exchange), the is an intermediate option, recently explored by Dong et al. in which they have performed ligand exchange at liquid-air interface.\textsuperscript{78} The ligand exchange happens to the film floating on the surface of the liquid. During the ligand exchange, extra flexibility is given for the superlattice film to shrink isotropically. The cracking of the films can be significantly reduced, and a highly coupled NC superlattice film can be obtained. Figure 4.1 shows the local order of NC superlattice by liquid-air interface ligand exchange, which is distinct from the sample by solid-state exchange A general schematics of liquid-air interface ligand exchange is depicted in Figure 2.5. We proposed that the liquid-air interface ligand exchange is also applicable to BNSL film, which generates strongly coupled NC superlattice structures with effective charge and energy transport.
Figure 4.1 (a) Low magnification and (b) high magnification SEM images of FePt NC superlattice after liquid-air and then solid-state ligand exchange with formic acid. (c) Low magnification and (d) high magnification SEM images of FePt NC superlattice film by solid-state ligand exchange only with formic acid. Reprinted from Dong et al. 78

4.2 GISAXS Background and Theory
The kinetics and extent of ligand exchange can be reflected by the structural transformation of the NC superlattice, which can be characterized by GISAXS technique. At 1989, the GISAXS is introduced as an advanced tool to characterize the growth of the gold thin film.
It takes the advantages of low beam damage, no restrictions on the substrate and large characterization area. It is a versatile technique to characterize the structural features of interface or thin film in micrometer and nanometer scale. A typical type of samples for GISAXS is the NC self-assemblies, thin-film block polymers, and silica mesophases.

GISAXS techniques are developed from the similar theoretical background with the more common small angle X-ray scattering (SAXS), but performed in a grazing-incidence geometry instead of transmission or simple reflection geometry. In GISAXS the X-ray beam is incident on the sample supported on the substrate so that the beam is at or near the critical angle for total reflection. Most of the beam is reflected or refracted by the substrate. But when part of the reflected or refracted beam interacts with the sample, the scattered beam encodes structural information related to the in-plane ordering.

When a monochromatic X-ray beam (λ as wavelength) hits a thin film sample, the scattering factor q can be expressed by equation (4.1). αᵢ is the incident angle of beam, αᵢ is the in-plane exit angle and 2θᵢ is the out-of-plane scattered angle.

\[
q = \begin{bmatrix} q_x \\ q_y \\ q_z \end{bmatrix} = \frac{2\pi}{\lambda} \begin{bmatrix} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}
\]

(4.1)

The scattered intensity can be described as

\[
I(q) = \langle |F|^{2} \rangle \mathcal{S}(q_{\parallel})
\]

(4.2)

in which the \( F \) represents the form factor and the \( \mathcal{S}(q_{\parallel}) \) is the total interference function.

The form factor correlates with particles’ size, shape and faceting. And the interference
function (Structure Factor) represents the inter-particle correlation. In a connected systems such as NC superlattice, the two terms are strongly correlated at small $q_y$ values.\textsuperscript{231}

The capability of \textit{in-situ} characterization makes GISAXS an even more powerful tool with which to investigate the kinetics and mechanism of NC growth and self-assembly process. The pioneering work of Renaud \textit{et al.} reveals the capability to deriving the particle size, shape, ordering and growth mode of NCs on the substrate.\textsuperscript{232} It can also help to determine the best conditions for NC growth. The schematics about using GISAXS to characterize the growth of gold NCs on the solid substrate can be found in Figure 4.2. Pietra \textit{et al.} use \textit{in-situ} GISAXS to study the self-assembly of CdS/CdSe colloidal nanorods at the liquid-air interface.\textsuperscript{22} The dynamics of self-assembly indicates a hierarchical self-organization model which explains the length-dependent mechanism of NRs self-assembly at the liquid/air interface. By performing GISAXS and GIWAXS combination experiment, Weidman \textit{et al.} tracked the translationally and orientationally order of superlattice during the process of self-assembly.\textsuperscript{21} Their experimental result shows the kinetics of self-assembly, the structural transformation from fcc to bct lattice, and reveals that the orientational alignment occurs at a faster time scale than the translational alignment. The NC superlattice takes 4.8 min to go from 5 to 95\% of its final c axis alignment, while the NC only takes 1.2 mins to go from 5 to 95\% of their maximum alignment.
4.3 *In-Situ* GISAXS Characterization of Ligand Exchange with Binary Nanocrystal Superlattice*

In a general process of ligand exchange, the choice of the anchoring group, the reaction time, and the extent of ligand exchange are significant factors to affect the performance of semiconductor NC devices. Combination of *ex-situ* and *in-situ* characterization techniques are required to understand the mechanisms of ligand exchange reactions on the surface of the NCs.\textsuperscript{72} Previously, NMR\textsuperscript{76,233-235} and EPR\textsuperscript{236,237} are used to study the kinetics of ligand exchange. These experiments require NCs to be well dispersed in the solution during the measurement, which is only applicable to a small proportion of ligands. Liquid-air interface ligand exchange allows to study the kinetics of ligand exchange through the combination

---

* The author acknowledges Blaise Fleury for his contribution to GISAXS characterization.
with *in-situ* GISAXS technique and is feasible to a board range of ligands. By analyzing the real-time GISAXS patterns, we could resolve the inter-particle spacing evolution, calculate the kinetics of ligand exchange, and investigate the structural transformation of the NC superlattice during the reaction.

### 4.3.1 In-Situ GISAXS Experiment Setup

The superlattice films can be prepared by NC self-assembly at the liquid-air interface. A general procedure is discussed in Chap. 2.21. Briefly, a drop (10 µL) of NC solution is drop-casted on to the surface of diethylene glycol in a Teflon well. A glass slide is used to cover the well to reduce the rate of evaporation. Once the solid film forms at the liquid-air interface, the Teflon well is transferred to a GISAXS solvent chamber. Additional diethylene glycol is injected to bring the meniscus above the edges of the well, allowing the X-ray incident beam to hit the sample directly through the Kapton windows. The experiment is performed at synchrotron beam station at Argonne National Lab.

To perform ligand exchange in GISAXS experiment, a pair of needles are placed at the diagonal corners of the Teflon well. One injects the guest ligand solution while the other withdraws the same amount of liquid, to keep the meniscus surface at the same level during the scattering experiment. The set up can be found in detail in Figure 4.3. This design allows the solvent front to move in one direction. To reduce the evaporation of the solvent and inhibit the change to the heights of meniscus surface, additional solvent is placed in the GISAXS cell, creating a high vapor pressure of the solvent. The GISAXS measurement and the syringe pump system are synchronized using an in-house program. When the reaction starts, 0.3 mL guest molecule solution in acetonitrile is quickly (0.54 ml/min)
injected into the diethylene glycol subphase. Since acetonitrile has a lower density (0.79 g/mL) than diethylene glycol density (1.12 g/mL), it stays between the liquid phase and the solid film. The reaction proceeds immediately when the solution front touches the film. The change of scattering pattern is instantly recorded at a time resolution of one frame of images per second. The ligand exchange reaction continues for 150-300 s.

**Figure 4.3** (a) Side view of GISAXS solvent chamber. The superlattice on top of the Teflon well can be seen through the Kapton window. (b) Top view of Teflon well in GISAXS solvent chamber. The injection and withdraw needles are fixed on the diagonal corner of the Teflon well. (c) A broad view of the solvent chamber on XYZ stage in the GISAXS hood. The solvent change is located at GISAXS beam stage in one of the Advanced Photon Source beam station in Argonne National Lab (4) Cartoon of the set-up about how the scattering diagram is collected.
Before the experiment, beam damage tests are performed to investigate whether the X-ray beam exposure will cause any change to the structure of superlattice and corresponding diffraction pattern. The test is performed under the same condition with *in-situ* experiment, by using 7.1 nm PbSe superlattice film with blank acetonitrile liquid. Figure 4.4 shows that no noticeable change occurs in the (111) scattering peak within 150 seconds of direct exposure, which is the timescale of a typical GISAXS experiment.

**Figure 4.4** Line-cut of the peak (11-1) in GISAXS diffraction pattern collected at 0 s, 30 s, 60 s, 90 s, 120 s, and 150 s. The sample is 7.1 nm PbSe superlattice treated with blank acetonitrile.
4.3.2 Ligand Exchange Kinetics on Single Component NC Superlattice Film

The in-situ GISAXS experiment is demonstrated with 3-mercaptopropionic acid (MPA), and oleic acid grafted 6.7 nm CdSe (quantum dot) NC superlattice. Owning to MPA’s small size and bi-functional anchoring group, it enhances the coupling of semiconductor NCs for efficient charge transfer, which makes it widely used small molecules to fabricate NC solar cells.238,239

The GISAXS diagrams of CdSe superlattices and MPA ligand exchange are shown in Figure 4.5 (a-b). It compares the scattering pattern taken at 0 s and 150 s of ligand exchange. The sharp diffraction peaks can be seen in both diagrams, which means the NC superlattice maintains crystal structural and long-range-order after the reaction. We perform line cut over the (11-1) scattering peak on the GISAXS diagrams taken by each second. Then we fit the curve with a Lorentzian model, from which we obtain the position and the full width at half maximum (FWHM) of the scattering peak. The position of scattering peak indicates the spacing between {11-1} plane, which correlates with the inter-particle spacing. The qy coordinate of each fitting is extracted and plotted against time to reflect the kinetics of ligand exchange in a NC superlattice (Figure 4.5 (e)). According to the analysis of the curve, the interparticle spacing reduces at a fast rate in the first 40 seconds. Then the reaction reaches equilibrium at around 80s. A general recipe to fabricate NC solar cells requires more than 30s for ligand exchange with MPA.240 Which is in good agreement with our characteristic time obtained from in-situ GISAXS measurements.
Figure 4.5 (a) GISAXS pattern of 6.7 nm CdSe NC superlattice film at 0s and (d) 150s of ligand exchange reaction with MPA. (b) TEM images of corresponding CdSe superlattice film at 0s (black frame) and 150s (red frame) of ligand exchange. The insert is small angle electron diffraction pattern of local area superlattice. The scale bars represent 50 nm (c) The time slices of (11-1) scattering peak of CdSe superlattice during ligand exchange. (e) The $q_y$ coordination of (11-1) scattering peak against the time during ligand exchange. (f) FT-IR spectra of the superlattice in (a) and (d).
Quantitative analysis of the scattering pattern shows that in the fcc type structure, the lattice constant is reduced from 12.6 to 11.7 nm, indicating a reduction of the inter-particle spacing (surface-to-surface) from 2.2 nm to 1.6 nm. *Ex-situ* FT-IR measurement in Figure 4.5 (f) shows ~65% reduction of the C-H stretching intensity by the end of the reaction, which is close to the reported result characterized by NMR.\(^7\) The coherence length of superlattice increased from 3959 nm to 4220 nm. It means the superlattice maintains and slightly improves the long-range order after liquid-air inter-face ligand exchange, which is also reported by Angang Dong’s publication.\(^8\)

Based on the assumption that the inter-particle spacing has a linear relationship with reaction yield, the kinetics of scattering peaks is comparable to the kinetics of ligand exchange. The kinetics of scattering peaks is fitted with a single exponential function,

\[
q = q_1 e^{-\frac{t}{t_0}} + q_0
\]

where \(q\) is the \(q_y\) coordinate of the (111) scattering peak. The characteristic time \(t_0\) is \(~16\) s for above CdSe/MPA ligand exchange. The reaction rates under different conditions are compared through the constant \(t_0\) in the following analysis.

*In-situ* GISAXS technique allows the investigation of NC’s size, shape, stoichiometry and the effect of these variables on the rate and yield of ligand exchange. So far there is no common agreement between the relationship of NC’s size and its ligand’s binding energy. Both positive\(^2\) or negative\(^3\) correlations are reported. Here we investigate the ligand
exchange kinetics of 4.9 nm CdSe NC superlattice and compare it with the 6.7 nm CdSe NC superlattice. The fcc-type superlattice from 4.9 nm NC gives a lattice constant of 10.1 nm, and the face-to-face inter-particle spacing of 2.2 nm. After ligand exchange with MPA, the spacing is reduced to 1.6 nm. According to the GISAXS diagram (Figure 4.6), the post-exchange spacing is identical for both 4.9 nm and 6.7 nm CdSe superlattice, indicating that the ligand exchange for two size CdSe NCs has a similar yield under the same reaction conditions. However, the grain size of the superlattice is reduced from 3457 nm to 587 nm, showing a lower degree of translational order in the final NC superlattice. The severe post-exchange disorder can be explained by the higher volume fraction of ligand in NC superlattice composed of small NCs. More free space is generated by ligand exchange, and the NCs get more freedom to rearrange. The time constant from the dynamic curve is 6.8s (Figure 4.7(a)), showing that the inter-particle spacing reduces at a faster rate for smaller particles. Two factors can contribute the faster reaction rate. First, the binding energy for the ligands on the surface reduces as the surface-to-volume ratio increases, according to the simulation result from Schapotschnikow et al.\textsuperscript{241} Second is the faster diffusion of the ligand molecules. Since ligand diffusion only occurs between NC cores, a higher ligand volume fraction and a larger number of defects in the NC superlattice will increase the accessible volume, and accelerate the ligand diffusion rate within the NC superlattice.
Figure 4.6 GISAXS diffraction pattern taken at (a) 0 s and (b) 150 s. The sample is 4.9 nm CdSe superlattice, ligand exchange with MPA.

1, 2-ethanedithiol (EDT) is widely used to efficiently remove the original ligands employed in NC synthesis, crosslink the neighboring NCs and enhance the efficient charge transfer in electronic devices. As a typical bidentate ligand, the two equivalent bonding sites give it strong binding ability. The GISAXS diagram reveals that the ligand exchange between EDT and CdSe superlattice give a time constant of 9.9s (Figure 4.7(b)). The inter-particle spacing is further reduced to 1.5 nm.

Above analysis is based on CdSe NC superlattice. In this study, the CdSe NCs are synthesized by cation exchange from PbSe template. The cation exchanged CdSe NCs, as discussed in Chap. 3.2, have a similar size, morphology, and binding ligand with the PbSe template. The PbSe and CdSe NCs are an ideal system to compare the surface chemistry of quantum dots during the investigation of ligand exchange. When EDT is used for ligand exchange with PbSe NC superlattice, the inter-particle spacing is further reduced to 0.6 nm (Figure 4.7 (c)), indicating a higher proportion of ligand replacement. FT-IR spectrum
(Figure 4.8) reveals that the intensity of C-H stretching peak declines by ~90%. The result shows the binding energy of ligand to the surface of PbSe and CdSe NCs is the determinant factor for the significant difference in inter-particle spacing between the two NC superlattices.

**Figure 4.7** The qy coordination of (11-1) GISAXS peak against time. The sample is (a) 4.9 nm CdSe SL with 0.02 M MPA, (b) 6.7 nm CdSe with 0.02 M MPA and 0.02 M EDT (c) 7.1 nm PbSe with 0.02 M MPA and 0.02 M EDT. (d) 7.1 nm PbSe with 0.02 M TBAC, TBAB and TBAI.
In ligand exchange, halide capping (Cl\(^-\), Br\(^-\), I\(^-\)) groups are widely used to passivate the surface of the NC, stabilize them under ambient conditions and give n-type electronic behavior.\(^{215,244}\) However there are few experimental investigations have probed the kinetics of halide anions in ligand exchange. Here we investigate the performance of 0.2 M tetrabutylammonium chloride (TBAC), bromide (TBAB) and iodide (TBAI) in ligand exchange. Figure 4.7 (d) shows different time constants for TBAC (17.05 s), TBAB (47.20 s), and TBAI (64.93s) reactions. The distinctive time constant of the halide anions can be explained by three aspects. First, according to the Born model, smaller radius ions of the same charge is more easily solvated, and the activity increase with solvation.\(^{245}\) Second, in the self-assembled superlattice, smaller ions are also expected to diffuse faster, leading to a shorter time to reach the NCs surface. Third, the Pb-Cl has highest binding energy while Pb-I has the lowest one, which makes Cl\(^-\) to bind to the surface of NC with a fast rate.\(^{246}\) Again, the extent of ligand replacement can also be extracted from the reduced inter-particle spacing. The lattice constants are increasing for TBAC (11.6 nm), TBAB (11.9 nm) and TBAI (12.2 nm), indicating a higher yield for the exchange from TBAI to TBAC. Corresponding GISAXS diagram and TEM images of PbSe superlattice after ligand exchange can be found in Figure 4.9. The FT-IR spectra confirm this result as the sample exchanged with TBAC has the lowest C-H stretching intensity while the TBAI exchanged sample has the highest one. Overall, among the three halide anions, Cl\(^-\) ions are the most efficient in ligand exchange, while I\(^-\) is the least.
Figure 4.8 FT-IR spectra of original 6.4 nm PbSe NC superlattice and the ones ligand exchange with TBAI, TBAB, TBAC, MPA and EDT for 150 s.
4.3.3 Structural Transformation of Superlattice in Ligand Exchange

The NC superlattice has collective properties from NC building blocks. The point group symmetry has a strong correlation with their long-range physical properties.\textsuperscript{247,248} Through the investigation of ligand exchange by \textit{in-situ} GISAXS, a structural deformation is found with the PbSe superlattice. At the steady state of ligand exchange, the $\alpha$ angle of fcc-type unit-cell varies between 91° and 96°, depending on the choice of ligand. For example, $\alpha=96°$ for MPA ligand exchange, $\alpha=92°$ for TBAB and TBAC ligand exchange, and $\alpha=91°$ for EDT ligand exchange. The $\alpha$ angle expansion indicates an anisotropic in-plane and out-of-

\textbf{Figure 4.9} GISAXS pattern and TEM images of 7.1 nm PbSe superlattice at 150s, ligand exchange with (a, b) TBAC, (c, d) TBAB, (e, f) TBAI. Each scale bar represents 200 nm.
plane reduction of interparticle spacing through ligand exchange. The $\alpha$ angle expansion only happens to all the PbSe superlattice but is rarely seen in CdSe superlattice.

Two potential driving factors can be put forward to explain the anisotropic expansion: one is the increasing attractions between NC and liquid phase by ligand exchange. Through liquid-air interface ligand exchange, the ligands with non-polar hydrocarbon groups are replaced by small but polar ligands, which enhances hydrophilic attraction between NCs and the interaction with the highly polar diethylene glycol sub-phase. The deformation of a unit cell reduces the energy of the whole NC superlattice on the liquid-air interface. However, that expansion is more prominent in the PbSe NC superlattices while almost no deformation can be detected in CdSe and Au NCs superlattices under the same conditions. It means the hydrophilic interactions may not be the dominant factor. The deformation relies on the structural features of PbSe NC superlattice.

The second explanation is an isotropic ligand exchange which reduces the inter-layer inter-particle spacing more than inner-layer inter-particle spacing. A discussion about the longitudinal and orientational alignment of the NC superlattice can be found in Chap. 3.4. Within the same layer of the NC superlattice, one PbSe NC touches 6 nearest neighbors with its two $\{100\}$ facets and four $\{111\}$ facets. Between two layers of the NC superlattice, the NC contacts with the 6 nearest neighbor NCs (3 on top and 3 below) through two $\{100\}$ facets and four bridges between $\{100\}$ and $\{111\}$ facets, vice versa. It means the $\{100\}$ facet takes a higher proportion in the out-of-plane inter-particle attachment rather than an in-plane inter-particle attachment. As have been discussed in recent investigations, oleic
acid on PbSe has smaller binding energy on \{100\} facets than \{111\} facets. The oleic acid on \{100\} fact can be replaced more easily, which makes the out-of-plane inter-particle spacing to be smaller than the in-plane inter-particle spacing, which further induces the isotropic shrinkage in an orientationally ordered NC superlattice.

4.3.4 Ligand Exchange with Binary Nanocrystal Superlattice Film
Different from typical fcc-type single component NC superlattices, BNSL films display diverse and complex crystal structures, which give it unique properties.\(^6,7,9,4,24\) Here we use in situ GISAXS technique to investigate the ligand exchange reaction in BNSL films. MgZn\(_2\)-type BNSL films can be prepared by self-assembly of 4.5 nm and 6.8 nm PbSe NCs at the liquid-air interface. Then, ligand exchange is induced with 0.1 M 3-mercaptopropionic acid (MPA). Figure 4.10 (a) and (b) show the images of an NC superlattice film at the liquid-air interface before and after ligand exchange. The macroscopic contraction of the film reflects the reduction of local interparticle spacing. FT-IR spectroscopy in Figure 4.10 (c) shows the extent of ligand exchange to the superlattice. Both the intensity of C-H stretching (2852-2954 cm\(^{-1}\)) and COO- stretching (~1539 cm\(^{-1}\)) are reduced by more than 60\%, while the O-H stretching mode from the free carboxyl group of MPA appeared at ~3369 cm\(^{-1}\). A red-shift of PbSe NC excitonic absorption band also can be found in the FT-IR spectra between 5000 and 6000 cm\(^{-1}\). It shows the enhanced electronic coupling of the NC building blocks by ligand exchange.
Figure 4.10 (a, b) Photographs of a typical film on top of diethylene glycol (a) before and (b) after ligand exchange with MPA. The scale bar represents 10 mm. (c) FT-IR spectra of BNSL film self-assembled with 4.5 nm and 6.0 nm PbSe NCs before and after ligand exchange with MPA. Reprinted from Wu et al.79

We use GISAXS to characterize the long-range-order of BNSL film before and after ligand exchange. According to Figure 4.11(d)-(e), the high intensity and distinct scattering pattern after ligand exchange show the preservation of long-range order of the BNSL films, and the shift of scattering peaks reflects the change in inter-particle spacing. Simulation of the GISAXS pattern gives lattice constant of a pristine unit cell, in which a=b 14.7 nm, and c=
25.6 nm. This lattice constant indicates a uniaxial lattice expansion of around 6% along c axis than a typical MgZn$_2$ unit cell. The uniaxial lattice contraction is often caused by the NC orientation, limitation in the formation of the NC superlattice or post-treatment to the superlattice. The lattice contraction of BNSL prepared on a solid substrate is reported to be caused by the evaporation of residual solvent during the formation of the superlattice.$^{250-253}$ In contrast, the MgZn$_2$ BNSL film forms at the liquid-air interface, which gives the freedom of contraction along the surface of the liquid. By ligand exchange, the lattice constants are reduced to $a = b = 13.2$ nm and $c = 20.2$ nm, which means $a$ and $b$ contracts by 9% while $c$ contracts by 25%.

In the MgZn$_2$-type unit cell, the small NC takes two sites, as is shown in the model in Figure 4.11 (c). The small particles are represented by light and dark blue spheres, while the large particle is represented by red spheres. The shortest inter-particle distance and the thickness of ligand shell between particle is 1.8 nm. After ligand exchange with MPA, this inter-particle distance is reduced to 1.1 nm, resulting in the stronger electronic coupling. By analyzing the FWHM of the diffraction pattern, we can figure out that the in-plane coherence length ($S$) remained at 220 nm, which means the NC superlattice preserve the long-range-order after ligand exchange.
The kinetics of ligand exchange is characterized with MgZn₂-type BNSL self-assembled with similar size PbSe NCs. On the scattering diagram, in-plane/out-of-plane contraction can be found by the radial expansion of scattering peaks along q_y and q_z axis. The lattice constant of a unit cell is reduced from a=b=14.7 nm, c=24.5 nm, to a=b=13.9 nm, c= 20.6 nm. The corresponding c/a ratio changes from 1.67 to 1.48, which means the out-of-plane contraction exceeds the in-plane contraction. The anisotropic contraction can be explained by the enhanced NC-substrate interactions. By ligand exchange with polar ligands, the
hydrophilic interactions give polar NCs stronger attraction with the liquid phase. Due to the relatively lower spacing filling ratio, the ligand exchange on MgZn₂-type NC superlattice has a faster reaction rate than single component NC superlattice. By performing linecut over the (112) diffraction peak along both qₓ and qₑ axis on each frame of the diffraction pattern, in-plan and out-of-plan ligand exchange kinetics can be revealed. The in-plane time constant is 4.1 s, which is comparable with the out-of-plane time constant of 4.5 s.
Figure 4.12 GISAXS diffraction pattern of MgZn$_2$-type BNSL films self-assembled with different size PbSe NCs at (a) 0 s and (b) 150 s of ligand exchange with MPA. The red and green rectangular in (a) mark the diffraction peaks from which we can get the (c) in-plane and (d) out-of-plane kinetics curves of ligand exchange. (e) Models of a MgZn$_2$-type unit cell and corresponding lattice constant at 0 s and (f) 150 s.
By replacing the small PbSe NC with similar size CdSe NC, we can also get MgZn$_2$-type BNSL of similar lattice constant. The original lattice constant of the unit cell is $a=b=13.3$ nm and $c=24.0$ nm, which gives $c/a$ ratio 1.80. By ligand exchange with MPA, the lattice constant is reduced to $a=b=12.2$ nm, $c=22.0$nm. The $c/a$ ratio remains to be 1.80, indicating an isotropic contraction in both the in-plane and out-of-plane directions. The time constants are 6.5 s for in-plane ligand exchange and 4.5 s for out-of-plane ligand exchange, respectively.

Although the BNSL structure of 4.5 nm and 6.0 nm PbSe NCs is maintained the long-range order after ligand exchange with MPA, it does not necessarily mean that this method is feasible for all other NC superlattice or ligands. In the following discussion, we will compare the ligand exchange reaction by tuning ligands and structure of NC superlattice. Without the ligand, the blank solvent-acetonitrile only results in a slight reduction in lattice parameters. It is because some free or loosely bond ligand is detached the surface in the process. By using TBAI instead of MPA, the in-plane lattice constant $a$ and $b$ is further reduced to 12.8 nm, while the out-of-plane lattice constant remains 20.2 nm. (Figure 4.13 (a)) This means the surface-to-surface inter-particle pacing changes to 0.9 nm and the coupling between NC building blocks will be enhanced. The in-plane coherence length is 350 nm, remains comparable to the original film. While TBAI maintains the long-range-order of the NC superlattice, NH$_4$SCN, and formic acid treatments are quite aggressive ligands causing the fusion of neighbor NCs and damage the local order of superlattice, which can be seen from TEM images in Figure 4.14.$^{254-256}$
Figure 4.13 (a-c) TEM and Fourier Transform images and (d-f) GISAXS patterns of BNSL films self-assembled with: (a,d) 4.5 and 6.0 nm NCs and ligand-exchanged with TBAI, (b,e) 3.2 and 4.5 nm NCs before ligand exchange, (c,f) 3.2 and 4.5 nm NCs ligand-exchanged with MPA. Scale bars represent 50 nm. Reprinted from Wu et al. 79

We also investigate the ligand exchange reaction to BNSL formed with NCs of the same chemical composition but of different sizes. Figure 4.13 (b, c) show TEM images of MgZn2-type BNSL with 3.2 nm and 4.5 nm PbSe NC. The GISAXS diagram of Figure 4.13 (e, f) shows that the diffraction pattern has increased smearing into rings, which reflects the polycrystalline features of the treated NC superlattice. The in-plane coherence length is 57 nm, which is much smaller than the same structure NC superlattice formed with large NCs. The lattice constants are $a = b = 11.8$ nm and $c = 23.5$ nm for the pristine
film. They are reduced to \( a = b = 9.9 \text{ nm} \) and \( c = 17.1 \text{ nm} \) by ligand exchange with MPA.

In the meantime, the in-plane coherence length is reduced to 35 nm, which means the increasingly severe shrinkage of the lattice introduces more defect to the NC film. The center-to-center interparticle spacing changes from 5.7 nm to 4.7 nm, which means the surface-to-surface spacing changes from 1.9 nm to 0.9 nm.

**Figure 4.14** TEM images of BNSL film (self-assembled with 4.5nm and 6.0 nm PbSe NCs) after ligand exchange with (a) 0.1M NH\(_4\)SCN in acetonitrile and (b) 0.1 M Formic acid in acetonitrile. Scale bars represent 100 nm. Reprinted from Wu et al.\(^79\)
4.4 Directional Carrier Transfer in Binary Nanocrystal Superlattice Characterized by Transient Absorption

Following the structural analysis, the ligand-exchanged superlattice with well-order crystal structure gives an ideal platform to understand the improvement of charge and energy within the heterojunction of the two coupled building blocks. The cyclic voltammetry measurement reveals that the 3.2 nm and 4.5 nm PbSe NCs form a Type-I heterojunction, which has conduction band offset of 0.25 eV and valence band offset of 0.05 eV. The near-infrared transient absorption (NIR-TA) spectroscopy is used to investigate the ultrafast carrier dynamics of a series of single-component and binary superlattice composed with 3.2 nm and 4.5 nm PbSe NCs. To perform the ultrafast measurement, the solid films are photoexcited with an ultrafast pump pulse (3.18 eV). The energy is above the band gaps of building blocks to ensure that both NCs are excited. In the meantime, we also limit the bandgap to be less than 4 times of the NC’s bandgap to limited the side effect of generating multiple excitons.257

The TA spectroscopy is introduced with the example taken from single component NC superlattice self-assembled with 4.5 nm PbSe NC. Figure 4.15 (a) shows the 2-D spectrum with a function of time and energy. 1-D slices from the 2-D spectrum compare the time evolution of spectrum in a more clear way, as is shown in Figure 4.16 (b). The first excitonic peak (1S<sub>h</sub> – 1S<sub>e</sub>) is at 0.89 eV and the second excitonic transition (1P<sub>h</sub> – 1P<sub>e</sub>) is at 1.12 eV.258,259 In the first 2 ps, we can see a shift of the primary feature which introduced

* The author acknowledges Siming Li for her contribution to transient absorption characterization.
by hot excitons\textsuperscript{260,261}. After ligand exchange, the first excitonic peak red-shifts by 25 meV with enhanced electronic coupling between neighbor NCs. This feature is also found in the FT-IR spectrum discussed in Figure 4.10 (c).

**Figure 4.15** (a) 2D plot of NIR-TA spectra of oleic acid (OAc)-capped 4.5 nm PbSe superlattice film. (b) NIR-TA spectra of Oleic acid-capped 4.5 nm PbSe superlattice film at several pump-probe delay times and the linear absorption spectrum. (c) Dynamics of the 1S bleach of 4.5 nm PbSe NCs under three conditions: dispersed in tetrachloroethylene, SL film before ligand exchange, and same film following a ligand exchange. Samples were pumped at 3.2 eV with 12-18 \( \mu \text{J/cm}^2 \). (d) Fluence-dependent dynamics of a superlattice film of MPA-capped 4.5 nm NCs (points) with global fitting by an Auger recombination process (lines). The fluence was 6.1 \( \mu \text{J/cm}^2 \) for \( N_0 = 1.9 \times 10^{18} \text{ cm}^{-3} \). Reprinted from Wu et al.\textsuperscript{79}
Figure 4.15 (c) compares the dynamics of 1S bleach of 4.5 nm PbSe NC in solution and solid-state films with the pristine and post-exchange ligand. Before ligand exchange, the dynamics are comparable for the NC in liquid and solid-state. After ligand exchange with MPA, the superlattice film shows a faster decay, which can be explained by two major factors. First, ligand exchange may introduce more trap states to the surface of NCs.\textsuperscript{262,263} Second, enhanced coupling coming with ligand exchange make charge and energy to be able to transfer to local states since NCs are not perfectly uniform in size and bandgap edges. In this circumstance, it is energy favorable for carriers to transfer to the nearby large particles, increase their carrier density and cause additional Auger recombination.\textsuperscript{264,265} We perform fluence-dependent studies and fit the decay rate, which is shown in Figure 4.15(d). At our typical pump fluence of 18 \(\mu J/cm^2\), the calculated Auger recombination’s time constants are 45 ps and 100 ps for 4.5 nm and 3.2 nm PbSe superlattice, respectively. In the following analysis, we will compare it with the time scale with carrier transfer in the superlattice.

Then, we perform TA measurement on the post-exchange MgZn\textsubscript{2}-type BNSL film from 3.2 nm and 4.5 nm PbSe NCs. We use 3.18 eV photons to excite both components in the superlattice. The 2D plot of TA spectra is shown in Figure 4.16 (a-c). It shows absorption features from both 3.2 nm and 4.5 nm PbSe NC building blocks.
Figure 4.16 2D plot of NIR-TA spectra as a function of both probe energy and the pump-probe delay time of MPA-capped NC films for (a) 3.2 nm NC SL, (b) 4.5 nm NC SL, and (c) BNSL film. (d) Cartoon showing the transfer of photoexcited carriers from 3.2 nm PbSe NC to 4.5 nm PbSe NC. (e) 1S bleach dynamics of 3.2 nm NCs in single-component SL and BNSL probed at 1.18 eV and 1.14 eV. (f) 1S bleach dynamics of 4.5 nm NCs in single-component SL and BNSL, probed at 0.87 eV. Reprinted from Wu et al. 79

Then, we compare the dynamics of the 1S bleach bands of 3.2 nm and 4.5 nm PbSe NC building blocks in both single component and BNSL whose ligands are exchanged with MPA under the same conditions. In BNSL, the 3.2 nm PbSe has a faster decay rate than in single component lattice, while the 4.5 nm PbSe has a slower decay rate than in single component lattice. The different kinetics indicates the directional carrier transfer from 3.2 nm PbSe to 4.5 nm PbSe. The wide-bandgap 3.2 nm PbSe serves as a donor and 4.5 nm PbSe serves as an acceptor. Meanwhile, 3.2 nm and 4.5 nm PbSe NCs in either pristine single component or binary NC superlattice show no significant difference in their rate of
decay. This means that enhancing the coupling of NCs in the BNSL can generate directional charge or energy transfer between the coupled Type-I heterostructure.

4.5 Conclusions
In this chapter, we demonstrate that the in-situ GISAXS is a powerful tool to investigate the kinetics of ligand exchange and real-time structural transformation of the superlattice in ligand exchange. It allows people to compare the time scale and extent of ligand exchange among a broad group of ligands, and the corresponding result is valuable for device fabrication. By performing ultrafast characterization, we reveal that the enhanced coupling can deliver directional carrier and energy transfer across the Type-I heterojunction in the BNSL. The method is also applicable for the superlattice films with Type-II heterojunction, which is expected to have promising photovoltaic properties.
5 3-D NANOCRYSTAL SUPERSTRUCTURES BY DESTABILIZATION-DRIVEN SELF-ASSEMBLY

5.1 Motivations for 3-D Nanocrystal Superstructure by Destabilization-driven Self-Assembly

In past two decades, a verity of superstructures has been developed relying on the use of Van der Waals interaction, steric interaction and covalent bonds. Semiconductor, metallic and magnetic NCs all have been used as building blocks for self-assembly. The 3-D NC superstructures give distinctive features, compared to their dispersed components, for application, such as surface-enhanced Raman spectroscopy (SERS) substrates, catalyst, and biosensors. Figure 5.1 shows a group of NC supercrystals formed with metallic NC with control over size and morphology.

The superstructures can be prepared through either “evaporation-driven” or “destabilization-driven” self-assembly. The “evaporation-driven” self-assembly allow solvents to evaporate at a controlled rate. As the NC concentration increase with solvent evaporation, the structural of NC aggregates transfers from disorder to order, and finally forms a crystalline superlattice. In a destabilization-driven process, the non-solvent gradually diffuses into the NC solution, which makes the environment unfavorable for NCs. To counter the increasing surface energy, the NCs tend to aggregate to have more overlapping of ligands and reduce the contact with non-solvent. The diffusion driven process is comparable to the crystallization of small molecules. By changing the conditions of self-assembly, superstructures of different size and morphology can be obtained.
Figure 5.1 SEM images of supercrystals formed from various Au–Pd core-shell (a) cubes, (b) truncated cubes, (c) cuboctahedra, (d, e) truncated octahedra, and (f–h) octahedra by the droplet evaporation method. Reprinted from Chiu et al.272
5.2 Preparation of 3-D Superstructures by Destabilization-Driven Self-Assembly
The destabilization driven self-assembly can be prepared under ambient conditions. A general procedure is shown in the schematic diagram in Figure 5.2 (a). NC is dispersed in non-polar solutions like hexane, toluene, and chloroform, at a concentration of 100-400 mg/mL. Then non-solvent (ethanol, isopropanol, etc.) is injected into the solution at a slow rate (50 µL/hr). Before the non-solvent/solvent ratio reached 1:1 ratio, most of the NCs have assembled and participated out, and the solution turns clear. The participants are washed by non-solvent for 3 times before they are transferred to substrate for characterization.

Figure 5.2 (a) Cartoon of the experimental setup for destabilization-driven self-assembly. (b) SEM image of the NC supercrystal self-assembled by 5 nm Au NCs (c). The superstructures have polyhedron morphology. And their size is in the range of 0.5 to 10 µL. (d) High-resolution SEM image to show the fcc lattice of supercrystal. (e) SEM image of a single supercrystal in (b).
Since the NC self-assembles by reducing energy, different NCs of the equivalent size and surface features are expected to assemble and randomly positioned in a superlattice. To verify the assumption, we mix the solution of the same size PbSe and Au NC at 1:1 ratio and allow the superstructure to form by adding non-solvent. The focused ion beam (FIB) is used slice the supercrystal and characterize the inner structure. As is shown in Figure 5.3 (a), the film shows a sandwich-like structure. From left to right, the three layers seen are the Platinum coatings, sliced supercrystal, and a silica substrate. The Platinum is a protective layer to reduce the damage from the ion beam. And the silica layer comes from the substrate which loads the superstructure. The sliced film shows an fcc-type close-packing lattice, from which Au and PbSe NCs are not distinguishable. By taking TEM image in dark field, the strong scattering spots identify the Au NC in the lattice, as is shown in Figure 5.3 (b). The image shows Au NCs occupy random positions in the NC superlattice.

In 2015, Cargnello et al. report that the Au and CdSe NCs can randomly mix in a two-dimensional superlattice film forming doped NC superlattice and the electronic properties are profoundly affected by the presence of Au NCs. Here we show that the random mixture structure can also be found in three-dimensional NC superstructures. It allows following investigations of its new optical and electrical properties.
Figure 5.3 (a) Bright field and (b) dark field TEM images of superlattice thin film which is sliced from superstructures. The superstructure is prepared by a mixture of PbSe and Au NC at 1:1 ratio. Bright spots in (b) show scattering from Au NCs.

Besides the compact polyhedral NC supercrystals, the application of external magnetic field allows the formation of nanorods when magnetic NCs are used in the assembly. The experimental set-up is shown in Figure 5.4 (a). The Zinc Ferrite NC solution (10 nm in size, 100mg/mL, 1mL) is loaded in a square glass vial. The vial is sealed and placed between a pair of magnets. Non-solvent such as ethanol, isopropanol is injected into the solution at a constant rate of 50µL/hr. After 24 hours, the liquid turns clear. All the NC aggregates into rod-like superstructures on the walls. The rods are purified multiple times and then transferred to a solid substrate for characterization. SEM image in Figure 5.4 (b) shows that the aggregates have uniform width around 10 µm and their lengths are in centimeter scale. TEM image of the tip of the rod (Figure 5.4 (b) insert) shows that locally the NCs are in close-packing structure. Following the reported recipe by Jiao et al., high-temperature thermal anneal at inert environment allows the carbonation of ligand. The
hydrochloric acid can etch the metal part of NCs and enables the formation of mesoporous carbon frameworks. Figure 5.4 (c) show the mesoporous carbon frameworks prepared from the rod-like superstructure. It is promising to be applicable for matter storage, exchange or the carrier of catalyst.

**Figure 5.4** (a) Picture of magnetic nanorods prepared in a glass vial. (b) SEM images of the rod self-assembled with iron oxide NCs. Insert is TEM image taken on the tip of the nanorod. (c) Mesoporous carbon framework prepared from the rod-like superstructure. The dark substance in the center of carbon framework is unreacted iron.

### 5.3 Stepwise Post-Treatment of 3-D NC Superstructures by Ligand Exchange and Thermal Anneal

The coupling of NC building blocks in a superstructure can be enhanced by removing the insulating long hydrocarbon chain ligands and initiate the atomic diffusion of NCs. The ligand exchange method has been well developed for 2-D superstructures. Since the 3-D
close-packed lattice is not favorable for the diffusion of guest ligands the same ligand exchange methodology is not directly transferable. On the other hand, the 3-D structure gives higher mechanical strength, which allows for multiple treatments under more rigorous conditions like long reaction time of ligand exchange (5-30 mins) and high thermal anneal temperature (~500 °C).

A series of control experiments reveal that the combination of ligand exchange and thermal annealing give the optimal conditions for the highly coupled NC superstructure. Figure 5.5 (a) shows the superstructure assembled from PbSe NCs. The orientational preference of NC in the superstructure is characterized by the select area electron diffraction patterns. The banana shape diffraction peaks indicate that the oriental coherence of NC building blocks is in an extent between perfect order and disorder. After ligand exchange with MPA, Figure 5.5 (b), the diffraction pattern smears, showing that the orientational order is degrading. The misorientation can be attributed to either surface-internal inhomogeneous ligand exchange or defects generated by removal of original ligands. Further experiments are required to validate the causes. Thermal anneal is also carried out with the pristine NC supercrystals, as is shown in Figure 5.5 (c). Thermal anneal breaks the orientational coherence, and diffraction rings can be obtained. However, by performing sequential ligand and thermal anneal, the supercrystal maintains the polyhedron morphology and gives bright and sharp diffraction patterns, which means the sequential treatments induce high orientational order superlattice.
Figure 5.5 TEM image (up) and electron diffraction pattern (down) of an NC supercrystal assembled from PbSe NCs (a) without extra treatment (b) ligand exchange with MPA (c) thermal annealing at 150°C in an inert environment. (d) ligand exchange with MPA, followed by ligand exchange with MPA at 150°C in an inert atmosphere.
Following the preliminary results, we investigate the effect of thermal annealing temperature and its correlation with the orientational order in the CdSe NC supercrystals. Figure 5.6 (a) shows TEM image and the electron diffraction pattern of CdSe NC film prepared by spin coating. Due to fast evaporation of the solvent in spin coating, the NCs initially display an entirely random orientation, and the electron diffraction gives homogeneous rings. Control experiments are done by performing MPA ligand exchange with the NC supercrystal self-assemble from these CdSe NCs, followed by thermal annealing. As is shown in Figure 5.6 (b-h), when the temperature ramps up from 150 °C to 500 °C, the supercrystal maintains the polyhedral morphology. However, the banana shape diffraction pattern gradually transforms into sharp and bright spots, indicating a high degree of orientational coherence for the NC building blocks in the lattice. Figure 5.14 (h) shows that the 500 °C annealed NC supercrystal maintains the polyhedron morphology and has the narrowest diffraction patterns. But defects generated by the lattice contract and atomic fusion also can be found under TEM. It is essential to consider the effect of these structural defects when investigating the optical and electrical properties of ligand exchange and thermally annealed supercrystals.
Figure 5.6 TEM image (up) and electron diffraction pattern(down) of (a) CdSe NC film by spin coating (b) CdSe supercrystal with ligand exchange and thermal anneal at 150 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, (f) 400 °C (g) 450 °C (h) 500 °C for 30 minutes.
5.4 Conclusion
In this chapter, we synthesized polyhedral shaped NC supercrystals by destabilization-driven self-assembly. Following that, we test ligand exchange and thermal annealing conditions with the as-synthesized supercrystals. Although any single step post-treatment breaks the orientational coherence, a stepwise ligand exchange and thermal annealing enhance the inter-particle coupling and initiate atomic diffusion, which further improves the orientational order of building blocks. We explore the optimized conditions for stepwise post-treatment. The strongly coupled NC supercrystals are expected to have distinctive electrical properties.
6  3-D NANOCRYSTAL SUPERSTRUCTURES FROM EMULSION CONFINED SELF-ASSEMBLY*

6.1 Motivations to Prepare 3-D NC Superstructures Through Emulsion Confinement

Emulsions are widely used in food, cosmetics, and pharmaceutical, paints, and coatings industries, etc. Among the diverse techniques in emulsion production, membrane emulsification has received increasing interest due to several distinctive advantages: 1) The membrane emulsification can prepare emulsion with high monodispersity. 2) The emulsion’s size can be tunable in a wide range by choosing the pore size. 3) The emulsions can be prepared under mild conditions and feasible for continuous production. 4) The emulsions can be prepared with complex multi-layer structures. (Figure 6.1) Owing to above advantages, emulsions can serve as ideal container and template for NC self-assembly and generate NC superstructures with uniform size and tunable morphology. In this chapter, we focus on the methodology to prepare 3-D NC superstructures through the emulsion confined self-assembly, and their diverse structures.

* The author acknowledges Mingliang Zhang for his contribution to microporous film preparation. The author acknowledges Zixuan Li for his contribution to self-assembly and structural characterization.
6.2 Preparation of Superstructures by Emulsion Confined Self-Assembly

The process to synthesize emulsion confined self-assembly can be split into two stages: 1) preparation of emulsions and 2) formation of superstructures through the diffusion of solvent. At the first stage, micrometer size (5-50 um) pores are created in silicon nitride films by electron beam lithography followed by chemical etching. These pores are symmetrically aligned to give emulsions out of each a uniform condition. The film is mounted on a Teflon chamber and then immersed in the continuous phase, which is usually mixtures of polar liquid such as isopropanol, methanol, and water. At the second stage, the dispersed phase, which is prepared by dissolving NC into non-polar liquids, such as hexane, octane or toluene, is pumped into the chamber and separated by the pores. The emulsions form as the liquid is extruded out of the pores, the microdroplets detach from the membrane and float up into the continuous phase. Figure 6.1 shows the schematics of the experiment setup and formation of droplet out of micropores and plastic needles.
Figure 6.1 (a) Cartoon about the formation of droplets through the mesoporous membrane. (b) Images of the emulsions which are pumped out of the member and dispersed into the continuous phase. The insert is microporous SiN film.

Traditionally, membrane emulsification technique generates oil-in-water or water-in-oil type emulsions, in which the two phases are not miserable. In our experiment, the non-polar organics in dispersed phase can diffuse into the continuous polar phase at a slow rate while the NC remains in the droplet. That means, at the second stage, the diffusion of non-polar organics out of the droplet reduces the size of droplets and increase the concentration of NCs inside the droplet. As the concentration increases, NCs aggregate into solid-state superstructures, in the template of the droplet. Figure 6.2 shows the shape of emulsions out of pores and the size reduction of the emulsions in the solvent diffusion process.
Figure 6.2 Pictures of droplet out of the (a) mesoporous film (b)-(g) plastic needles as a function of time. The pictures are taken by DLS camera in high-speed mode.

6.3 Structural Diversity and Formation Mechanism
The size of the superstructure formed by emulsion confinement self-assembly can be tunable from 10 µm to 90 µm. A series of controlled experiments have been done to investigate the driving factors to control their size, shape, and inner structure. Different from previous investigations, the out-of-pore droplet size is independent of continuous phase’s flow rate. By tuning the flow from 0.07 mL/min to 0.15 mL/min, we see a linear correlation with the bubble rate (Figure 6.3 (d)), which is defined by the number of bubbles per minute. Within this range of flow rate, the produced superballs are in the same size.
When above 0.15 mL/min, high inner pressure causes the film to break. By tuning the concentration of NCs in dispersed phase, we see the changes to superstructure’s size, shape, and inner structure. The size changes from 30 µm to 63 µm, by tuning the concentration of solution between 0.2 mg/mL and 1 mg/mL.

![Graphs showing size and distribution of superstructures](image)

**Figure 6.3** (a) size and distribution of superstructures which can be prepared by the emulsion confined self-assembly from the microporous film. (b) Size of the superstructure as a function of solvent concentration. (c) Size of the superstructure as a function of flow rate. (d) The rate of bubbles out of the film as a function of flow rate (pumping rate).
SEM is used to compare the morphology of these superstructures and focused ion beam is used to slice the NC superballs to reveal their inner structure. As is shown in Figure 6.4, four different morphologies can be prepared by tuning the concentration of continuous phase: a) hollow sphere with a dimple on the surface b) hollow sphere with one hole on the wall c) the hollow sphere with an intact shell d) the pear shape NC superstructure. In a previous publication, Remigijus et al. discussed the formation mechanism of hollow micro-particles from polymers, which is similar with the superstructure self-assembled from NC: When the emulsions are pumped out of the micropore membrane, solvent transfers into the continuous phase through diffusion and convection, whereas the NCs remain in the droplet. As emulsion size reduces, the concentration of NC gradually increases, especially at the interface. Gradually, the NCs near the surface transfer into a solid or semi-solid phase and the condensed shell further block the solvent to transfer into the continuous phase. When the outer layer of droplet becomes highly condensed, the solvent transfer is inhibited. And the residual solvent in the superball cause phase separation. During the prolonged incubations, the combined action of interfacial tension force, and dissolving-consolidation dynamics make the solvent to come out through a hole in the shell. For the emulsion with low concentration dispersed phase, phase separation happens before the solid shell forms, in which case a dimple forms on the surface. Conversely, when droplet concentration is high enough, the thick and solid shell eliminates the diffusion of the solvent through the hole, then a hollow sphere with integrate wall forms. (Figure 6.4 (c)) It is reasonable to believe that the size of the superstructure is determined by the size of the emulsion when its surface becomes solid. It also explains why higher
concentration droplet generates larger size superballs. When the concentration is even higher (Figure 6.4 (c)), the semi-solid shell deforms under the shear force while the droplet flows up, in which case a solid and pear-like superball forms.
Figure 6.4 SEM images and cartoon to show the morphology of superlattice from emulsion confined self-assembled. The morphology changes as a function of dispersed phase concentration.
The inner structure of superball is characterized by the FIB microscope and GISAXS. A piece of shell from the superstructure is sliced by the FIB. Figure 6.5 (a-c) shows a general procedure to get 20-40 nm thick film from superball and transfer it to the copper base for imaging. As is shown in Figure 6.5 (e-f), NCs form a polycrystalline fcc-type superlattice. Both [111] and [100] plane can be found. GISAXS is used to characterize the long-range-order of assembly in the superball. Figure 6.5 (d) confirms the polycrystalline fcc-type superlattice. The width of the scattering peak reveals the average grain size to be about 400 nm, which is smaller than the micrometer grain size of superlattice formed at the liquid-air interface.

**Figure 6.5** (a) SEM image of a typical hollow core superball. (b) The inner structure of a superball sliced by the FIB (c) SEM image of the thin film which is sliced from (b) and transferred to a copper bar. (d) The GISAXS diffraction pattern of superstructures. (e) and (f) TEM images of the sliced thin film in (c).
6.4 Spike-Like Superstructure through Emulsion-Confined Self-Assembly

The morphology of superballs has a high correlation with their distinctive optical, electrical or magnetic properties. In the process of emulsion-confined self-assembly, the morphology of superstructure is defined by either the interaction of building blocks or the shape of the droplet as a template. For example, Wang et al.’s report reveals that the anisotropic interaction of CdSe-CdS nanorods leads to the single domain, needle-like superstructures (Figure 6.6). Unidirectional alignment of superstructures enables the generation of linearly polarized photoluminescence at a polarization ratio of 0.88.

Figure 6.6 (a) Scheme of the needle-like superstructure synthesis. (b) SEM images of the needle-like superstructure. (c) TEM images of the needle-like superstructure. Reprinted from Wang et al..
There are few reports about tuning the morphology of superstructure by changing the shape of emulsion template. In general, the surface tension requires the emulsion to stay spherical in self-assembly, which delivers spherical superstructures. However, our experiment reveals that by a combination of external magnetic field and magnetic NCs, spike-shape superstructures can be prepared with distinctive magnetic properties from un-assembled NCs.

![Figure 6.7](image)

**Figure 6.7** (a)-(c) SEM images of magnetics of different aspect ratio. (d) the cartoon to show the formation of magnetic spikes. (e) length and (f) aspect ratio distribution analysis of magnetic spikes in (a), (b) and (c)

The experimental setup is shown in schematic diagram in Figure 6.7 (d). The Zinc ferrite NC solution is pumped through the micropores. The emulsions flow up and pass the
magnetic field, which is generated by the magnetic bar on opposite side of the reactor. The emulsion is stretched in the field along with the magnetic flux, together with the diffusion of solvent to the continuous phase. After the surface solidified, the superstructure maintains the spike-like morphology with uniform distribution. By tuning the magnetic field, the aspect ratio can be varied from 1.8 to 5.

6.5 Conclusion
In this chapter, we develop the synthesis of superstructures through emulsion-confined self-assembly. With home-design setup, we prepare high uniform NC superstructures of distinctive morphology and complex structure. In the magnetic field, we can also obtain spike-like superstructures with tunable size and longitudinal ratios. Following that, we investigate the formation mechanism and their inner structures. The emulsion-confined superstructures are expected to function as a new generation of drug capsule and controlled drug release materials.
REFERENCES


Chem. C 2017, 121 (33), 18186.


2007, 6, 115 EP.


(85) Kovalenko, M. V. Nat Nano 2015, 10 (12), 994.

(86) Okada, Y. Optical Society of America: Canberra, 2014; p PTu4B.2.


Gao, Y.; Demir, H. V.; Xiong, Q. *Nanoscale* **2014**, *6* (11), 5592.


(111) Kwon, S. G.; Piao, Y.; Park, J.; Angappane, S.; Jo, Y.; Hwang, N.-M.; Park, J.-


Justo, Y.; Sagar, L. K.; Flamee, S.; Zhao, Q.; Vantomme, A.; Hens, Z. ACS Nano 2014, 8 (8), 7948.


(135) Lalatone, Y.; Richardi, J.; Pileni, M. P. 2004, 3, 121 EP.
(138) Lalatonne, Y.; Richardi, J.; Pileni, M. P. 2004, 3, 121 EP.
(141) Hamaker, H. C. Physica 1937, 4 (10), 1058.


Hodges, J. M.; Morse, J. R.; Williams, M. E.; Schaak, R. E. J. Am. Chem. Soc. 2015, 137 (49), 15493.


(204) Ting, H.-W.; Lin, Y.-K.; Wu, Y.-J.; Chou, L.-J.; Tsai, C.-J.; Chen, L.-J. J.

119


Müller-Buschbaum, P. European Polymer Journal 2016, 81 (Supplement C), 470.


Renaud, G.; Lazzari, R.; Leroy, F. Surface Science Reports 2009, 64 (8), 255.


Ma, Y.; Chechik, V. Langmuir 2011, 27 (23), 14432.


Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. 2014, 13, 796 EP.


Lippert, E. Angew. Chem. 1960, 72 (16), 602.


Lippert, E. Angew. Chem. 1960, 72 (16), 602.


Gdor, I.; Sachs, H.; Roitblat, A.; Strasfeld, D. B.; Bawendi, M. G.; Ruhman, S. ACS Nano 2012, 6 (1), 3269.


Gao, J.; Fidler, A. F.; Klimov, V. I. Nature Communications 2015, 6, 8185.


Misztka, K. Nature Publishing Group 2011, 10 (11), 872.


