Polymer assisted synthesis of functional nano-materials

Liang, Yen Nan

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NANYANG
TECHNOLOGICAL
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POLYMER ASSISTED SYNTHESIS OF FUNCTIONAL NANO-MATERIALS

LIANG YEN NAN

School of Materials Science and Engineering

2013

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LIANG YEN NAN

School of Materials Science and Engineering

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This thesis is dedicated to my parents:

Liang Ah Kau & Chong Tau Lin

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List of Symbols and Abbreviations

[X]	Concentration of X
$[\text{Cu}^{2+}]:[\text{COOH}]_0$	Binding ratio of Cu^{2+} towards COOH
$[\text{Cu}^{2+}]:[\text{COO}^-]$	Binding ratio of Cu^{2+} towards COO^-
AAS	Atomic absorption spectroscopy
BE	Binding energy
CIGSe	$\text{Cu}_x\text{In}_y\text{Ga}_z\text{Se}_w$
CISe	Copper indium selenide, CuInSe_2
COOH	(Protonated) carboxylic acid group
COO^-	Deprotonated carboxylic acid group/ carboxylate ions
$\text{Cu}(\text{acac})_2$	Copper acetylacetonate
Cu-ISE	Cupric ion selective electrode
CuO_x	Copper oxide
CZTSe	$\text{Cu}_x\text{Zn}_y\text{Te}_w\text{Se}_z$
DBE	Dibenzyl ether
DFT	Density functional theory
DLS	Dynamic light scattering
DPE	Diphenyl ether
DS	Degree of supersaturation
EDX	Energy-dispersive X-ray spectroscopy
EXAFS	Extended X-ray absorption fine structure
HOMO	Highest occupied molecular orbitals, a.k.a. valence band
HSAB	Hard soft acid base
$\text{In}(\text{acac})_3$	Indium acetylacetonate
ITC	Isothermal Titration Calorimetry
k	Binding constant
LS	Light-scattering
LUMO	Lowest unoccupied molecular orbitals, a.k.a.conduction band
MEH-PPV	Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene)
MRI	Magnetic resonance imaging
MW	Molecular weight

M^{x+}	Metallic ions
N	Binding ratio
NMR	Nuclear Magnetic Resonance
P3HT	Poly(3-hexyl thiophene)
PAA	Poly(acrylic acid)
PAA-Cu ²⁺	Complex resulting of binding of Cu ²⁺ to PAA
PAA-b-P4VP	Poly(acrylic acid)-b-poly(4-vinylpyridine)
PDADMAC	poly(diallyl dimethylammonium chloride)
PEI	Poly(ethyleneimine)
PELs	Polyelectrolytes
PEO	Poly(ethylene oxide)
PEO-b-PAA	Poly(ethylene oxide)-b-poly(acrylic acid)
pK ₀	Intrinsic dissociation constant
pK _a	Acid dissociation constant
PMMA-b-PMAA	Poly(methyl methacrylate)-b-poly(methacrylic acid)
PPH-PVP	Polyphenylene-b-poly(2-vinyl pyridine)
PS-b-P4VP	Poly(styrene)-block-poly(4-vinyl pyridine)
PS-b-PAA	Poly(styrene)-b-poly(acrylic acid)
PT	Potentiometric titrations
QD	Quantum dot
R ₃ P	Tri-alkyl-phosphine
SAED	Selective area electron diffraction
SLS	Static light scattering
TEM	Transmission electron microscopy
TFXRD	Thin film x-ray diffraction
T _m	Melting temperature
TOP	Tri-n-octylphosphine
TOPSe	Tri-n-octylphosphine selenide
UV-Vis	Ultra-violet visible absorption spectroscopy
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray photoelectron spectroscopy
ΔH	Enthalpy change
ΔS	Entropy change

Θ	The fraction of COOH occupied by Cu^{2+}
α	Degree of deprotonation
χ	Electronegativity

Abstract

Polymer assisted solution synthesis is a common and versatile strategy for preparation of colloidal inorganic nano-materials with novel morphological and functional properties. Although block copolymers are usually employed, homopolymers are attractive substitutes for them, considering cost and scalability. This however requires further understanding and more stringent control of the interaction between homopolymer and precursor species.

The objective of this work is to utilize functional homopolymers to control the structural properties and chemical compositions of synthesized nano-materials. This objective is approached through detailed studies on two hybrid material systems useful for energy-related applications: (i) aqueous-based poly(acrylic acid) (PAA) templated synthesis of copper oxide (CuO_x); and (ii) organic solvent-based poly(3-hexyl thiophene) (P3HT) assisted synthesis of CuInSe_2 (CISe) nano-particles. The chosen homopolymers are good representatives of its own category: PAA has an aliphatic, flexible, and ion conducting backbone; while P3HT is an aromatic, rigid, and semiconducting polymer.

The bridging of the theoretical studies of PAA-Cu^{2+} interaction and PAA templated synthesis is attempted. In the CuO_x project, investigation on the PAA-Cu^{2+} interaction was carried out. Important factors including $[\text{Cu}^{2+}]:[\text{COOH}]_0$, chain conformation, and non-uniform equilibrium charge distribution were identified to have contributed to counterion induced copolymer-like assembly of the PAA-Cu^{2+} complexes, eventually producing nano-tubular CuO_x .

The challenging control of stoichiometry and its uniformity is known to be an issue in tailoring the functional properties of CISe nano-particles. In the CISe project, CISe

nano-particles having novel stoichiometric gradient (i.e. increasing In:Cu ratio from core to shell) and coordinated with P3HT were prepared. Synthesis systems without P3HT were carefully studied and a mechanism leading to novel core-shell-like stoichiometry is proposed. With employment of P3HT as functional ligands, the stoichiometric gradient could be moderated.

This work investigates fundamental molecular-level phenomena associated with the starting precursor conversion, stabilized intermediate state, and eventual crystal growth. The concept and methodology developed can be extended to relevant material systems. This work highlights the vast opportunities remained to be explored in utilizing functional homopolymers for controlled synthesis of nano-materials. It can contribute to the fields of fundamental polymer science, inorganic nano-materials formation chemistry, as well as technological applications for printed electronics.

Chapter 1

Introduction

Nano-structured inorganic materials, having potential for various advanced applications such as optoelectronics, photovoltaics, and sensing, can be prepared by solution synthesis. Organic molecules, e.g., surfactants, block copolymers, and polyelectrolytes (PELs) are often used in the synthesis as ligands or additives. Functional hybrid nano-materials containing both organic and inorganic phases can potentially be prepared in single step. Polymer assisted solution synthesis is attractive as the unique long-chain characteristics of polymer can tailor, not only the structural properties (e.g., hierarchical structure), but also the functional properties (e.g., electronic passivation) of the nano-materials or their hybrid nano-composites. Specific coordination of polymers with precursor/monomer/crystallite is critical towards the nucleation or the growth phases. This is dependent on the functionality, molecular architecture and chain conformation of polymer.

Although successful templated formation of inorganic nano-materials is widely demonstrated via utilization of block copolymer self-assembly, the costly and tedious copolymerization process may limit the template synthesis scalability and practical application. It is therefore desirable to use functional homopolymers as possible substitutes for block copolymers. Great potential of homopolymers in assisting nano-materials synthesis has been shown in the literatures; with the focus on their roles as growth confinement reagent and heterogeneous nucleation sites. However, the functions of homopolymers in terms of structural directing and compositional regulating can be studied further. Despite the simplistic structures of homo-polymers, many parameters e.g., the chain conformation (and its variation), coordinating functionality, variable charge fraction, could be utilized for synthesis of nano-materials with interesting properties. This work identifies several gaps awaited to be bridged; which can be also viewed as research opportunities.

So far, many hybrid nano-composites with regular structure are prepared by utilizing self-assembly of amphiphilic block copolymers. In fact, homopolymers can also be used to achieve regular nano-structured materials. Furthermore, insulating ligated species is widely recognized to be one limiting factor for functional device performance. This ligand issue, together with the stoichiometric issue of ternary (or quaternary) chalcogenide materials can be tackled by using conducting polymeric coordination species.

The objective of this work is to study the unique roles of functional homopolymers during the synthesis of hybrid nano-materials. It is envisaged that the interaction manner between the precursors and homopolymers has profound effect on the structural properties of the hybrid nano-materials by regulating their growth; leading to unique control of nano-crystal size, morphology and chemical compositions.

Two representative hybrid material systems with potential for clean energy and environment related applications were chosen for this study:

- I. Aqueous medium, PEL templated synthesis: poly(acrylic acid) (PAA) templated synthesis of nano-tubular copper oxide (CuO_x).
- II. Organic solvent medium, conducting polymer assisted synthesis: poly(3-hexyl thiophene) (P3HT) assisted hot-injection synthesis of CuInSe_2 (CISE) nano-particles.

The two chosen functional homopolymers, i.e., PAA and P3HT, possess molecular structures that are representative of two important categories of functional polymers. PAA is an aliphatic and annealed ionic conducting polymer electrolyte with flexible backbone; and has been utilized in different applications including energy storage and water treatment. While P3HT, a semiconducting polymer with fully aromatic and rigid backbone, has shown great potential in polymeric photovoltaics and transistors. Both CuO_x and CISE nano-particles have been extensively studied for energy conversion, apart from many other applications.

The organization of the thesis is as following. In Chapter 2, literature review focusing on solution synthesis, polymer assisted synthesis, and formation mechanism of colloidal nano-materials is done.

Chapter 3 discusses PAA- Cu^{2+} interaction mechanism. An in-depth investigation of molecular-level PAA- Cu^{2+} interactions has been carried out. The interdependent relationship among α , pH, and $[\text{Cu}^{2+}]:[\text{COOH}]_0$ has been established quantitatively. Discussion was also done by relating these parameters to spatial conformation of PAA- Cu^{2+} complexes.

Chapter 4 includes the PAA templated synthesis of nano-tubular CuO_x . The synthesis proceeded through binding of Cu^{2+} with COO^- on PAA, hydrolysis, and thermally aided reduction. This work reveals the importance of chain conformation variation and metallic counterions induced copolymer-like assembly of the PAA-Cu^{2+} complexes.

Chapter 5 is about hot-injection synthesis of ternary chalcogenide CISE nano-particles. With the end-goal i.e., preparation of P3HT coordinated CISE nano-particles in mind, this work started from synthesis without P3HT due to novel non-intuitive core-shell-like stoichiometry of CISE nano-particles. The determination of the accurate stoichiometry and its uniformity of the synthesized CISE nano-particles is very important for elucidation of role of specific coordination towards monomer formation kinetics.

Chapter 6 proposes the formation mechanism of CISE nano-particles with stoichiometric gradient; supported by further experimental results. Till today, there remained controversy in the chalcogenide formation mechanism. The reactivities of individually Cu- and In-based organo-metallic precursors are critically dependent on the coordination species present. Further synthesis of CISE nano-particles with P3HT as functional coordinating species not only could change the monomer formation kinetics (tailoring the stoichiometric gradient); it also created intimate P3HT/nano-particle interface beneficial for charge dissociation and transport.

Lastly, chapter 7 concludes with the summary of this work on functional homopolymer assisted formation of inorganic nano-materials; together with recommended future works and outlook.

This work demonstrates the previously unexplored potentials of utilizing functional homopolymers in controlling hybrid nano-materials synthesis. It clearly underlines the

fact that mechanisms involved in the nucleation and growth phases are not only dependent on the intrinsic precursor properties, but also on the essential specific coordination manner between polymers and precursors.

Chapter 2

Literature Review

In this chapter, literature review focusing on four main topics is done:

1. Colloidal semiconducting nano-crystals: material properties and applications
2. Solution synthesis of inorganic nano-materials
3. Polymer-assisted solution synthesis of inorganic nano-materials
4. Nucleation and growth mechanism of nano-crystals in solution synthesis

2.1 Colloidal semiconducting nano-crystals: material properties and applications

Semiconductors possess electronic band structures that consist of valance band (a.k.a. HOMO) and conduction band (a.k.a. LUMO) separated by material specific empty energy interval called bandgap. Simply speaking, electrical conductivity of semiconductors is contributed by the net movements of charges (either electrons or

holes). Many novel electronic and opto-electronic properties rely on phenomena associated with the charges; such as electron-hole recombination and tunnelling. Both inorganic and organic materials could be semiconducting either intrinsically or through extrinsic doping. This review focuses on inorganic semiconductors. The bulk bandgaps of semiconductors can be generally defined to vary from ~ 0.2 eV to 4 eV; corresponding to photons having wavelength ~ 6200 nm to 310 nm. The different bandgap corresponds to different potential application of the specific materials. For instance, silicon with suitable indirect bandgap (~ 1.1 eV) and corresponding strong absorption across the sunlight spectrum is useful for photovoltaic application. Nonetheless, many applications utilize defect energy level instead of the direct/indirect bandgap. More importantly, when the 1D to 3D dimensions of semiconductors are confined down to nano-meter scale, the bandgap is variable and their material properties exhibit novel changes; generally termed as ‘quantum confinement’ (to be discussed later) [1, 2].

- Physical properties

The high surface energy of nano-crystals (and large surface-to-volume ratio) resulted in size-dependent properties [3], e.g., depression of melting temperature (T_m) [4]. Difference in surface energy of dissimilar crystal facets can be utilized for achieving anisotropic growth of nano-crystals [5]; some reported approaches include control of growth kinetic and ‘selective-adhesion effect’ [6]. Mechanical properties of nano-crystals are highly sensitive to crystal planes sliding and crystallographic defects. The stress-strain response of individual quantum dot (QD) (e.g., InGaAs/GaAs [7]), nanowire (e.g., Au [8]), self-assembled supercrystal (e.g., PbS, CdSe, and CoPt₃ [9]), and nano-crystals thin film (e.g., electrophoretically deposited CdSe [10]) were directly or indirectly probed. Characterization techniques that were employed in nano-

mechanics include AFM, STM, nano-indentation, photo-luminescence, and Raman microprobe analysis.

- Chemical Properties

Chemical properties of nano-crystals are of a very broad scope that it is not straightforward to categorize them. Reactions often take place at the surfaces or interfaces of the nano-crystals. ‘Nanocatalysis’ is a research field dealing with utilization of nano-crystals for homogeneous (same phase as reactants) or heterogeneous catalysis (different phase from reactants) [11]. The catalytic behaviour is especially important for petro-chemical industry. The transport and dissociation of charge carriers at nano-crystals interface affect the catalytic efficiency; which are dependent on properties of crystal facets such as sign of charge and type of surface atoms [12]. Catalytic properties of transition metallic (e.g., Au, Pt, Cu, Ni), or bimetallic (e.g., PtSn, PtPb, PdAu, FePt) nano-crystals are widely studied [13]. Note that quantum confinement effect renders the metallic nano-crystals to be semiconducting (to be discussed later).

Photo-catalysis represents another important application of semiconducting nano-crystals [14]. For instance, TiO_2 is an attractive photo-catalyst for water splitting and water/air purification [15]. In photo-catalytic process, electron-hole pairs (generated upon irradiation) dissociate and transport toward the nano-crystals surface; catalysing surface reactions such as oxidation/reduction. Other examples of semiconducting photo-catalytic materials include: CdS, CdSe, SiC, Ta_2O_5 , ZrO_2 , ZnO, In_2O_3 etc. Different approaches were adopted to improve photo-catalytic efficiency, e.g., using redox mediator, noble metal surface metal ion doping, metal ion implantation, and dye sensitization [16].

Strictly speaking, ‘surface chemistry’ of nano-crystals is another research field (still related to photo-catalysis) that involves the studies on (i) constituent surface atoms, (ii) the interfaces of nano-crystals and ligands, and (iii) interaction between ligand and external media. Surface chemistry is relevant to some unique phenomena including surface plasmon resonance and oriented attachment of nano-crystals. For instance, defect energy levels caused by dangling bonds on nano-crystals surfaces can be utilized for photo-emission applications. These surface defects could be controlled or ‘repaired’ by capping of ligands. Affinity of functional groups of ligands to the nano-crystal and packing density of ligands are two important parameters. There are many reviews that discussed the physics and chemistry of interaction between ligands and nano-crystals, as well as strategies of ligand exchange [17, 18]. It is an attractive option to combine chemical properties by preparing nano-structured semiconductors containing different components with dissimilar chemical composition i.e., hetero-structured nano-crystals. Examples include bimetallic nano-rod (e.g., CuPt [19]), hetero-structured nanorods (e.g., CdSe+ CdTe [20]), core-shell nano-crystals [21], and hybrid nano-crystals with various morphology [22].

- Magnetic properties

The unique magnetic properties of nano-crystals have been studied both theoretically [23] and experimentally [24, 25]. The magnetic properties are dependent on mean flipping time of magnetic moment that is affected by nano-crystal morphology and anisotropy force [26]. At nano-scale level, superparamagnetism manifests and can be utilized for applications including data storage and ferro-fluidic based devices [27]. No heating (no hysteresis loss) takes place during magnetization in single magnetic domain; this is especially important for applications involving fast alternating magnetic field. Magnetic nano-crystals of different compositions and morphologies

such as Fe, Co, Ni, FePt, and CoPt were synthesized [28]; sometimes obtained through doping of established fluorescent nano-crystals (e.g., doping Mn into CdSe [29]). Magnetic nano-crystals possess high potential for advanced medical applications, e.g., magnetic resonance imaging (MRI), hyperthermic cancer treatment, and guided drug delivery [30, 31]. Therefore, biocompatible surface coating of magnetic nano-crystals for in-vivo medical applications is very important [32].

- Electronic, optical, and opto-electronic properties

Many unique properties are exhibited by ‘quantum dot’ (QD), referring to the nano-crystals with all their three dimensions smaller than the characteristic exciton Bohr’s radius (main distinction in definitions for ‘QD’ and ‘nano-crystal’). The fact that the electrons are confined within several nano-meter spatial regions significantly affects their momentum/energy and distorts the electronic band structures. This ‘quantum confinement’ effect causes size-dependent separation/quantization of originally overlapped energy states into discrete energy levels (see Figure 2.1).

Figure 2.1. Schematic illustrations showing: (a) the difference in density of states of metallic and semiconducting materials in their atomic, nano-crystal and bulk form. For metal, overlapping of atomic orbitals forms the continuous energy states. For semiconductor, there exist a bandgap where electron energy states are forbidden; (b) difference in density of states with their dimensionality [1].

Different types of unique electronic or opto-electronic properties could be observed on nano-crystals. In fact, tunable fluorescence of QDs has been a widely pursued topic and significant advances have been achieved in past two decades; built on the much better controlled nano-crystal synthesis. Gold and silver nano-crystals exhibit surface plasmon resonance with tunable absorption and emission wavelength [33]; this collective wave propagation phenomenon is useful for nano-scale photonic circuit or photonic storage device. It is also possible to manipulate the charge carrier transport at well-defined discrete energy levels to achieve multiple-state memory device [34]. Multiple exciton generation (i.e., generation of multiple excitons with single absorbed photons) of QD is promising in enhancement of the power conversion efficiency of

solar cells [35]. Effective electronic passivation, e.g., through ligands capping and core-shell architectures, is critical to ensure reliability of device performances.

- Applications of nano-crystals in thin film and composite form

Unique properties of nano-crystals can be utilized by incorporating them inside organic matrix to prepare blend [36, 37], composite particles [38], and biomimetic materials [39, 40]. For device applications, inter-particle energy coupling, interfacial charge dissociation and transport, and charge collection at the contacts are important parameters [41, 42]. They rely on intimate interface between the nano-crystals and organic coordination species. The processability of hybrid materials can also be improved by existence of organic phase. Hybrid solar cell employing functional nano-composites is widely studied; the nano-crystals help sensitizing/improving electron-hole pair generation and charge separation [43]. Other applications include non-linear photonic crystal (e.g., Ag nano-particles doped poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) [44]), photorefractive material (e.g., LiNbO₃ sensitized poly(N-vinylcarbazole) [45]), fluorescent composite (e.g., CdTe in polystyrene [46]), photoconductor (e.g., CdSe in MEH-PPV [47]), single electron memory device (e.g., Si [48]), and so on.

2.2 Solution synthesis of inorganic nano-materials

In this section, less emphasis is placed on substrate-based heterogeneous growth or deposition techniques; the focus is on the creation of colloidal nano-materials synthesized and stabilized in solution phase. Preparation techniques of nano-materials can be broadly categorized into 'top-down' and 'bottom-up' approaches. 'Top-down' approaches reduce the dimensions of bulk materials into small entities through physical or chemical methods, e.g., ball-milling and laser ablation; large amount of

energy is required in the process. ‘Bottom-up’ approaches employ atomic or molecular precursors as building blocks to synthesize nano-crystals. Examples are different types of solution synthesis routes, vapor-phase deposition, and electro-deposition. Solution synthesis, which can be carried out in either aqueous medium or organic solvent, is very attractive to printed electronics industry. The unique advantages of solution synthesis include the facile tailorability of material properties through variation of synthesis parameters, large library of selectable material systems, good scalability, and so on. Well crystallized metallic or semiconducting (e.g., oxides, sulfides, nitrides) nano-crystals with controllable and novel morphologies could be prepared by solution routes. Semiconducting nano-crystals can be categorized into II-VI (i.e., IIB-VIB; e.g., CdSe, HgTe), III-V (i.e., IIIB-VB; e.g., InAs, PbS), IV-VI (i.e., IVB-VIB; e.g., PbS, PbSe), I-VII (i.e., IB-VIIB; e.g., CuCl, AgBr) types based on their group numbers and old European IUPAC system inside periodic table. Comparing to gas-phase techniques, solution synthesis is carried out at lower temperature (<300-350 °C); limited by the thermal decomposition temperature of precursors and boiling point of the solvents and ligands.

- Aqueous-based versus organic solvent-based nano-material synthesis

Compared with synthesis using organic solvents, aqueous-based synthesis is more environmental friendly, potentially bio-compatible, more economical, and easier to be scaled-up. There are different types of aqueous synthesis methods which include: reduction/oxidation [49], sonochemical [50] co-precipitation [51], and hydrothermal [52]. Aqueous synthesis is widely used for synthesizing inorganic materials including metal oxides (e.g., HfO₂ [52], TiO₂ [53], iron oxide [54]), metallic or bimetallic materials (e.g., Ag, Pt, Pd [55], Au [56]), and semiconductors (e.g., InP [57], ZnS [58]).

Different types of reagents or precursors are used for either aqueous or organic solvent-based synthesis. Many metallic salts possess good solubility inside aqueous media, which fulfilled the first but important prerequisites of aqueous synthesis. Aqueous-based biomimetic or bio-inspired growth of hierarchical meso-crystals represents a very attractive research direction in preparing functional or structural-supporting crystals with complex architectures [39].

Interactions among the solvent molecules, ligands, and precursor species are critical considerations. Solvent properties such as polarity, boiling point, and coordination capability affect the synthesis results. For example, solvent type and mixed solvent ratio affect the growth behaviour and solubility of nano-crystals. Precursors can be of different types such as salt, organo-metallic compound, single molecular precursor, or elemental form. Molecular integrity of precursors (e.g., before and after decomposition) is important especially when multiple precursor species exist inside the reaction solution. The kinetics of the chemical reaction is critical.

Organic molecules are very often included in the synthesis for functions such as templating or confining the growth of inorganic nano-materials. For surfactant molecules (charged or un-charged), utilization of their micelles or reverse micelles to synthesize nano-materials in aqueous or mixed solvents is widely reported [59]. Organic molecules with longer aliphatic chains are however hydrophobic in nature and insoluble in aqueous media; but they can effectively stabilize nano-materials inside organic solvent. In principle, to solubilise inorganic nano-materials inside aqueous media, the following strategies can be adopted: (i) using ligands with one hydrophilic end (e.g., OH^- and COO^-) for aqueous solubility and another hydrophobic end for nano-crystals capping; (ii) using amphiphilic diblock or triblock copolymers or phospholipids to interleave the commonly found alkylphosphine ligand through

hydrophobic interaction, while hydrophilic center-block helps to solubilise [31]. Apart from those, there are various techniques for surface modifications of inorganic nano-crystals to suit different solvent environment [18]. Specifically for polymer-assisted solution synthesis, another section will be devoted later.

Of course, aqueous-based techniques are not without limitations. The synthesis temperature cannot be too high; limited by the boiling point of water. The degree of crystallinity could also be poorer due to temperature limitation. Hydrothermal method indeed uses higher temperature, but it also requires pressurized atmosphere that is not straight-forwardly controllable. Besides, compared with organic solvent based synthesis, the size of aqueous-based synthesized products is usually larger (up to several hundreds nanometers or microns); and the size dispersity is more difficult to be controlled. Longer growth time is usually needed for aqueous synthesis, but slow growth under milder conditions is essential for producing micro- or nano-scale crystals with well-defined and novel morphologies, e.g., octahedron and hierarchical structures.

The types of interaction among the reactant species in aqueous media or organic solvents is of course different. In aqueous synthesis, ionic interaction is the dominant type of interaction; the hydrophobic interaction, hydration structures, polarity of both the metal ions and the organic additives are important parameters. In organic solvent-based synthesis, the conversion/decomposition process of the precursors into ‘monomer’ is very critical; which is heavily influenced by the coordination bonding of intermediate nature between covalent and ionic bonding. Here, the ‘monomer’ refers to, for instance, $[\text{CdSe}]^0$ (two atoms) of CdSe nano-crystals. Organic solvent-based synthesis is capable of producing large quantities of well-crystallized mono-dispersed nano-crystals or QDs; which is contributed by possibly high solvent boiling point and availability of strong capping organic ligands. Certain conditions could be difficult to

be achieved via aqueous routes. The ability to disperse the synthesized nano-materials in aqueous system depends most of the time on ionic stabilization (considering zeta-potential); while in organic solvent, ligands that could interact with the solvent and nano-crystals are required to cap the high-surface-energy nano-crystals and maintain good dispersion.

The ligand species (with functional groups e.g., -NH_2 , -SH , -COOH , $\text{-R}_3\text{P}$, $\text{-R}_3\text{P=O}$, -PO_4^{3-}) can be coordinating/non-coordinating, mono-dentate/multi-dentate, ionic/non-ionic, and templating/non-templating; these properties affect the formation mechanism and colloidal stability of nano-materials [31, 60]. Besides organic ligands, inorganic chalcogenide based ligands were reported by Kovalenko et al.; heat treatment could convert the ligand into inorganic phase to ‘glue’ nano-crystals together for device fabrication [61]. Addition of non-solvent or lowering of temperature can precipitate colloidal nano-materials capped with ligands. Synthesized products can be purified by repeated ‘washing’ with solvent; before re-dispersed inside suitable solvent.

- Different solution synthesis techniques of nano-materials

Many solution-based techniques have been reported; each of them possessing their own strengths and weaknesses. For instance, some of them offer good size control, while others offer simpler procedures or good product yield. Summarized inside the Table 2.1 are some common solution synthesis techniques; note that not all of them can be distinguished into solely aqueous or organic solvent-based systems.

Table 2.1. Common solution synthesis techniques.

Solution-based techniques	Description
Hot Injection (thermolysis) [62]	Injecting organo-metallic and chalcogen-based precursors into reaction solution containing capping ligands at high temperature. Upon injection, thermal decomposition of precursors happens, generating monomers; followed by rapid nucleation. At lower temperature, crystallization takes place within the ‘shell’ of capping ligands. The ligands confine the nano-crystal growth, limit the inward transport of additional ‘monomers’, and passivate the surface atoms.
Hydrothermal/ solvochemical [63]	Mixture of reactants is sealed inside autoclave and reaction proceeds by heating. High pressure is generated under the condition. Various materials can be synthesized including oxide, sulfide, halide, nitride, and chalcogenide. Morphology of nano-materials is tailorable by ratio of mixed solvents, surfactants and ligands. For instance, citrate ions bind to the (0001) plane of ZnO and inhibit the c-axis growth; promoting lateral growth.
Sonochemical [64]	Using sonic wave (e.g., ultra-sonication) to assist synthesis by acoustic cavitation; involving creation of localized high-temperature and high-pressure bubbles as the reaction sites.
Polyol reduction [65]	Using polymer with multiple hydroxyl (–OH) groups (e.g., diethylene glycol) to chemically reduce the precursors. The polyol species serve as both reaction solvent and chelating agents. This method can produce metallic nano-crystals, phosphates, sulfides, and chalcogenides. The reaction can be assisted by microwave irradiation.

Sol-gel method [66, 67]	Using hydrolysis and polycondensation of sol-based precursors to form nano-crystallites, thin film or interconnected crystallized network. Typical precursors are metal alkoxides and chlorides; and metal oxide is synthesized. Morphologies of crystallites are affected by surfactant, ligands or ionic species.
High-energy irradiation Synthesis [68]	Using high energy irradiation such as γ -ray to generate localized reaction through decomposition of precursors or reductive mechanism (e.g., by creation of aqua OH^-).
Micro-emulsion method [69]	Mixture of different ratios of oil-phase and water-phase organic species forms emulsion droplets (dispersed phase in continuous phase: 'oil-in-water' (direct) or 'water-in-oil' (reverse)) as micro- or nano-reactor. With precursors and surfactants, reaction takes place within the droplets and greatly influenced by the interfacial interaction. The generation and homogenization of the droplets can be assisted by ultra-sonication.
Precipitation by hydrolysis/ oxidation/ reduction [49]	Hydrolysis, reduction or oxidation of homogeneously dispersed precursors inside solutions. Organic additives are always used to control the growth and to encapsulate the synthesized products. The oxidation/reduction can be achieved through physical (e.g., heating) or chemical (e.g., NaBH_4) means. This encompasses also co-precipitation.
self-assembled polyelectrolyte multi-layer templated synthesis [70]	By depositing polyelectrolyte (PEL) multi-layers with alternating signs of charges on substrates e.g., Si or polystyrene nano-spheres; which absorb counterions that are subsequently hydrolyzed/reduced/oxidized into inorganic nano-materials. The PEL multi-layers can be removed by thermal decomposition or chemical dissolution.

As a short summary, for solution synthesis of colloidal nano-materials, research directions pursued generally include: (i) developing chemistry to synthesize nano-materials with controllable and novel morphologies, compositions, crystal phases, and functional properties; (ii) improving the solution synthesis routes to be more facile and environmental friendly; (iii) studying ligand chemistry to achieve good colloidal nano-materials stability or special functionality (e.g., electronic passivation); and (iv) fabricating functional devices with good interfacial charge dissociation and transport by solution techniques.

2.3 Polymer-assisted solution synthesis of inorganic nano-materials

This section discusses the literatures that utilized long-chain polymers in nano-material synthesis. The focus will be on utilizing the polymers to tailor the nucleation and growth behaviours of the synthesized nano-materials. Less emphasis will be given to studies that reported physical blending of pre-formed nano-crystals and polymer [71], stabilization of the nano-crystals by capping [17], on-substrate polymer brush synthesis [72], or polymerization on the nano-crystal surface [73].

Polymers that are used in solution synthesis of inorganic nano-materials can be categorized into different categories: hydrophilic polymers (e.g., poly(ethylene oxide) (PEO)), PELs (e.g., PAA, poly(ethyleneimine) (PEI)), block copolymers (e.g., poly(styrene)-b-poly(4-vinyl pyridine) (PS-b-P4VP)), and conducting polymers (e.g., P3HT). Although proteins are also considered as polymers, relevant topics are not supposed to be discussed further here due to its extensiveness [74, 75]. Nevertheless, discussions on non-classical crystallization in the context of bio-mineralization and biomimetic synthesis will be included later on; in which protein play important role. As mentioned previously, due to the polymer solubility limit in aqueous media,

aqueous synthesis usually involves hydrophilic polymers or PELs (both of them in at least certain segments).

Functions of polymers are not so dissimilar as compared to those of surfactants or oligomeric ligands, normally including (i) random confinement through capping of in-situ generated nano-materials (e.g., PbS in MEH-PPV [76]); (ii) self-assembled 'nano-reactor' confining the reaction inside certain volume (e.g., calcium phosphate in poly(methyl methacrylate)-b-poly(methacrylic acid) (PMMA-b-PMAA) micelle [77]), or (iii) structural directing agent with utilization of the interaction between the functional groups and nano-crystals (e.g., growth of ZnO hexagonal plate directed by polypyrrolidone [78]). The most important attribute, that differentiates polymers apart from shorter chain surfactants and ligands, is of course the long-chain structures, which poses considerations on steric hindrance, chain rigidity, and chain conformation variation. For instance, whether the chain is of aliphatic or aromatic repeating unit influences the chain conformation (e.g., coil-like, planar, or twisted). It is equally important to understand the interaction of the polymers with precursors/monomers/nano-crystals, as well as with surrounding media. In polymer assisted synthesis, larger diffusion constraint is exerted on monomers to attach to the growing crystal.

Usually, the polymeric matrix provides protection or passivation for the functional nano-crystals and facilitates further device fabrication processes. Polymers can also be used to prepare colloidal hybrid functional nano-materials or thin films [36, 38]. For instance, conducting polymer, either as matrix or coordination agents, provides good interface for charge transport between the nano-materials and external contacts [79, 80]. Besides charge carrier conduction, many novel functions (e.g., electrochromic and optoelectronic) were reported for hybrid nano-composite containing conducting

polymers and inorganic nano-materials [81]. In thin film architecture, the polymeric template could be thermally or chemically removed after the nano-materials formation.

Block copolymer assisted synthesis is another important research topic. The block copolymers offer unique structural and chemical properties: e.g., amphiphilicity, segmental coordination, segmental chain stiffness, nano-scale phase separation capability, and so on. Novel hybrid nano-materials can be produced using block copolymers, for instance, (i) patterned thin film with spatially distributed inorganic nano-particles [82, 83] or epitaxial crystals [84]; and (ii) colloidal nano-materials with novel morphology such as hollow spheres [85]. As shown in Figure 2.2 are selected examples of nano-materials prepared using block copolymer assisted synthesis. One interesting example is a report that synthesize P3HT-b-poly(zinc methacrylate acetate) block copolymer; which was hydrolysed to produce P3HT-ZnO blend for photovoltaic applications [86]. The trend of directly preparing functional nano-composites by utilizing or modifying functionality of polymers is recognized.

Figure 2.2. Representative examples of hybrid materials prepared by block copolymer assisted synthesis: (a) meso-structured ZnO nano-tubes [87]; (b) micro-capsule encapsulated single gold nano-particle [88]; (c) meso-porous boron nitride of hexagonal cylindrical or lamellar structure [89]; (d) hollow spherical calcium phosphate [77]; (e) hybrid rod-like assembly containing ZnO nano-particles [86]; (f) palladium nano-particles synthesized in-situ macro-phase separated block copolymer [83].

Despite the versatility of using block copolymer to assist synthesis of inorganic nano-materials, from a pragmatic aspect, the method is expensive and tedious. It would be of great research interest to utilize much structurally simpler and potentially cheaper homopolymers for nano-materials synthesis (in both colloidal and thin film forms); this strategy however warrants better understanding of the fundamental molecular phenomena from both academic and technological perspectives.

This extends beyond (i) simply using homopolymers as non-coordinating additives during nano-materials formation; (ii) addition of homopolymer in block copolymer blend which tunes the phase separation behaviour. For homopolymers, their unique

properties such as chain end effect can be potentially used for synthesis control. For instance, as a homopolymer, poly(N-alkylacrylamide)s was demonstrated to be able to assemble into novel organic micro-spherical structures [90]; although in the work, such homopolymer assembly phenomenon was not utilized for directing synthesis of inorganic nano-materials. Nevertheless, utilization of the usual functions of homopolymers such as confinement, selective absorption, or steric-related templating were reported to have produced nano-materials with novel morphologies; some representative examples are given in Figure 2.3.

Figure 2.3. Examples of homopolymers used for synthesis of nano-materials with novel morphologies: (a) Cu₂O/PEG400 composite hollow spheres [91]; (b) Cu₂O cubic nanoparticles [92]; (c) CdS nano-rods templated by P3HT [93]; (d) PbS nano-rods in situ generated and aligned in MEH-PPV, proposed due to dipole-induced oriented attraction [94].

2.4 Nucleation and growth mechanism of nano-crystals in solution synthesis

The understanding of the formation mechanism is essential for achieving controllable synthesized nano-crystals with uniform and reliable quality. Continuing research efforts have been put into investigation of the formation mechanism of nano-crystals, so to achieve good synthesis control. Despite the fact that general picture of formation mechanism of certain material systems is understood, existing theories are most of the time taken for granted. In fact, the existing theories but could be inadequate to fully elucidate the formation of synthesized products. By tailoring the nucleation and growth kinetics, nano-crystals with novel morphologies can be achieved. For instance, ionic species, surfactants or ligands might enhance or inhibit the growth rate of selective crystal plane(s) and resulted in anisotropic growth.

This section will start from the general classical theory on homogeneous and heterogeneous nucleation and growth; followed by discussions on the limitations of the theories and some reported variations dependent on specific scenarios. The theories are applicable to the formation of semiconducting, metallic, and transition metallic nano-crystals.

- Classical theory on homogeneous and heterogeneous nucleation and growth

Formation mechanisms of nano-crystals depend on various factors including material systems (i.e., precursors, solvents, ligands, and additives), synthesis routes, and synthesis parameters (e.g., reaction temperature and duration). In nano-crystals synthesis, ‘precursors’ generally refer to molecules that are converted (e.g., through thermal decomposition or chemical conversion) into ‘monomers’ which combine to

form crystal nuclei. Herein, ‘monomer’ is defined as the basic entity that constitutes the nano-crystals.

Classical nucleation mechanism is nonetheless fundamentally similar to that of melted solid solution upon super-cooling. Nucleation may happen via ‘homogeneous’ or ‘heterogeneous’ manner. ‘Homogeneous’ nucleation, taking place without any foreign seeds, is thermodynamically driven and proceeds following the supersaturation of the constituent monomers. ‘Heterogeneous’ nucleation takes place with the presence of foreign seeds or nucleating agents (e.g., substrates and organic molecules) inside the reaction solution [95]; the free energy barrier is lower in this case. ‘Seed-mediated’ synthesis that utilizes heterogeneous nucleation can isolate the nucleation phase from growth phase. The classical nucleation is described by the LaMer model [96] (see Figure 2.4(a)), which is dependent on: (i) the monomer concentration, (ii) the number of nucleus’ atom (also called nano-cluster size), and (iii) the free energy barrier of nucleation. Finney and Finke recently reviewed nucleation of transition metallic nano-clusters and discussed several variations of classical nucleation theory [97].

Figure 2.4. (a) The originally proposed LaMer mechanism illustrating three regions of evolution of concentration of dissolved molecular sulfur throughout the nucleation and growth phases: I: homogeneous nucleation, II: burst nucleation, III: ‘diffusion-controlled’ growth; (b) illustration of classical nucleation theory that shows the relationship between free energy change and nano-clusters radius. Both diagrams are abstracted from [97].

For homogeneous nucleation, free energy change (ΔG) of the overall system due to the formation of nano-crystals consists of two parts: volume energy and surface energy [5]:

$$\text{Equation 2.1:} \quad \Delta G = -\frac{4}{3V}\pi r^3 k_B T \ln(S) + 4\pi r^2 \gamma$$

(V: molecular volume of the precipitated species; r: radius of the nuclei; K_B : Boltzmann constant; S: saturation ratio; γ : free energy per unit surface area)

Saturation ratio:

$$\text{Equation 2.2:} \quad S = \frac{C - C_s}{C_s}$$

(C_s : saturation concentration)

The 1st term at the right hand side of Equation 2.1 is the decrease of volume energy and the 2nd term is the increase of surface energy upon nucleation.

The nucleation rate (J) can also be calculated [98]:

$$\text{Equation 2.3:} \quad J = J_0 \exp\left[\frac{-16\gamma^3 V^2}{3K_B^3 T^3 (\ln S)^2}\right]$$

(J_0 : nucleation rate constant, representing the maximum nucleation rate)

The ‘embryos’ or ‘clusters’ are only stable as nuclei when their radii exceed critical radius (material specific); below which the embryo dissolves. Critical nuclei radius (r^*) can be obtained by setting $\frac{d\Delta G}{dr} = 0$ to give (also see Figure 2.4(b)):

$$\text{Equation 2.4:} \quad r^* = \frac{2V\gamma}{K_B T \ln(S)}$$

From Equation 2.4, it can be observed that the r^* depends on synthesis system, monomer concentration (and its supersaturation), and temperature. Since monomer

concentration changes throughout the synthesis course, the magnitude of r^* changes. The implication of above statement: there are two feasible approaches to obtain mono-dispersed nano-crystals [99]: (i) burst nucleation induced by fast supersaturation of monomers and (ii) maintaining supersaturation of monomers (e.g., through intermittent replenishment of precursors) for ‘size-focusing’ event during growth phase.

- Extended beyond classical theory of nucleation and growth: other considerations

Classical nucleation theory was built on ‘diffusion-limited’ condition (Gibbs-Thompson equation). This refers to the condition when the ‘rate of monomer diffusion from bulk solution towards the nuclei’ is slower than the ‘rate of chemical attachment of monomers to seed nuclei’. ‘Reaction-controlled’ condition implies the reverse condition. Classical nucleation theory can however be extended to encompass both ‘diffusion-controlled’ and ‘reaction-controlled’ (or ‘kinetic-controlled’) reaction [100]; by considering the number of atom, atom attachment rate, atom dissociation rate, solubility, and temperature. Even so, there exists distinct discrepancy in formation mechanism of nano-crystals especially during ‘size focusing’ event [101]. Examples of limitations of classical nucleation theory are (i.e., it is unable to account for): (i) high saturation (and usually accompanied by fast depletion) of monomers; (ii) low solubility of nano-crystals; (iii) effects of ligands or additives towards monomer attachment and dissociation; (iv) magic-size clusters i.e., localized stable thermodynamic energy states of a cluster constituting small number of atoms; (v) size-dependent chemical stability; and (vi) no information regarding size and size distribution.

Furthermore, classical theory is also not directly applicable for anisotropic growth that produces 1D (e.g., nano-wire), 2D (e.g., nano-platelet), or 3D (e.g., spiky sphere) nano-structured crystals; it is another important research field that investigates crystal shape evolution [102]. Some examples of other updated theories describing nucleation include: balanced nucleation-growth model, Randolph-Larson model, two-step mechanism, and four-step mechanism [97, 98, 103].

More insights and understandings on various phenomena involved at the initial nucleation stages are required; for instance, decomposition/conversion of precursors, reduction/oxidation of monomers, and polymer-counterion complexation. The challenge of experimentally studying the nucleation phase is the availability and development of reliable and robust techniques to characterize the atomic-scale phenomena at ultra-short time interval within a transient time frame. Examples of some usually adopted techniques include absorption spectroscopy, dynamic light scattering (DLS), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR), and some advanced x-ray spectroscopies (e.g., X-ray Absorption Near Edge Structure (XANES), Extended X-ray absorption fine structure (EXAFS)).

The nucleation of semiconducting nano-crystals is significantly dependent on the stage when conversion of precursors into monomers [104]. For instance, the fast rate of nucleation and slow growth rate in hot-injection synthesis is opposite to conditions described by classical nucleation theory.

The proposed ‘ligand-controlled nucleation’ theory emphasizes that favorable binding between ligands and monomers inhibits nucleation; while favorable binding between ligands and crystal nuclei inhibits growth [105]. For instance, stronger affinity of oleic acid towards cadmium monomers increases critical radius r^* (i.e., low supersaturation

ratio) and results in higher solubility of embryos. The interaction among nano-crystals also affects the formation mechanism. The existence of small nano-crystals was found to prevent the dissolution of large nano-crystals [106]. In-situ TEM observation of the formation of platinum nano-crystals, as reported by Zheng et al., showed that both ‘monomer attachment’ and ‘particles coalescence’ contribute to the final mono-dispersed nano-crystals [107].

Rempel et al. divided the nano-crystals formation into five consecutive stages based on kinetic modeling of temporal evolution of the mean size, size distribution, reaction yield, monomer concentration, and total cluster concentration [104]. As shown in Figure 2.5(a) is the schematics of these regions: (i) generation of monomers; (ii) small cluster formation and size broadening; (iii) size focusing caused by precursor depletion; (iv) invariant size and size distribution; (v) increase in size and size distribution. Their theory discussed different monomer attachment and dissociation rate constant; which are affected by temperature modulation and additives.

Xie et al. proposed three non-overlapped reaction regimes (Figure 2.5(b)): (i) ‘reaction-controlled’ formation, (ii) ‘nucleation-controlled’ formation, and (iii) dissolution region; the regimes are defined and continuously separated by different range of monomer concentration and embryo solubility [108]. Magic-size clusters with close-shell atomic configuration have essentially lower solubility and different morphologies, resulting in obvious discrepancies from classical nucleation theory.

Figure 2.5. (a-I) Five nucleation and growth regions (modeled for CdSe) showing different trend of σ_R/μ_R ('radius variance'/mean radius') and μ_R versus scaled time (τ); (a-II) different trend of cluster concentration (C_{tot}), monomer concentration (C_1), and reaction yield (Y) versus scaled time (τ) [104]. (b) Monomer concentration versus size of clusters/crystals within the three different non-overlapped regions; which also serves as an illustration of the solubility limits of smaller nuclei (S_{∞}) and bulk crystal (S_{max}). The dips of monomer concentration in the initial small cluster size region is due to the formation of magic-size clusters [108].

After the nucleation and initial growth of the nano-crystals, Ostwald ripening [109] and aggregation [110, 111] may ensue. These phenomena produce large size and size

dispersity of nano-/micro-particles or aggregates of crystallites. To put it simply, Ostwald ripening refers to the condition when large crystals grow by consuming materials coming from dissolution of small crystals. It happens at relatively slower growth and lower monomers concentration, and is generally encountered in the later stage of nano-crystal growth phase or during storage period. Lifshitz–Slyozov–Wagner (LSW) theory is generally adopted to describe Ostwald ripening; which involves quantitative predictions based on diffusional mass exchange [109]. Park et al. modeled the collision and secondary aggregation of embryos (‘singlets’) into secondary particles, and suggested a growth that is sensitive of surface energy (faster aggregation of smaller nano-crystals), resulting in size selection [110]. Talapin et al. carried out Monte Carlo analysis to simulate change of size distribution due to Ostwald ripening under ‘diffusion-controlled’ and ‘reaction-controlled’ situation [112]. For nano-particle ensembles with size smaller than 20 nm, Ostwald ripening occurs faster and gives smaller size distribution; especially under strong ‘diffusion-controlled’ condition.

As another important research topic on non-classical nucleation and growth, natural bio-mineralization that involves genetically defined phenomena that build up nano-crystals into complex hierarchical crystal structures will be discussed here. Fascinated by bio-mineralization, researchers develop or design ‘bio-mimetic’ synthesis methods through imitating the crystallization principles of those phenomena. For this purpose, marine organisms e.g., mollusk, sea urchin, and diatom are usually studied. These studies are not only important for understanding the fundamentals of natural crystallization, but also for advanced applications such as preparation of artificial bio-material (e.g., bone repair), cell-growth scaffold, biosensor, superhydrophobic surface, and even meta-materials.

Bio-mineralization involves interplay of inorganic and organic species; contributing to the final crystal structures. This is the reason why bio-mineralization could not be explained simply based on classical theories. Of course, this research topic overlaps with the organic molecules assisted synthesis of inorganic nano-materials. Organic species including poly(acrylic acid), poly(ethylene oxide), poly(aspartic acid), collagen, and cellulose have been used in biomimetic synthesis under mild reaction conditions. Different biological inorganic materials including silica, calcium carbonate, calcium phosphate, and hydroxyapatite have been prepared using relevant methods; a broader scope may include metallic and semiconducting inorganic nano-materials. Control of crystallite morphology, composite structures, and polymorphism is possible. In fact, bio-mineralization is so complicated that new insights are constantly generated for specific organism. There are many good and detailed reviews on this topic [113-116]. To keep this section concise, the following discussion will only focus on the important nucleation and growth phenomena in bio-mineralization or biomimetic synthesis.

Figure 2.6 showed several examples of different biomimetic crystal structures prepared in mimicking their natural counterparts. The complexity of the bio-mineralization of course could not be fully replicated in laboratory. However, these studies suggested that the bio-mineralization phenomena could be studied and closely re-created from physicochemical aspects; instead of from more complicated biological or genetical aspects.

Figure 2.6. Examples of different crystal structures synthesized using biomimetic methods, together with the comparison with the natural crystals: (a-1) synthetic nacre versus (a-2) original nacre (*H. laevigata*) [117]; (b-1) oriented ZnO helical columns versus (b-2) nacreous CaCO_3 columns and layers (abalone) [118]; (c-1-a) calcite induced by proteins from calcitic shell and (c-1b) aragonite induced by protein of aragonitic shell [119] versus (c-2) typical shell structure of mollusc (*M. californianus*) [120].

In bio-mineralization, the dynamic shapes of vesicle (e.g., elongation) formed by proteins and bio-molecules confine the nano-crystals growth; eventually modulate the building blocks for hierarchical crystals. The ion-pump-like function of biological

membrane includes expelling or concentrating certain salt species plays important role. Certain inorganic species inhibits the formation of specific crystal phase (note: not plane), producing amorphous particles with well-defined shape [121].

For bio-mineralization, the (i) stabilization of embryonic crystals with high surface energy and (ii) further anisotropic growth represent two important stages [122, 123]. In the pre-nucleation stage, ‘stabilized cluster’ is recognized to be an important intermediate [124]. For instance, the adsorption of metallic ions (e.g., Li^{1+} , Mg^{2+}) onto selective crystal faces could stabilize metastable crystal phases. The difference of surface energy of dissimilar crystals faces needs to be considered. Moreover, the nucleation phase is affected by the presence of biological species (e.g., fatty acids) that coordinate to the nucleating precursors. Based on functionalities, specialized protein species can be prepared to template heterogeneous nucleation. Proteins can be considered as polyelectrolytes, with complex and genetically determined molecular structures. Simply speaking, the effects of inorganic-organic interface manifest in terms of stereochemical selection, chain conformation effect, and change in energy barrier [125].

From the thermodynamic aspects, intermediate metastable energy levels are created which modulate the nucleation during bio-mineralization. Polymeric structures were demonstrated to be utilized for kinetic control and preferential templating of metastable crystals [126]. The combined effect of stabilization and surface energy could result in change of nucleation kinetics or correlated assembly during the growth phase [127]. It was found that in some organisms, the kinetically stabilized amorphous phase is important for further structural evolution [128, 129].

In the further growth phase, the coordination and stabilization (e.g., electrostatically, sterically) are important in determining the final structures. The formation or assembly mechanism of natural hierarchical single- or meso-crystal structures remain largely conjecture; despite that, their physicochemical principles are generally known. Oriented attachment or formations of meso-crystals are frequently discussed in this context [130]; illustrated in Figure 2.7 are the relevant phenomena.

Figure 2.7. The illustration of the oriented self-assembly and mesocrystals formation [131]. The difference between them is that organic ligated species are removed in the process for oriented assembly; while those in mesocrystals remain. The bottom right illustration shows that large single crystal is possibly formed after fusing of the aligned smaller nano-crystals.

Mesocrystals can possess both crystalline and amorphous properties. In bio-mimetic synthesis, the organic bound phase inside mesocrystals could be retained or removed through physical or chemical means. For mesocrystals found in living organism, the intercalation of macromolecules or proteins improve the mechanical toughness more than that of the inorganic materials; this is very beneficial for structural supporting function. Both oriented attachment and mesocrystals formation are highly dependent on the molecular recognition, hydration structure (i.e., hydrogen bonding), and ionic species. Both of the products obtained via such phenomena appear single crystalline in

diffraction behaviour; but in fact consist of well-aligned nano-crystals in the same crystal direction. The mechanism of such alignment is still not fully understood, although it is usually attributed to the polarity of the nano-crystals.

2.5 Summary

The literature review done in this chapter underlines the versatility of polymer assisted solution synthesis of inorganic nano-materials; the polymer not only acts as coordination or confinement agents, but also induces the non-classical nucleation and growth behaviours. There are much potential left to be explored for utilizing functional homopolymers for such purposes. The vision of templated generation of macroscopic single crystal or mesocrystal with nano-scale morphologies (confined in 1D to 3D) via solution-based techniques is highly beneficial for many applications including catalysis, sensing, optoelectronic, or even meta-materials. Over the years, many intriguing phenomena have been demonstrated, scrutinized, and utilized. However, looking at the vastness of the synthesis and material systems, more in-depth understanding and insight on relevant and specific research topics are deemed to be generated in coming decades.

Chapter 3

Study on Interaction

Mechanism of Poly(acrylic acid) with Cu^{2+} Counterions

3.1 Introduction

3.1.1 Interaction of polyelectrolytes with metallic counterions

Polyelectrolytes (PELs) are long chain organic molecules with distributed charged functional groups. They can interact with metallic counterions (denoted as $\text{M}^{\text{x}+}$ in future appearances) through electrostatic interaction, complexation, and so on. (Note that organic counterions are not discussed here.) Specific examples of the PEL- $\text{M}^{\text{x}+}$ interaction include expulsion of inert salt species or solvent molecules, charge regularization/fluctuation, physical or chemical binding of $\text{M}^{\text{x}+}$, intra-/inter-chain bridging, and so on. These events could be observed macroscopically, e.g., as chain shrinkage and precipitation. The understanding and utilization of the PEL- $\text{M}^{\text{x}+}$ interactions are of interest for both academic research and the technological/industrial applications; they are useful for many applications such as targeted bio-imaging or

waste-water treatment. Summarized inside Table 3.1 are some intrinsic and extrinsic properties of three main components inside PEL-M^{x+} mixture that affect their interaction.

Table 3.1. Summary of properties of three main components inside PEL-M^{x+} mixture that affect their interaction.

	Intrinsic Properties	Extrinsic Properties
PEL	Molecular composition, functionality, architecture, molecular weight, poly-dispersity	Concentration, solubility, chain mobility, chain flexibility, persistence length, degree of ionization (α), chain conformation, entropy
Metallic counterions	Valency, sign of charge, electronic structure, atomic size	Concentration, solubility, configurational entropy, hydration structure
Solution environment	Dielectric constant, polarity	Ionic species, ionic strength, pH, temperature

Theoretical studies on PEL-M^{x+} interaction by looking into the phenomena such as electrostatic interaction, complexation, or counterion condensation have been conducted for decades [132-134]. ‘Counterion condensation’ refers to a phenomenon involving binding of counterions which rapidly condense onto the PEL backbone of certain charge density. There are several fundamental models that describe the counterion condensation, including Oosawa-Manning model [135], two zone model [136], and ion binding/localization model [137]. Based on principle of free energy and chemical potential, these models can provide information on (i) the fraction and distribution of M^{x+} at the chain vicinity of PEL, and (ii) conditions for counterion condensation. These fundamental models can be effectively used as guidelines for PEL assisted synthesis of inorganic nano-materials, judging by the critical influence of the PEL-M^{x+} interaction towards morphology of synthesized products.

PEL chain conformation represents one critical parameter affecting the PEL-M^{x+} interaction. It is important to be able to predict and utilize PEL chain conformation under various physicochemical conditions, with or without the presence of M^{x+}. Theoretical studies of PEL chain conformation correlate many parameters, e.g., Bjerrum length, persistence length, and charge screening length [138]. The ‘necklace model’ is normally adopted to describe flexible PEL as connected electronic blobs; with properties defined by the number of monomer per blob, charge density, ionization fraction, and counterion valency [139, 140]. Note that in the literature, the ‘monomer’ usually used for such context refers to ‘repeating unit’; instead of the basic entities of inorganic crystals. A scaling approach can predict chain conformation within different regimes of concentration and charge fraction [141, 142]. PEL chain conformation manifests as measurable solution properties including viscosity, turbidity, osmotic pressure, pK_a-α (dissociation behavior), hydrodynamic radius, solution conductivity, thermodynamic enthalpy change, and so on [134, 138, 143, 144]. It is important to highlight here that these solution properties often involve inter-chain interaction; on top of phenomena contributed by only single PEL.

3.1.2 Interaction of poly(acrylic acid) (PAA) and Cu²⁺ counterions

PAA and Cu²⁺ has been widely studied as a model system of PEL-M^{x+} interaction [145-147]. Other M^{x+} of various valency and electronic nature (e.g., alkali species, alkali earth species, and transition metallic species) that were studied include Na⁺, Ba²⁺, Co²⁺, Ca²⁺, Mg²⁺, and Cd²⁺. The understanding on complexation of Cu²⁺ with PAA is still being built up and constantly updated; as newer and more accurate characterization methods are developed. ‘Complexation’ is a term usually used when there is certain degree of overlapping of electronic orbitals of two coordinating entities. PAA-Cu²⁺ interaction is reported to be distinctly different from interaction of PAA

with alkaline earth metal ions, e.g., Ca²⁺ [148]. PAA as an annealed PEL possesses different degree of deprotonation ($\alpha = \frac{[\text{COO}^-]}{[\text{COOH}]_0}$); under different physicochemical conditions. Depending on α , Cu²⁺ may bind in 1:1 (low α) or 1:2 (high α) ratio with COO⁻ [149]. Intra-chain or inter-chain bridging bidentate structure may form between COO⁻ and Cu²⁺ [150]. Deprotonation of the COOH stabilizes when the equilibrium ion exchange of H⁺, Cu²⁺ or other inert ionic species (e.g., Na⁺, K⁺) within COO⁻ vicinities is reached. Other important factors that influence the PAA-Cu²⁺ interaction and cannot be neglected include Cu²⁺ hydrolysis and variation of PEL chain conformation. More molecular-scale characterization results are needed to provide better insights on PAA-Cu²⁺ interaction; especially from the aspect of PAA chain conformation.

3.1.3 Scope and objectives

In the project of aqueous PAA templated synthesis of CuO_x nano-materials, the PAA-Cu²⁺ interaction mechanism was firstly studied. Secondly, the mechanism was correlated to the PEL chain conformation, which determined the morphology of CuO_x nano-materials obtained in synthesis experiments. This chapter (Chapter 3) focuses on discussing the interaction mechanism.

Different symbols have been used to represent Cu²⁺ concentration under different conditions. For concentration of titrated Cu²⁺, [Cu²⁺]_t is used. For concentration of measured Cu²⁺, [Cu²⁺]_m is used. As for [Cu²⁺], it refers to general meaning of Cu²⁺ concentration; for instance, a solution with [Cu²⁺]:[COOH]₀=0.5 is a solution prepared by simple mixing of two components (PAA and CuCl₂ solution), which does not involve any titration or [Cu²⁺] measurement.

Precise morphological control requires not only accurate quantification of both binding limit of PEL-metal ions (i.e., [Cu²⁺]_t: [COOH]₀ in this work) and pH variation,

but also the understanding of their effects towards PEL chain conformation. The windows of the pH or reagents concentration used in the interaction mechanism study corresponded to the synthesis parameters. A new characterization methodology, combining two complementary characterization techniques i.e., isothermal titration calorimetry (ITC) and potentiometric titration coupled with cupric ion-selective electrode, was employed. Besides that, absorption spectroscopy was also carried out.

3.2 Experimental

3.2.1 Materials and methodology

CuCl₂·2H₂O (Fisher Scientific) and poly(acrylic acid) (M_n= 124,500 g/mol, PDI= 1.25, Polymer Source) were purchased and used in experiments without further purification. Throughout the interaction mechanism study, concentration of carboxylic acid groups (i.e., [COOH]₀) was fixed at 1.25mM and ionic background of 0.01M NaNO₃ was used for all samples. As shown in Figure 3.1 is the graphical outline of the methodology used.

Figure 3.1. The methodology used for studying mechanism of PAA-Cu²⁺ interaction. (k: conductivity, ΔH: enthalpy change)

3.2.2 Titration experiments

Potentiometric titrations coupled with cupric ion-selective electrode (denoted as 'PT+Cu-ISE' in future appearances) were carried out using Metrohm Titrando 905 titration system connected with conductivity module 856. Cupric ion concentration (i.e., [Cu²⁺]) was measured using Orion 9629BNWP Cu-ISE. The Cu-ISE was calibrated using freshly prepared Cu²⁺ standards (of [Cu²⁺] = 0.001mM, 0.01mM, 0.1mM, and 1mM) before each set of measurement. All the titrations were done at 25 °C; temperature was regulated by linking jacketed vessel (containing titrand with initial volume of 60mL) to water circulator. Two sets of titration experiments were designed and carried out:

- Experiments A: Using PT+Cu-ISE to measure unbound (free) [Cu²⁺]_m to determine binding limit of Cu²⁺ onto PAA at different initial pH.
 - Titrating 20mM, pH 5 CuCl₂·2H₂O (titrant) into 1.25mM PAA of variable initial pH (titrand).
 - Conditions: pH 6.6, pH 6, pH 5.75, pH 5; only applied for PAA solution.
- Experiments B: Studying dissociation behaviour (pK_a versus α) via pH and conductivity measurements.
 - Titrating 50mM NaOH (titrant) into 1.25mM PAA with different [Cu²⁺]:[COOH]₀ ratio (titrand).
 - Conditions: [Cu²⁺]:[COOH]₀ ratios= 0, 0.05, 0.075, 0.125, 0.175, 0.25, 0.375; pH of titrand was adjusted to ~3.3 prior to the start of titration.

In titration experiments, 30μL titrant was titrated into 60mL titrand at 180 seconds interval.

3.2.3 Isothermal Titration Calorimetry (ITC)

ITC experiments were conducted using MicroCal VP-ITC. The pH of 8mM CuCl₂·2H₂O and 1.25mM PAA solutions were adjusted to same desired initial value prior to the start of ITC experiments. Four different initial pH values were used in ITC experiments: pH 5, pH 4.7, pH 4.4, and pH 3.6. pH 5 was selected as upper pH limit to avoid hydrolysis of 8mM Cu²⁺; which may cause formation of insoluble hydroxide species; while pH 3.6 was used as the lower limit as it is lower than intrinsic dissociation constant (pK₀) of PAA i.e., no deprotonation of COOH is expected at pH 3.6. The CuCl₂·2H₂O solution (titrant) was loaded into the injector; from where it was titrated/injected into the PAA solution (titrand) loaded inside the sample cell with volume of ~1.455mL; according to a series of designed titration steps of variable pre-set titrant volume with time spacing of 300 seconds between each injection. The injector also functioned as mechanical stirrer to effectively mix the titrant with titrand, and the enthalpy change (ΔH) at each injection was measured. The sequential titration steps are included in Table 3.2. Note that the increasing titrant volume in the process is necessary to reveal especially the rapid events taking place in the starting of PAA-Cu²⁺ interaction. The last 10-20 injections are to verify that no further interaction of thermodynamical significance took place.

Table 3.2. The programmed sequences used for ITC experiments.

Injection sequence	Injected titrant volume (μL)
1 to 20	1
21 to 40	2
31 to 60	5
61 to 70	10

3.2.4 UV-Vis absorption spectroscopy

UV-Vis absorption spectroscopy of mixture of CuCl₂·2H₂O and PAA was carried out using UV-Vis spectrophotometer (UV 2501PC, Shimadzu).

3.3 Results and Discussion

In aqueous system, deprotonation of COOH on PAA takes place and its degree of deprotonation (α) increases with increasing pH: $COOH \rightleftharpoons COO^-$. At high α (i.e., high pH), PAA chain conformation expands due to like-charge repulsion and the chain is of high stiffness. It is generally known that when Cu²⁺ is added inside the PAA solution, electrostatic attraction rapidly brings the Cu²⁺ to the vicinity of COO⁻. Further binding of Cu²⁺ with COO⁻ takes place via: $Cu^{2+} + 2COO^- \rightleftharpoons [Cu^{2+}(COO^-)_2]$. The [Cu²⁺]:[COO⁻] ratio need not be strictly 1:2 as multiple bridging is possible [151]; this is affected by parameters such as pH, ionic strength, and ionic species. The interaction between COO⁻ and Cu²⁺ (i) consists of coordination with characteristics between ionic and covalent; (ii) involves overlapping of d-orbital of Cu²⁺ with the electron configuration of COO⁻; and (iii) involves counterion condensations; on top of many other phenomena. The actual interaction however is sensitive to physicochemical conditions.

Another critical factor is hydration behaviour of Cu²⁺. Principal hydrolysis reaction of copper is [152]: $2Cu^{2+} + 2H_2O \rightleftharpoons Cu_2(OH)_2^{2+} + 2H^+$. At high pH, Cu²⁺ that are not bound to COO⁻ may be hydrolysed into insoluble Cu(OH)₂ based on: $Cu^{2+} + 2H_2O \rightleftharpoons Cu(OH)_2 \downarrow + 2H^+$. The reduction capability of electron rich PAA (due to COO⁻) reduces the bound Cu²⁺ into Cu through $Cu^{2+} \xrightarrow{+2e^-} Cu$.

UV-Vis absorption spectroscopy was used to investigate the complexation phenomenon at different [Cu²⁺]:[COOH]₀ [147, 153]; the absorbance spectra are shown inside Figure 3.2.

Figure 3.2. Absorbance spectra of PAA and CuCl₂.2H₂O mixture at different initial pH of PAA and [Cu²⁺]:[COOH]₀ ratio; the [COOH]₀ was fixed at 1.25mM. After mixing CuCl₂.2H₂O with PAA, absorbance peak of purely CuCl₂.2H₂O at around 810nm disappears and new absorbance peak at around 700nm emerges; indicating complexation of Cu²⁺ and COO⁻. This 700nm peak undergoes slight blue-shift with increased [Cu²⁺]; this was explained to be due to varied ratio of two types of PAA-Cu²⁺ complexes at different [Cu²⁺]: either mono-nuclear (1 Cu²⁺) or bi-nuclear (2 Cu²⁺) [147, 153].

The importance of understanding the influence of interaction mechanism towards the morphological control of synthesized nano-materials cannot be emphasized more. Also, the chain conformation and chain stiffness of PAA are directly affected by binding of Cu²⁺. To study this interaction mechanism, there are some considerations that have to be kept in mind. It is required that: (i) PAA has small molecular weight (MW) poly-dispersity and (ii) PAA concentration is dilute enough to minimize the inter-chain interaction. Hydrolysis of Cu²⁺ represents another important consideration, which is dependent on the pH and concentration of Cu²⁺ [154, 155]. To avoid hydrolysis phenomenon that produces insoluble Cu(OH)₂, a small window of pH (below 6.6) and [Cu²⁺] was used in all the experiments and analyses in this work.

Hydrolysis adds complication to the morphological uniformity of nano-particles, caused by divergence of PAA-Cu²⁺ interaction mechanism. Within the [Cu²⁺]_t range used in this study, Cu(OH)₂ is expected to only noticeably form at pH value above 7.

3.3.1 Quantification of binding limit of Cu²⁺ onto PAA at different initial pH

There are very few synthesis works reporting quantification of the actual binding limit of weak PELs; which is pH dependent and usually deviates considerably from the deduced binding limit (i.e., assuming 100% deprotonation). The binding ratio of PAA-metal ions is affected by inter-dependent factors including PEL charge fraction, metal species and its concentration, ionic background, and so on. Therefore, on one hand, often only low nano-particle concentrations were produced; indicating that the metal ion concentration were far below the binding limits [156, 157]. On the other hand, when metal ion concentration exceeded the binding limits very much, larger size crystals with poor size dispersity would be obtained [158, 159].

The synthesis strategy employed in this work involves employing PAA homopolymer for complexation with Cu²⁺ and templated formation of CuO_x nano-materials. The hypothesis stems from the notion that the state of metal counterions (Cu²⁺ in this case) in the PEL solution (PAA in this case) considerably affects the morphological uniformity of the nano-crystals. This means that preventing the co-existence of bound and unbound Cu²⁺ on PAA chains can ensure single formation mechanism, to prevent non-uniform nano-crystal morphology. The bound Cu²⁺ were non-detectable by Cu-ISE. When the [Cu²⁺]_t: [COOH]₀ binding limit is reached, further Cu²⁺ added became detectable by Cu-ISE; Figure 3.3(a) plots the [Cu²⁺]_m detected by the Cu-ISE versus [Cu²⁺]_t: [COOH]₀ ratio at different initial pH (titration experiment A). Table 3.3 further summarized the estimated binding limits in term of [Cu²⁺]_t: [COOH]₀ at different pH.

The binding limit increases with initial pH due to increasing α within the pH window that was investigated. The maximum $[\text{Cu}^{2+}]_t:[\text{COOH}]_0$ binding limit (at initial pH value of 6.6) is only 0.18, far below the theoretical limit of 0.50. This large shortfall is certainly due to combination of many factors, including α and PAA chain conformation.

Furthermore, based on the pK_a - α curves (to be discussed in next section), a 3D diagram of α , pH and $[\text{Cu}^{2+}]_t:[\text{COOH}]_0$ was constructed; as shown as the inset in Figure 3.3(a). The details of analysis method are included in Appendix A1. Based on this 3D diagram, numerical interpolation was used to re-define the binding limits by plotting measured $[\text{Cu}^{2+}]_m$ versus $[\text{Cu}^{2+}]_t:[\text{COO}^-]$ at different initial pH values; as shown in Figure 3.3(b). Bear in mind that the pH constantly varies during the titration of Cu^{2+} into PAA. For Figure 3.3(b), the seemingly faster increase of $[\text{Cu}^{2+}]_m$ at high pH is not reflecting a time-dependent trend; because at the same $[\text{Cu}^{2+}]_t:[\text{COO}^-]$, the data points are of different time, $[\text{Cu}^{2+}]_t$, and $[\text{COO}^-]$. Therefore, it cannot be correlated to the chain conformation. As for Figure 3.3(a), the slopes of increasing $[\text{Cu}^{2+}]_m$ of all samples are similar; because the x-axis possesses a linearly increasing time frame (titration is of constant-rate).

The $[\text{Cu}^{2+}]_t:[\text{COO}^-]$ values corresponding to the binding limits are also given in Table 3.3. Figure 3.3(b) clearly shows that the binding stoichiometry in terms of $[\text{Cu}^{2+}]_t:[\text{COO}^-]$ for PAA solutions at different initial pH values converged towards 0.50. This is an important indication showing, regardless of the α and its variation during Cu^{2+} titration, Cu^{2+} bind to COO^- following the stoichiometric ratio of ‘one Cu^{2+} to two COO^- ’. This suggests that under the experimental conditions in this work which are of relatively low pH values (when Cu^{2+} hydrolysis is unlikely), the

evolution of PEL chain conformation has negligible effect towards the accessibility of the COO⁻ for Cu²⁺.

Figure 3.3. (a) Concentration of unbound Cu²⁺ measured by Cu-ISE through titration of pH 5 CuCl₂·2H₂O (titrant) into 1.25mM PAA (titrand) of different initial pH (i.e., 5, 5.75, 6, 6.6). The inset at top-left corner is the 3D diagram showing the relationship among pH, α , and $[Cu^{2+}]_i:[COOH]_0$; plotted based on results of titration experiment B. (b) By using the interpolated α , the re-plotted curves of concentration of unbound Cu²⁺ (i.e. $[Cu^{2+}]_m$) versus $[Cu^{2+}]_i:[COO^-]$; showing that the binding limits converge at $[Cu^{2+}]_i:[COO^-] = 0.5$.

Table 3.3. The binding limit of Cu²⁺ onto PAA at different initial pH determined using Cu-ISE; represented by both [Cu²⁺]_t: [COOH]₀ and [Cu²⁺]_t: [COO⁻].

pH	[Cu ²⁺] _t : [COOH] ₀	[Cu ²⁺] _t : [COO ⁻]
5	0.044	0.41319
5.75	0.1	0.49174
6	0.132	0.48923
6.6	0.18	0.61560

It needs to be stressed again that the pH values discussed so far are the initial pH values of the PAA solutions prior to addition of Cu²⁺; and pH is expected to decrease upon titration of Cu²⁺ into PAA; this affects the α . α is a critical parameter in the PAA templated nano-materials synthesis because it is not only quantitatively linked to the bound M^{x+} concentration or the [M^{x+}]_t: [COOH]₀ binding limit, it also determines PAA chain conformation. For example, whether PAA chains adopt expanded (at higher pH) or compact (at lower pH) conformation affects the accessibility of (i) COOH for deprotonation, and (ii) COO⁻ for Cu²⁺ binding. Although these factors discussed above have significant effects on the morphology of the nano-materials prepared, so far, previous works on PEL assisted synthesis of metal oxide have largely overlooked this important aspect.

3.3.2 Effects of Cu²⁺ counterions towards deprotonation behaviour of PAA

As mentioned earlier, the binding limit issue was further approached by quantifying the relationship among α , pH and [Cu²⁺]_t: [COOH]₀ using pK_a- α curves. The curves can also provide important information about the deprotonation behaviour; and they are obtained by titrating NaOH into mixture of PAA with different fixed [Cu²⁺]_t: [COOH]₀

ratios (titration experiments B), pK_a - α curves as shown in Figure 3.4 were plotted based on the modified Henderson-Hasselbalch equation: $pK_a = pH + \log\left(\frac{1-\alpha}{\alpha}\right)$. The identification of boundaries at $\alpha=0$ and $\alpha=1$ was based on the standard methodology of looking at the slope change conductivity curves. No further discussion on this methodology will be done here.

Figure 3.4. pK_a - α relationship of mixture of 1.25mM PAA and $CuCl_2 \cdot 2H_2O$ with different $[Cu^{2+}]:[COOH]_0$ ratio. To facilitate curve reading, (i) arrows are drawn in the direction of increasing $[Cu^{2+}]:[COOH]_0$; (ii) a vertical line is plotted in the graph separating region with $\alpha < 0.5$ and $\alpha > 0.5$.

The pK_a - α curves can show the range of pK_a (or pH) that the PEL deprotonates. The interesting shape of the pK_a - α curves require analysis based on different regions of α and $[Cu^{2+}]$:

- a) *Low α ($< \sim 0.5$) & Small $[Cu^{2+}]$ ($[Cu^{2+}]:[COOH]_0 < \sim 0.5$):* Increase of $[Cu^{2+}]$ resulted in lower pK_a at same α . Cu^{2+} induced deprotonation of COOH (easier deprotonation); thus lowering the pK_a . The PAA adopted a slightly compact chain

conformation. This is indeed the regions of pH and [Cu²⁺] which are most relevant to the synthesis conditions used in this work.

- b) *Low α ($<\sim 0.5$) & High [Cu²⁺] ([Cu²⁺]:[COOH]₀ $<\sim 0.5$):* Increase of [Cu²⁺] resulted in higher pK_a at same α . COOH deprotonated easier with increased [Cu²⁺] (lower energy barrier) and COO⁻ complexed rapidly with Cu²⁺. PAA had compact chain conformation and large stiffness; causing low accessibility of neutralization sites to OH⁻ (hence higher pK_a).
- c) *High α ($>\sim 0.5$) & Small [Cu²⁺] ([Cu²⁺]:[COOH]₀ $>\sim 0.5$):* Increase of [Cu²⁺] resulted in higher pK_a at same α . The stiff PAA chain caused by high degree of complexation of COO⁻ and Cu²⁺ inhibited the neutralization. Hydration behaviour of Cu²⁺ at high pH is another critical factor toward the PAA-Cu²⁺ interaction [152]. At high pH, Cu²⁺ that are not bound to COO⁻ can be hydrolysed. Insoluble hydrolyzed Cu²⁺ species are wrapped by the PAA; this event further stiffened the PAA chain.
- d) *High α ($>\sim 0.5$) & High [Cu²⁺] ([Cu²⁺]:[COOH]₀ $>\sim 0.5$):* Almost constant slope of pK_a- α curves within intermediate α region followed by fast increase at higher α region; clearly indicating that an initial compact conformation inhibited the neutralization. Until higher enough α , the chain expanded and its COO⁻ were neutralized due to increased accessibility. It is important to highlight that this was not simply a well-recognized helix-coil transition [160]. Expansion of the PAA chain with increased α (followed by neutralization) competed with the collapse of the chain due to counterion condensation. At even high pH and higher [Cu²⁺]:[COO⁻] (e.g., ratio of 0.75 is larger than theoretical binding limit), stiffness of PAA chain further increased due to the wrapping of insoluble hydrolyzed Cu²⁺

species. The electrostatic effect leading to the chain expansion was likely to be counter-balanced by possible bridging of COOH [161].

The above discussions are summarized in Table 3.4 below, aided with illustration:

Table 3.4. The summary of analysis of potentiometric titration of PAA-Cu²⁺ system at different [Cu²⁺]:[COOH]₀ and pH. Notice that the estimated boundaries as $\alpha \sim 0.5$ was deduced from the pK_a- curve; which is not a strict value. As for the [Cu²⁺]:[COOH]₀ ~ 0.5 is based on theoretical full loading of Cu²⁺ onto 100% deprotonated PAA. The Cu²⁺ ions had been left out from the illustrations for clarity.

	$\alpha < \sim 0.5$	$\alpha > \sim 0.5$
[Cu ²⁺]: [COOH] ₀ <~0.5	<p>(a)</p> <ul style="list-style-type: none"> • slightly compact chain conformation • Cu²⁺ induce further deprotonation • SYNTHESIS CONDITION 	<p>(c)</p> <ul style="list-style-type: none"> • Deprotonation induced expansion counteract with Cu²⁺ induced collapse • Large stiffness • Unavoidable non-solubilized hydrolyzed species
[Cu ²⁺]: [COOH] ₀ >~0.5	<p>(b)</p> <ul style="list-style-type: none"> • compact chain conformation and large stiffness • low accessibility of COO⁻ 	<p>(d)</p> <ul style="list-style-type: none"> • Similar to condition 3, but more Cu²⁺ induced collapse • More non-solubilized hydrolyzed species

3.3.3 Thermodynamic aspects of PAA-Cu²⁺ interaction

Usual ITC done on biological molecules (e.g., proteins) is kept at constant pH and ionic strength; by using buffer solutions. However, ITC done on binding phenomenon of PAA-Cu²⁺ is dynamic, i.e., involved variation of pH and α ; therefore, the data could not be interpreted straight-forwardly. During consecutive injection of CuCl₂·2H₂O into PAA, pH and α changed due to: (i) concentration dependent hydration of Cu²⁺ and (ii) Cu²⁺ shifting equilibrium of deprotonation of COOH.

Figure 3.5. The enthalpy change (ΔH) measured by ITC of samples versus $[\text{Cu}^{2+}]_i:[\text{COOH}]_0$ at different initial pH.

The enthalpy change (ΔH) versus $[\text{Cu}^{2+}]_i:[\text{COOH}]_0$ is shown inside Figure 3.5; the values were obtained after subtracting signals from ‘blank runs’ (titrating CuCl₂·2H₂O into 0.01M NaNO₃ solution at corresponding initial pH). One transition of ΔH from definite value down to near zero denotes a binding phenomenon; with positive ΔH referring to endothermic reaction. The PAA-Cu²⁺ interaction is therefore entropically

driven. The COO⁻ (hydration) is more hydrophilic than COOH (hydrogen bonding); counterion condensation renders PAA more hydrophobic and reduces the solvation power of PAA-Cu²⁺ clusters. The ITC results obtained in this work are similar to what was obtained previously in PAA-Ca²⁺ system [162]; however, as mentioned previously, Cu²⁺ is expected to interact much differently with PAA as compared to that of alkali earth species. Three stages of PAA-Cu²⁺ interaction could be identified from ITC curves: (i) electrostatic interaction, (ii) complexation, and (iii) counterion condensation. Rapid electrostatic interaction brought the Cu²⁺ to the deprotonated PAA chain vicinity. The positive ΔH is due the disruption of hydration structure near the carboxylate groups; at the same [Cu²⁺]_t: [COO⁻], the larger ΔH at higher pH is due to the greater change of the entropy of water molecules. This is affected by different strengths of hydrogen bonding. Complexation of Cu²⁺ and COO⁻ followed and the ΔH diminished as the α of PAA decreased. The ΔH consisted of the interaction enthalpy from several interactions, including: (i) Cu²⁺ replaced H⁺ and induced deprotonation; (ii) Cu²⁺ complexed with COO⁻; (iii) Cu²⁺ lost configurational entropy; (iv) expulsion of ionic species (i.e., Na⁺) from chain vicinity; (v) two steps of complexation (i.e., one Cu²⁺ can bind to two COO⁻). Easier 2nd step complexation (i.e., $[Cu^{2+}(COO^{-})]^{+} + COO^{-} \rightleftharpoons [Cu^{2+}(COO^{-})_2]$) is possible for linear PAA [163]. Counterion condensation happened above certain [Cu²⁺]_t: [COOH]₀ ratio. Eventually, the interaction enthalpy is zero as the PAA-Cu²⁺ complexes fully collapsed (L-type precipitation [164]) and no more binding occurred. The ITC data could be further fitted to standard model (assuming single binding mechanism), which gives important thermodynamic parameters to the binding phenomenon; the data are summarized in Table 3.5.

Table 3.5. Thermodynamic parameters including N (binding ratio), k (binding constant), ΔH (enthalpy change, in cal/mol) and ΔS (entropy change, in cal/mol/°) obtained through fitting of ITC data.

pH	N (+/-)		k (M ⁻¹) (+/-)		ΔH (cal/mol) (+/-)		ΔS (cal/mol/°)
5	8.92E-2	9.06E-4	1.17E+5	7.54E+3	4.15E+3	7.23E+1	37.1
4.7	8.35E-2	8.56E-4	2.17E+5	1.68E+4	3.38E+3	7.46E+1	35.7
4.4	6.23E-2	6.76E-3	1.91E+4	3.31E+3	2.03E+3	2.78E+1	26.4
3.6	*_	-	-	-	-	-	-

. * Data fitting cannot be done due to negligible binding trend.

The binding constant $k = \Theta / \{(1 - \Theta) \cdot [X]\}$; in which Θ is the fraction of COOH occupied by Cu²⁺ and [X] is the free [Cu²⁺]. Note that the different of N and Θ is their intrinsic meaning; N is the total number of sites (not necessarily occupied). And relationship of X_t (bulk [Cu²⁺]) and M_t (bulk [COOH]₀) is: $X_t = [X] + n\Theta M_t$

Note that the data fitting assumes a single binding mechanism; which is unable to fully account for the complexity of PAA-Cu²⁺ which could involve two (or even more) stages of complexation. In fact, the 2nd binding is usually of much higher reaction constant. Indeed, further investigation need to consider such complicated multiple-stage complexation. Nevertheless, the fitting data can give an overall binding ratio (N) and binding constant (k). The values as given in Table 3.5 quantitatively highlighted the critical role of chain conformation and pH (i.e., α). With decreased pH, the decrease of N, ΔH , and ΔS are directly due to lower α ; i.e., less COO⁻. The interesting observation is the increased k from pH=5 to pH=4.7, which is followed by decreased k from pH=4.7 to pH=4.4. Especially from pH=4.7 to pH=4.4; a 10 times decrease in k is not able to be attributable to experimental error; hence must possess certain meaning. The larger the k value, the more favorable the complexation (as a forward reaction) is. When pH is lowest (pH=4.4), the lowest k value is attributable due to compact chain conformation at such pH, limiting the accessibility of the COO⁻ (adding to the effect of

low [COO⁻]). Comparing the lower k value at pH=5 with that of pH=4.7, chain rigidity is playing a main role. This result explicitly suggests the importance of chain rigidity (conformation).

Details of further analysis of ITC that considers the pH variation adjustment had been included inside Appendix A2. With the help of estimated pH (see Figure A2.1) and 3D diagram (of α , pH, and [Cu²⁺]:[COOH]₀) (Figure A1.2), the α could be obtained. The measured ΔH versus [Cu²⁺]_t: [COO⁻] (Figure A2.3(b)) can provide information relating to the structural evolution of PAA-Cu²⁺ complexes.

3.4 Conclusion

To study PAA-Cu²⁺ interaction mechanism which involves complexation phenomenon, it is important to choose suitable parameter window to avoid multiple interaction mechanism. The windows correspond to conditions to be used for PAA templated CuO_x synthesis. The [Cu²⁺]_t: [COOH]₀ limits at different initial pH values were determined by ISE; the synthesis should take place under the condition when all the Cu²⁺ counterions are effectively bound to the PAA backbones. Multiple interaction mechanism will cause non-uniform nano-materials morphologies as the crystals may form through different manners. Furthermore, the PAA with larger MW and higher pH was chosen to ensure high enough spatial Cu²⁺ atoms for crystallization.

In this work, study on the dissociation behavior gives insights on the chain conformation, chain stiffness, and accessibility of the deprotonated sites. ITC on PAA-Cu²⁺ is carried out for the first time; probably because the complexation phenomenon involves pH variation thus requiring a non-standard data interpretation. Besides this, the change of hydration structure during binding could be very clearly deduced from ITC results. This also shows that the PEL backbones become more hydrophobic when

Cu²⁺ is bound; this event gives significant impact when the PAA templated synthesis is concerned. These understandings are essential to elucidate the morphology of synthesized Cu-based nano-materials obtained (to be discussed in next chapter).

Chapter 4

Aqueous Poly(acrylic acid)

Templated Synthesis of

CuO_x Nano-materials

4.1 Introduction

4.1.1 Aqueous synthesis of copper based nano-materials

Nano-sized metallic copper and its oxides (denoted as CuO_x in future appearances) possess good potential for catalytic [165], photo-catalytic [166], photovoltaic [167], and sensing [168] applications. Their potential bio-related usages including fouling control and nano-toxicology is also of great interest [169, 170]. Wet-chemical hydrolysis and reduction is the most commonly reported synthesis method of CuO_x micro- and nano-crystals [171, 172]. Other solution-based techniques include double-jet precipitation [173], hydrothermal [166], micro-emulsion [174], and solvothermal [175] methods. The synthesis often employs organic ligands or surfactants to render the desired particle morphology and dispersion. Although well-defined CuO_x crystallites with size of several nanometers can be readily prepared in organic solvent

media, aqueous medium synthesis is a more desirable and attractive option due to its biocompatibility and eco-friendliness. Synthesis of wide range of CuO_x nanostructures (e.g., hollow sphere, cube, porous whisker etc.) and their assemblies in aqueous medium had been attempted [176]. Compared to high temperature thermolysis, mild reaction conditions inside aqueous media could be critical in the formation of nano-crystal with thermodynamically stable novel hierarchical morphologies.

4.1.2 Polyelectrolyte assisted synthesis of inorganic nano-materials

Hydrophilic polymers, especially polyelectrolytes (PELs), can be employed as versatile mediating or structural directing agents in the aqueous synthesis of inorganic nano-crystals by utilizing the interactions between polymer chains and metal counterions. Some examples of block-PEL and homo-PEL include: poly(methyl methacrylate)-b-poly(methacrylic acid) (PMMA-b-PMAA), poly(styrene)-b-poly(acrylic acid) (PS-b-PAA), PS-b-poly(4-vinylpyridine) (PS-b-P4VP), PAA-b-P4VP, poly(ethylene oxide)-b-PAA (PEO-b-PAA), PAA, poly(ethyleneimine) (PEI), poly(diallyl dimethylammonium chloride)(PDADMAC) etc. Some of them were reported to exhibit self-assembly properties inside solution (especially block copolymer); however, in the specific works, they were not employed further for directing inorganic nano-materials growth [177, 178].

The functions of hydrophilic polymers during synthesis are multifold, e.g., (i) as self-assembled nano-reactors [77, 179]; (ii) facilitating anisotropic crystal growth via selective adsorption of polymer chains on crystal facets [78]; and (iii) simply providing random confinement for the bio-mimetic growth of nano- or meso-crystals in a concentrated polymer solution or hydrogel [156]. Substrate-based PEL multi-layer

can be employed for layer-by-layer templated formation of inorganic nano-materials [180, 181].

Chain conformation which is dependent on physicochemical conditions, as a unique characteristic of PEL, influences the complexation phenomenon in terms of accessibility of binding sites, diffusion mobility of metal ions, charge correlated chain expansion, and so on. Consequently, PEL chain conformation impacts greatly the formation mechanism, morphology, and solubility/dispersity of the nano-materials. The potential of manipulating the chain conformation provides opportunities to synthesize nano-materials with novel morphological and functional properties.

Poly(acrylic acid) (PAA) (as block copolymer segment or homopolymer), due to its structural simplicity, biocompatibility, and availability in different molecular weights, represents one of the most widely employed PELs in inorganic nano-materials synthesis. It can be considered as one type of functional polymer since its variable charge density can give rise to many interesting phenomenon. PAA hydrogel has been used as medium for sol-gel synthesis of nano-particles (PAA in dispersed state) [182] or bio-mineralization of meso-crystals (PAA in semi-solid state) [183]. PAA has also been employed for random capping and confinement of synthesized nano-particles [156, 157]. In block copolymer, PAA often acts as the hydrophilic segments that absorb and concentrate metallic counterions [184]; at the same time providing good aqueous solubility. As shown in Figure 4.1 are some representative examples of PAA (as block copolymer segment or homopolymer) assisted synthesis.

Figure 4.1. Representative examples of PAA (as block copolymer segment or homopolymer) assisted synthesis of inorganic nano-materials: (a) PAA as microgel, producing teardrop-shaped or hollow spherical SiO₂ meso-particles [185]; (b) PAA as gel-like substrate for surface absorption of reactants, producing hollow spherical SiO₂ meso-particles [182]; (c) PAA-b-PS for reverse micelle synthesis of CdS, producing spherical assembly of CdS nano-crystals [159]; (d) PAA as gel, producing periodic laminated structures of hydroxyapatite [186]; (e) PAA as anionic PEL in LbL multi-layer, producing spherical gold nano-particles [187].

Most reports on PEL assisted synthesis adopted phenomenological approaches and focused on correlating the resultant crystallite morphology with synthesis parameters. Furthermore, the reported nano-materials syntheses typically used PELs within relatively concentrated regime, which is one of the conditions when the theoretical counterion binding models deviate [156, 188]. Many reports also did not pay attention

to the actual binding limits of Cu²⁺ onto available COO⁻ on a charged PAA chain and the variation of pH [87, 158]; which could complicate the formation mechanism.

4.1.3 Scope and objectives

In the templated synthesis (2nd part of PAA-Cu²⁺ project), the coordination of PELs onto already formed crystallites are not the main topic of discussion. The focus is instead placed on the influence of the PEL towards the nucleation and growth of the inorganic nano-materials. A better bridging of the fundamental understanding on PEL-M^{x+} interaction and nano-material formation mechanism can lead to more intelligent synthesis designs. The concentration of PAA within slight semi-dilute regime employed in this work was critical in minimizing inter-chain interaction but still providing reasonable product yield. Herein a new phenomenon is reported, under a carefully controlled condition, the nano-crystals formed by PAA-Cu²⁺ complex bear striking resemblance to those formed via the self-assembly of an amphiphilic rod-coil-rod triblock copolymer.

4.2 Experimental

4.2.1 Materials and methodology

Same chemicals as what were used in interaction mechanism study (Chapter 3) were used for templated synthesis experiments. As shown in Figure 4.2 is the methodology employed for aqueous PAA templated synthesis of CuO_x nano-materials.

Figure 4.2. Methodology employed for aqueous PAA templated synthesis of CuO_x nano-materials; including both the synthesis steps and characterizations.

4.2.2 Templated synthesis

Desired amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (initial $\text{pH}=5$), based on beforehand measured $[\text{Cu}^{2+}]_i : [\text{COOH}]_0$ binding limit (i.e., 0.175), was mixed with PAA solution (initial $\text{pH}=6.6$); the mixture was stirred at room temperature for 14 hours. After that, excess amount of 1M NaOH (32 times in molar number than $[\text{COOH}]_0$) was added into the solution to induce hydrolysis; and further stirring was done at room temperature for 5 hours. The samples were heated subsequently at 55°C for 3 hours; under stirring. After the heating step, the products were washed with DI water through sonication; followed by centrifugation to precipitate the solid content. The supernatant portion was discarded and the solid content was re-dispersed in DI water aided by sonication. This washing step was repeated 3 times.

4.2.3 Characterizations

Transmission electron microscopy (TEM) and selective area electron diffraction (SAED) are the main characterizations and were carried out using JEOL 2010 TEM (accelerating voltage= 200kV). TEM sample was prepared by drop-casting aqueous product onto copper grid and excess liquid was wicked away using filter paper. UV-Vis absorbance spectra were measured using UV-Vis spectrophotometer (UV 2501PC, Shimadzu).

4.3 Results and Discussion

In the 2nd part of the PAA-Cu²⁺ work, aqueous based PAA templated synthesis of nano-structured CuO_x was carried out. In the first step of the synthesis, complexation of the PAA with Cu²⁺ at room temperature was done based on the experimentally determined binding limit [Cu²⁺]_t: [COOH]₀. No free/un-bound Cu²⁺ should exist inside the solution; as all Cu²⁺ were condensed strongly onto the deprotonated PAA chains. Secondly, hydrolysis by raising the pH rendered all the non-deprotonated COOH to deprotonate. This step stiffened and ‘froze’ the structure of the PAA-Cu²⁺ complexes. Lastly, solution heating provided energy for the reduction of Cu²⁺ (aided by electron-rich PAA) and crystallization of the CuO_x nano-materials.

For the characterizations of synthesized products, UV-Vis absorption spectroscopy was firstly employed to study the absorbance of the reaction solutions at different stages of the synthesis; the results are as shown inside Figure 4.3.

Figure 4.3. Absorbance spectra of solutions containing 1.25mM PAA and CuCl₂.2H₂O with [Cu²⁺]:[COOH]₀= 0.175 at different stages of the synthesis. Notice that heating longer than duration or at higher temperature than what were mentioned in experimental section was done to check the effect of oxidation.

As observed from Figure 4.3, there was no characteristic absorbance peak of usual Cu nano-crystals (usually at ~580nm) and this was attributed to its low concentration. Oxidation of the Cu with prolonged heating could be observed from small absorbance peak at ~360nm and increased overall absorbance across the entire measured wavelength range. Interestingly, clear appearance of NO₃³⁻ absorption peak ($n \rightarrow \pi^*$ transition) at ~300nm after the hydrolysis step was observed. This peak was not observed inside (i) PAA solution with NaNO₃ or (ii) mixture of all three components (PAA, CuCl₂ and NaNO₃) (results not shown). This directly evidenced that the chemical species at vicinity of COO⁻ (i.e., the PAA chain) undergoes changes, as repulsion of NO₃³⁻ from COO⁻ sites happened during hydrolysis. This result also suggests, after the hydrolysis step, the structure of PAA-Cu²⁺ complexes is highly

condensed and the Cu²⁺ are strongly bound to the backbone (repelling the inert salt species).

Preliminary light scattering (LS) studies were also carried out on samples with other pH and [Cu²⁺]:[COOH]₀. Although the conditions used were dissimilar from what were used in the successful preparation of the CuO_x nano-materials (to be discussed in subsequent section), the LS results provided valuable information on the evolution of structural conformation of PAA-Cu²⁺ complexes. The results are included and discussed in Appendix A3, Figure A3.1.

4.3.1 Morphology of synthesized CuO_x nano-materials

Note that the synthesized product used for TEM observation was obtained after 3 hours of heating (at 55 °C). Figure 4.4(a) is the TEM images showing the morphology of CuO_x nano-materials obtained via our aqueous PAA templated synthesis; in which the [Cu²⁺]:[COOH]₀ (i.e., 0.175) was fixed at just below the binding limit. As mentioned in Chapter 3, the binding limit [Cu²⁺]_t: [COOH]₀ is ~0.18 when initial PAA pH=6.6. At first glance, it seemed that nanorod-like structures were obtained. However, closer examination revealed that they were in-fact well-crystallized hollow tubular nanostructures with diameter of 40-60 nm and length of 30-40 nm; having typical wall thickness of ~10 nm. As shown as the top-right inset, SAED pattern proved that the nano-tubes consists of both Cu and Cu₂O crystal phases, and this fact is further supported by lattice spacings measured from high resolution TEM images. It is not unusual that both Cu and CuO_x coexist as products in previously reported synthesis [189]. Pure Cu nanotubes are believed to form first and they were slowly oxidized into Cu₂O. TEM observation on stained assembled structure was done by

using phosphotungstic acid and it was evident that PAA phase existed in overall tubular Cu nano-structure (see Appendix A4, Figure A4.1(a)).

Figure 4.4. (a) TEM images of obtained hollow nano-tubular structures. It is proved by SAED (inset) that the product is a mixture of Cu and Cu_2O phase. (b) High resolution TEM images showing that lattice fringes at the nano-tube edge (side view) have d-spacing $\sim 0.34\text{nm}$, corresponding to Cu_2O (211); while those at the central portion of the nano-tubes has d-spacing $\sim 3.6\text{ nm}$, corresponding to Cu (200) plane (top view).

4.3.2 Proposed formation mechanism of nano-tubular CuO_x

More intriguing finding is that such nano-sized tubular structure was not observed in usual homopolymer assisted synthesis and cannot be simply explained by known mechanisms in terms of selective polymer capping or confinement of crystal growth. In fact, the nano-structure as observed in Figure 4.4 resembles those obtained from certain self-assembled block copolymers [190]. Despite imperfect size-dispersity, there is no doubt that copolymer-like assembly is the most plausible explanation.

This finding prompted us to hypothesize that a unique interaction between Cu²⁺ and PAA is responsible for such regular self-assembled nano-structure. Searching of literatures revealed that there are detailed theoretical studies on charge distribution in PELs based on single chain using density functional theory (DFT) and Monte Carlo simulations [191, 192]. As shown in Figure 4.5 are the schematics of the charge distribution along the chains; extracted from literatures [191, 192]. The essence of these works is that the charge distribution is non-uniform along a PEL chain in solution; where charges (COO⁻ in our case) are concentrated at end segments of the chain due to charge repulsion along the backbone and favourable energy minimization. This charge distribution was reported to be affected by a range of factors including temperature, solvent condition, charge density, Debye length and chain flexibility. In our study, as all these conditions are fixed, therefore, the addition of Cu²⁺ is believed to be the only reason for the change of PAA chain structure. As illustrated in Figure 4.6 are the proposed mechanism of how Cu²⁺ affects the PAA chain structure; together with the self-assembly of the PAA-Cu²⁺ complexes into nano-tubular structure.

Figure 4.5. The simulated charged distribution under different scenarios: (a) Debye length (ρ : charge density, $\langle\rho\rangle$: mean charge density, λ_D : Debye length, a : distance between ionizable groups) (solid, dashed and dot-dashed lines correspond to theoretical results of $\lambda_D=1.8a$, $5.8a$, and $12.9a$ respectively) with different chain rigidity [191]; (b) fraction of charge (f : charge fraction, $\langle f\rangle$: average charge fraction). See references for simulation details [192].

Figure 4.6. Schematic illustrations of (a) non-uniform charge distribution on PAA chain; (b) preferential binding of Cu^{2+} onto more deprotonated PAA chain ends via electrostatic attraction; (c) formation of triblock copolymer-like PAA-Cu^{2+} complex due to change in chain stiffness and hydrophilicity (top right insets show the PAA-Cu^{2+} complex formed by complexation of one Cu^{2+} with two COO^- , restricting the structural rotation); and (d) self-assembly of PAA-Cu^{2+} into nano-tubular structure. Note that in (b), the chain center would still have negligible bound Cu^{2+} ; the illustration here is the ideal scenario.

Figure 4.6(a) illustrates a possible charged structure of a PAA chain in solution at certain pH. According to earlier theoretical studies, the equilibrium charge distribution is inhomogeneous and the charge density is higher near the chain ends than that in the central segment of a PAA chain. This illustration is of an ideal situation as the central segment is not completely un-charged; this is to highlight that the PAA chain ends are more deprotonated. This inhomogeneous charge distribution and change of PAA chain conformation during addition of Cu²⁺ are believed to be ultimately responsible for the nano-tubular structure as observed in Figure 4.6. It can be reasonably deduced that, when CuCl₂ is added into the PAA solution, preferential Cu²⁺ binding to PAA chain ends occurs rapidly via electrostatic attraction (Figure 4.6(b)). The Cu²⁺ are concentrated near the chain ends, while the central segments of the chains would be comparatively Cu²⁺ free. This preferential Cu²⁺ complexation not only gives rise to a unique structural inhomogeneity of the PAA-Cu²⁺ complex, it also leads to (i) chain stiffening due to steric hindrance of rotation (i.e., note that PEL stiffening effect (in term of persistence length) due to metal ions was discussed in theoretical and experimental studies [193]) and (ii) change in hydrophilicity (note the order of hydrophilicity: COO⁻ > COOH > COO₂Cu). Therefore, such unique interactions between Cu²⁺ and PAA have effectively rendered the homo-PAA chain the characteristics of an amphiphilic rod-coil-rod triblock copolymer; as depicted in Figure 4.6(c). As a result of the relatively rigid and more hydrophobic nature of PAA-Cu²⁺ complex at chain end segments, and based on the knowledge of block copolymer self-assembly, it is logical that such tri-block copolymer-like PAA-Cu²⁺ complex could self-assemble into the nano-tubular structure as depicted in Figure 4.6(d); in which the central segments folded and the Cu²⁺ was ‘locked-in’ as a bi-layered uni-lamellar hollow tubular assembly [194]. At higher concentration regime, self-assembly

behaviour of rigid rod-like homo-PEL is possible [177]; but such behavior was not reported on flexible homo-PEL. During the heating steps, the nano-tubular crystallites formed via a non-classical crystallization route (similar to biomimetic crystallization) since diffusion of Cu²⁺ ions is inhibited due to their strong complexation with COO⁻ inside the assembled structure.

4.3.3 Further discussion on the parameter windows used for templated synthesis

The templated synthesis leading to self-assembly is a phenomenon very sensitive to physicochemical parameters. Figure 4.7 shows the boundaries of three essential parameters: pH, [Cu²⁺], and [Cu²⁺]:[COOH]₀ which are carefully determined or selected in this work. They are discussed in details in subsequent paragraphs by relating to the self-assembly phenomenon; although briefly mentioned previously.

Figure 4.7. The parameter window identified for studying PAA templated CuO_x synthesis.

- pH:** The boundaries of pH is decided by intended degree of deprotonation of PAA as well as the Cu²⁺ hydrolysis limits. High pH is required to deprotonate the PAA, but the pH cannot be too high which may induce hydrolysis of Cu²⁺ (giving insoluble Cu(OH)₂ species). The upper limit i.e., pH=6.6 was chosen as it is near the Cu²⁺ hydrolysis pH (note: the limit is dependent also on the [Cu²⁺]). The lower limit i.e., pH=5 could provide certain extent of deprotonation, but was in fact not much higher than pK₀. The triblock copolymer-like structures relies on a high enough α to manifest the amphiphilic contrast. Such conditions have to be carefully tuned in the first step of synthesis.
- [Cu²⁺]:[COOH]₀:** The upper limit, i.e., ~0.18 at initial pH=6.6, was determined through PT+Cu-ISE experiment (titration experiment A, see Chapter 3). The Cu²⁺ loading close to the upper binding limit as it is important to induce such triblock copolymer-like self assembly. Furthermore, low [Cu²⁺]:[COOH]₀ cannot provide enough spatial Cu²⁺ atoms for nucleation of stable embryonic nucleus. If the [Cu²⁺]:[COOH]₀ exceed the binding limit, multiple interaction mechanisms will take place, which could also cause the formation of large crystallites (to be discussed later).
- [COOH]₀:** This refers to the PAA concentration. Within the range of MW that was used, such triblock copolymer-like self-assembly is not possible in dilute regime. This can be understood with a concept similar to that of a critical micelle concentration: certain concentration is required for correlated interaction for the self-assembly to take place. However, PAA within concentrated region cause the crystal formation to take place in hydrogel or gel-like matrix; which is distinctly different from the scope of this work. Non-

desirable inter-chain metal ion bridging may take place when the [COOH]₀ is too high.

Other considerations, extended beyond this study, are discussed here. Firstly, the molecular weight distribution of the PAA should be sufficiently narrow for the self-assembly of the pseudo block copolymer to occur (PDI of the PAA used in this study is 1.25). Interestingly, the obtained results showed that pH is the principle reason affecting the binding limit, instead of the MW (results not shown). Also a suitable PEL concentration needs to be used. Bear in mind that copolymer self-assembly is itself highly sensitive to many intrinsic and extrinsic factors. For example, it is not uncommon that products with multiple morphologies are observed in copolymer self-assembly, e.g., rod-like with spherical micelles [195]. In fact, even in this work, a small amount of spherical Cu nanoparticles is observed to coexist with the nanotubes (see Appendix A5, Figure A5.1).

To further highlight the importance of selection of suitable parameters towards morphological control, supplementary syntheses were also carried out using parameters deviated from the specific parameter window mentioned. The morphological results are shown in Figure 4.8.

Figure 4.8. The morphologies of nano-crystallites that formed at different synthesis conditions; unless specified, other parameters are same as what are included in experimental section. (a) PAA with MW of 10k was used. Spindle-like crystallites oriented aggregates formed and the morphology had been described by a model included in the top right inset (abstracted from [196]). (b) $[\text{Cu}^{2+}] = 6\text{mM}$ and $\text{pH} = 6$. Needle like structures formed. (c) $[\text{COOH}]_0 = 0.15625\text{mM}$, $[\text{Cu}^{2+}] = 6\text{mM}$, and $\text{pH} = 6$. Large rectangular block-like crystallites formed.

As shown in Figure 4.8(a), spindle-like crystallites formed, consistent with the previously reported oriented aggregation of nano-crystals. Several points are to be added here. The morphology is a result of the fact that at low MW, (i) the steric effect of the polymeric chains is low, leading to not only high mobility of the PAA-Cu^{2+} complex, (ii) the charge non-uniformity is of lesser extent, and (iii) thermodynamic penalty of chain bending is higher. At low bound $[\text{Cu}^{2+}]$, whether due to low pH or low $[\text{Cu}^{2+}]:[\text{COOH}]_0$, a gel-like complex without nano-particles would be obtained (results not shown). If the $[\text{Cu}^{2+}]$ is higher than the binding limits, the interaction and crystal formation mechanisms are of multiple nature, resulting in agglomeration of clusters that give rod-like crystallites as shown in Figure 4.8(b). In the growth stage, the attachment of diffusing unbound Cu^{2+} sustains the growth. Further reduction of the $[\text{COOH}]_0$ (i.e., exceeding the binding limit even more) gave strikingly uniform

rectangular block-like crystallites (see Figure 4.8(c)). The templating function of the PAA is lost, instead, only the coordination function of the PAA towards the outer surface of the crystallites is taking effect. Indeed, the diffusion mobility of Cu²⁺ would be much higher also (compared to that shown in Figure 4.8(b)). Lastly, synthesis without adding in PAA had also been carried out and it produced Cu₂O nano-whiskers (see Appendix A4, Figure A4.1(b)). This outcome again clearly showed the critical role played by PAA in templating the morphologies of nano-tubular CuO_x.

4.3.4 PAA-templated Fe₂O₃ nano-particle synthesis

In fact, the mechanism and concept discussed above should be of certain universal nature in terms of types of PELs, metal ions, and complexed assemblies, in other words, they are not restricted to PAA-Cu²⁺ system only. However, in order to apply this new mechanism of metal ion binding induced self-assembly, the prerequisites and conditions discussed above need to be re-established. While the concept is extended to other transition metals, each metal ion has its unique characteristics and interaction behaviour with the PEL. Therefore, a detailed systematic study is required each time for a different set of metal ions or PELs.

To illustrate this point, additional experiments utilizing the same templating principle were carried out on Fe based nano-materials. The experiments and results will be briefly discussed in this section. This prepared PAA-wrapped Fe based material provides good potential for applications that utilize magnetic nano-particles in aqueous environment. The synthesis was done using the same process as what was used for CuO_x, except that FeCl₃.6H₂O was employed instead of CuCl₂.2H₂O. The binding limit of Fe³⁺ towards PAA could not be straight-forwardly determined by ISE due to availability of electrode. Therefore, conductivity measurement was done instead, and the binding limit of Fe³⁺ was found to be ~0.128 at pH 6 (result not shown). This is

based on the fact that a different slope in the conductivity curve would be observed when the binding ended. During the synthesis, 80% loading was done, i.e., $[\text{Fe}^{3+}]:[\text{COOH}] = 0.1024$. As shown in Figure 4.9 are the morphology of the Fe_2O_3 nano-particles prepared. A lower pH ($\text{pH}=5$) and lower loading did not give any nano-particles in the experiments (results not shown). In this case, no nano-tubes could be observed; therefore, Cu^{2+} with certain electron configuration that results in orbital overlapping with COO^- is believed to be responsible for the novel nano-tubular morphology observed. Despite the initial nonequilibrium charge distribution, the weaker binding of Fe^{3+} could not render strong enough amphiphilic contrast, and there will be a rapid charge re-distribution on PAA backbone. The results obtained in this Fe-based system are considered preliminary and more study is required.

Figure 4.9. The TEM images of synthesized Fe_2O_3 nano-particles templated by PAA. (a) The overview showing good size uniformity, and (b) HRTEM showing d-spacings of $\sim 0.27\text{nm}$ and $\sim 0.33\text{nm}$, corresponding to Fe_2O_3 (104) and (211) planes (JCPDS# 330664).

4.4 Conclusion

In this work, unique nano-tubular CuO_x nano-materials were synthesized by the PAA homopolymer assisted synthesis inside aqueous medium. The formation of such

unique morphology is proposed to be due to a counterion induced triblock copolymer-like self-assembly of the PAA-Cu²⁺ complexes. This self-assembly behaviour arises from the combination of the following sequential phenomena: (i) non-uniform charge distribution along the PAA chains, (ii) preferential Cu²⁺ binding on deprotonated carboxylic groups which concentrate at the chain ends, and (iii) Cu²⁺ complexation induced changes in chain conformation (via chain-stiffening) and hydrophilicity at the chain ends. The initially flexible coil-like PAA chain essentially became a pseudo rod-coil-rod triblock copolymer with rigid rod-like chain end segments; while the central segments remained flexible. This was found to be affected by several factors such as pH and PAA concentration, but critically relied on a strict quantitative control of [Cu²⁺] in the PAA solution in relation to the [Cu²⁺]:[COOH]₀ binding limit. This work has revealed one new dimension of nano-material synthesis by employing homo-PEL as the morphology-directing templates. With caution, the application of this proposed new concept of metal ion induced copolymer-like PEL assembly can be extended to other PELs and transition metal ions.

Chapter 5

Hot-injection Synthesis of CuInSe₂ Nano-particles

5.1 Introduction

5.1.1 Copper indium selenide: material properties and applications

Copper indium selenide (CuInSe₂, CISE) is a ternary chalcogenide material with high potential for photovoltaic applications due to its favourable bandgap (1.04eV), high absorption coefficient ($\sim 10^4$ - 10^5 cm⁻¹), tunable n- (indium rich, donor) or p- (copper rich, acceptor) type semiconducting properties, and processing stability [197, 198]. Although both 'CIS' and 'CISE' are used to represent copper indium selenide, 'CISE' is chosen for this thesis; as sometimes researchers also use CIS for CuInS₂. The stoichiometry of CuInSe₂ can deviate from ideal molar ratio Cu:In:Se=1:1:2 as defects (e.g. vacancies) and off-stoichiometric compounds may form; this is heavily dependent on fabrication parameters and initial precursor composition (see phase diagram of CuInSe₂ in Appendix B1, Figure B1.1). Besides CISE, many other types of

chalcogenides, e.g., CuInS₂, CuInGaSe (CIGSe), and CuZnTeSe (CZTSe), constitute one widely researched material category. One attractive opportunity is that controlling/tailoring elemental compositions and stoichiometry can significantly modify the material properties to suit different application. Furthermore, the chalcogenide materials are not as toxic as other functional or fluorescent nano-crystals containing cadmium. Other than being employed for photovoltaics (fully inorganic [199, 200] or hybrid [201]), CISE nano-particles can also be utilized for photo-conductors [202, 203].

5.1.2 Solution synthesis methods for copper indium selenide

Different fabrication techniques can be employed to prepare CISE in the forms of thin film, micro-/nano- crystals, or quantum dots. The most established preparation method for high performance CISE thin film solar cell is still vacuum-based method i.e., co-evaporation [204, 205]. Other methods include stacked-layer selenization [206, 207], magnetron reactive sputtering [208], pyrolysis of single molecular precursor [209], solvothermal method [210], and so on. Among them, solution-based techniques, adopted from nano-materials synthesis until patterning for device fabrication, offer advantages including low cost, low energy consumption, and good processability. These attributes are important for printed electronics industry. Subsequent introduction will focus on the solution synthesis techniques of CISE nano-particles.

Solution synthesis techniques of CISE nano-particles are widely studied and can be broadly categorized into: (i) heating-up method [211], (ii) autoclave solvothermal method [210, 212], and (iii) hot-injection method [213]. Besides them, other reported solution synthesis techniques include hydrothermal method [214], bubbling method [215], and polyol method [216]. Among them, hot-injection method is attractive due to

its (i) potential to separate nucleation and growth phases, and (ii) ability to produce highly mono-dispersed nano-crystals with good electronic and optical properties. Hot-injection synthesis of cadmium chalcogenide materials using organo-metallic precursors was firstly reported by Murray et al. [217] While Malik et al. firstly applied this method for synthesis of ternary CISE nano-particles [213]. Using hot-injection synthesis method, reaction starts from burst nucleation due to supersaturation of monomers (after pyrolysis of organo-metallic precursors) upon high temperature injection; followed by crystal growth at lower temperature. Note that the definition of ‘monomer’ is different from those appeared in Chapter 3 and Chapter 4. In CISE project, CISE refers to the binary monomer such as $[\text{CdSe}]^x$, $[\text{CuSe}]^x$, and $[\text{InSe}]^x$. Besides organo-metallic precursors (e.g., acetate, acetylacetonate), halide compounds of copper and indium are also often used as reaction precursors [203, 218]. Dependent on the selection of solvents and ligands, hot-injection synthesis usually involved relatively high temperatures ($>180\text{ }^\circ\text{C}$). Solution synthesized CISE nano-particles with different novel morphologies (e.g., trigonal pyramidal [219], nano-ring [220], and dandelion [221]) and crystal phases (i.e., chalcopyrite, sphalerite [219, 220] and wurtzite [203, 222]) were reported.

5.1.3 Scope and objectives

It will be of high research interest to investigate the phenomena when a conducting polymer was employed to assist the formation of CISE nano-particles. This method can produce functional hybrid nano-composites at one-step. To approach the objective of studying the conducting homopolymer assisted synthesis, investigation on the synthesis systems without the conducting polymer was firstly carried out. Although hot-injection has been widely employed for preparation of chalcogenide nano-particles, the understanding of the formation mechanism requires further insights. This is

important especially when various types of organo-metallic compounds could be used as the precursors; and their kinetics of decomposition into monomers are different. The characterization results show that the synthesized CuInSe_2 nano-particles possess novel core-shell-like stoichiometric, which was of course critically dependent on the decomposition kinetics. In this chapter, the 1st part of the CISE project will be discussed, which are the hot-injection synthesis and characterization results of CISE without using conducting polymers. The proposed mechanism will be discussed in next chapter; with further verification based on additional experimental results focusing on conducting polymer assisted synthesis.

5.2 Experimental

5.2.1 Materials and methodology

Copper acetylacetonate ($\text{Cu}(\text{acac})_2$) (Sigma-Aldrich), indium acetylacetonate ($\text{In}(\text{acac})_3$) (Sigma-Aldrich), selenium powder (Se) (Sigma-Aldrich), tri-n-octylphosphine (TOP) (Sigma-Aldrich), and dibenzyl ether (DBE) (Aldrich) were used in syntheses without further purification. The synthesis procedures are schematically illustrated in Figure 5.1.

Figure 5.1. Schematic illustration of hot-injection synthesis method used for preparation of copper indium selenide (CISE) nano-particles.

5.2.2 Hot-injection synthesis

Weighed amounts of $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$ of 1:1 molar ratio were added to DBE inside a three-neck flask; this mixture is referred as the ‘precursor solution’. TOPSe was prepared in separate flask by dissolving Se inside TOP (aided by stirring at 55 °C); this preparation was done inside N_2 filled glove box. In fact, the selenium used was in excess and was about 8 times more than Cu and In, in term of the molar number. The ‘precursor solution’ was heated at 100 °C in N_2 for 3 hours, followed by heating at 140 °C for 1 hour to obtain a homogeneous reaction solution. The ‘precursor solution’ was then heated to hot-injection temperature, and swift injection of TOPSe was done. The reaction was considered to have started after the injection, and was allowed to proceed for certain durations; aliquots were extracted for characterizations at several designed time intervals. The synthesized products were allowed to cool down to room temperature before ethanol was added inside to induce flocculation. After sonication for 20 minutes, synthesized products were centrifuged at 4500rpm for removal of reaction by-products. Further purification was carried out by sonicating synthesized products in ‘toluene: ethanol mixture’ (2:1 volume ratio) for 20 minutes, before centrifugation at 9000rpm for 15 minutes. The supernatant portion was discarded and the solid content was re-dispersed in toluene: ethanol mixture aided by sonication. This purification process was repeated three times. After the 3rd purification, the synthesized products were dispersed inside toluene and used for further characterizations. The main synthesis parameters are summarized inside Table 5.1.

Table 5.1. Reaction parameters used for CISE nano-particles synthesis.

Sample	Cu(acac) ₂ (mg)	In(acac) ₃ (mg)	Se (mg)	DBE (ml)	TOP (ml)	Injection temp. (°C)	Growth temp. (°C)
A1 (290 °C +260 °C, higher conc.)	87.7	138.1	216	3.375	3.375	290	260
A2 (290 °C +260 °C)	87.7	138.1	216	10	2	290	260
A3 (260 °C)	87.7	138.1	216	10	2	260	260

5.2.3 Characterizations

Thin film x-ray diffraction (TFXRD) was done using Shimadzu X-ray diffractometer equipped with a Cu k- α ($\lambda=1.54$ Å) x-ray source operated at voltage=40kV and current=30mA. Transmission electron microscopy (TEM), high resolution TEM (HRTEM), and selected area electron diffraction (SAED) were done using JEOL 2100 TEM. UV-Vis NIR absorption spectroscopy was done using Shimadzu UV-3101PC; using CISE nano-particle samples dispersed inside toluene. Atomic absorption spectroscopy (AAS) was carried out using flame-based Perkin-Elmer AAnalyst100 system. The AAS samples were prepared by digesting CISE samples inside 69% nitric acid inside hydrothermal bomb (100 °C, 3h); and further diluted in DI water to measurable concentration ranges. X-ray photoelectron spectroscopy (XPS) was done using AXIS HSI-165 Ultra, Kratos Analytical, equipped with Al K α X-ray source. XPS samples were prepared by drop-casting concentrated CISE nano-particle samples onto silicon wafer.

5.3 Results and Discussion

The hot-injection synthesis involved the decomposition of organo-metallic precursors and formation of monomers upon injection of TOP-Se. The temperatures during the injection (denoted as ‘hot injection temperature’) and the growth (denoted as ‘growth temperature’) are both critical parameters. The initial high temperature at injection phase ensures burst nucleation and high nuclei concentration. 290 °C was chosen for injection because the boiling point of DBE (solvent) is 298 °C. For subsequent crystal growth, a lower-temperature is usually used to reduce probability of further nucleation during the growth stage. Therefore, 260 °C was chosen as the growth temperature in this work based on experimental optimization. As seemed in Figure B2.1 in the Appendix B), when lower growth reaction temperatures were used, the conversion from intermediates (Cu_{2-x}Se or In_2Se_3) to the CISE crystals was incomplete even after extended reaction time.

The structural, absorption and stoichiometric properties of the synthesized copper indium selenide (CISE) nano-particles had been characterized.

5.3.1 Structural properties of CISE nano-particles

- Nano-particle morphologies

As shown by the TEM images in Figure 5.2, the morphologies of synthesized CISE nano-particles obtained using different synthesis parameters was of near spherical but slightly irregular shape; consistent with previous report when acetylacetonate precursors were used [218]. The morphologies observed clearly show that both the precursor concentrations and reaction durations are critically affecting the morphological uniformity and size dispersity of the CISE nano-particles. A closer

examination could be based on the estimated size as measured from the TEM images; as summarized in Figure 5.3.

Figure 5.2. Morphologies of CISE nano-particles synthesized using different synthesis parameters: (a) sample A2 (290 °C+ 260 °C); (b) sample A1 (290 °C+ 260 °C, with higher precursors concentrations ($\sim 3\times$)); (c) sample A3 (260 °C). The insets at each images are the SAED patterns and HRTEM images (the d-spacing of ~ 3.35 Å corresponds to crystal plane (112) and could vary slightly due to the stoichiometric deviation from ideal Cu:In:Se=1:1:2 ratio).

Figure 5.3. Sizes of ClSe nano-particles synthesized using different synthesis parameters: (a) sample A2 (290 °C+ 260 °C); (b) sample A1 (290 °C+ 260 °C, with higher precursors concentrations (~3×)); (c) sample A3 (260 °C). At least 50 measurements are taken from TEM images of the samples at different conditions.

It is understood that hot-injection method is beneficial in producing nano-particles with good size dispersity following a burst nucleation process and short growth duration. Even better size dispersity could be achieved through ‘size focusing’ event

by approaches such as intermittent replenishment of TOP-Se [6]. Prolonged growth that involves Oswald ripening could undesirably broaden the size dispersity. Therefore, as shown inside Figure 5.2, the general trend is that small and uniform nano-particles grew into nano-particles of larger size and poorer size dispersity with longer duration. The CISE nano-particles with best size dispersity were obtained with high hot-injection temperature (290 °C) and lower growth temperature (260 °C); as shown in Figure 5.2(a). Under this condition, the size of the CISE nano-particles of synthesis duration up to 1 hour are still small (< 10nm) and centralized at around 7nm (see Figure 5.3(a)). As mentioned previously, this is because high injection temperature is essential for creating high degree of supersaturation of monomer ($[\text{CuSe}]^x$ and $[\text{InSe}]^x$) i.e., an efficient burst nucleation phenomenon. The lower growth temperature, besides slowing down Ostwald ripening, is also necessary for preventing concurrent nucleation during the growth phase.

With higher precursor concentration (about 3 times in molar number in samples of Figure 5.2(b) than that in sample of Figure 5.2(a)); CISE nano-particles of less uniform shape and broader size dispersity was observed; this is especially obvious at longer growth duration. This observation will be discussed in details later when the difference in conversion kinetics of Cu and In based precursors into individual monomers were considered. Simply speaking, high precursor concentration of course led to higher degree of supersaturation and this could result in more imbalance monomer formation kinetics. As shown in Figure 5.2(c), a lower injection temperature gave nano-particles with small size dispersity at the beginning of the reaction; however, further growth rendered the nano-particles more non-uniform in terms of both of the size dispersity and shape. In fact, this sample showed the worst size dispersity; as shown in the TEM image in Figure 5.2(c-iii)) (although not clearly shown in the measured size in Figure

5.3(c)). This result firstly showed the importance of high injection temperature for burst nucleation event. Secondly, it is believed that a sluggish or incomplete nucleation phenomenon took place throughout the entire synthesis duration, not only at the time of TOP-Se injection.

- Nano-particle crystal phases

Figure 5.4(a) shows the TFXRD spectra of CISE nano-particles synthesized at different hot-injection temperature and growth temperature; at the start of the reaction (i.e., based on 6 mins samples). Note that 6 mins was chosen because synthesis at even shorter reaction duration gave poor product yield. No obvious peak broadening was observed from XRD spectra of nano-particles samples due to the broad size range of the nano-particles. When higher concentration of precursors was used (sample A1), existence of Cu based intermediates was more obviously observed in the XRD spectrum.

The XRD spectra of sample A1 (290 °+260 °C) are included in Figure 5.4(b); which shows purer CISE crystal phase formed with longer synthesis durations. Additional XRD spectra of sample A2 and A3 are included in Appendix B3, Figure B3.1. The XRD results indicate formation of binary intermediates (CuSe , Cu_{2-x}Se and In_2Se_3) in synthesis of short duration or low temperature; before they reacted and formed CuInSe_2 of chalcopyrite phase (JCPDS# 40-1487) with good crystallinity. This is consistent with the literatures which often describe a growth phase for Cu and In based monomers that require long enough duration for reaction completion. Synthesis at lower temperature using a less reducing solvent which is diphenyl ether (DPE) (greater extent of electron delocalization at two benzene rings) instead of DBE was also carried out; the results clearly show the formation of binary intermediates (see Appendix B3, Figure B3.2). Scherrer's equation was also employed to calculate the size of the

synthesized CISE nano-particles; the calculated sizes are summarized in Appendix B4, Table B4.1; together with the average measured sizes from TEM images.

Figure 5.4. TFXRD spectra of synthesized CISE nano-particles of (a) 6 minutes reaction duration using different synthesis parameters; (b) sample A1 (290 °+260 °C, higher precursor concentrations) at different synthesis durations.

One important observation is that the XRD spectra do not clearly show the In_2Se_3 phase, which is believed to be due to the small and not well-crystallized structure

formed from $[\text{InSe}]^x$ monomers (details to be discussed in next chapter). Another point to be highlighted here is the fact that prominent XRD peaks position (JCPDS# 46-1129) of Cu_{2-x}Se are similar compared to those of CuInSe_2 ; the peaks were not quantitatively distinguishable from XRD spectra obtained from diffractometer used in this work. Therefore, a more detailed crystal phase analysis requires supplementary absorption studies of the synthesized CISE nano-particles.

5.3.2 Absorption properties of CISE nano-particles

Figure 5.5 shows the representative absorbance spectra of sample A2 CISE nano-particles synthesized with different growth durations. Additional absorbance spectra of sample A1 and A3 are included in Appendix B5, Figure B5.1. All the absorbance spectra of CISE sample synthesized without P3HT are consistent with those in the literatures, which the CISE nano-particles absorb usually below 1200 nm and across the entire visible light wavelength range. No obvious shift of absorption band edge was observed. This is because the Bohr's radius of CISE is 10.6nm [209]; size-dependent quantum confinement effect was not reflected by absorption spectroscopy.

The absorbance spectra not only show the absorbance band-edge, they also help with the identification of Cu_{2-x}Se nano-particles. The definite absorbance shoulder of synthesized products within NIR wavelength range can be used to prove formation of Cu_{2-x}Se [223]. CISE does not absorb within this wavelength range. Note that small amount of Cu_{2-x}Se could be identified with absorption spectroscopy due to the higher absorption coefficient of Cu_{2-x}Se as compared with that of CISE ($\sim 10^7 \text{ cm}^{-1}$ versus $\sim 10^4\text{-}10^5 \text{ cm}^{-1}$) [224]. The disappearance of broad absorbance shoulder with time indicates that the In^{3+} had been incorporated into Cu-rich nano-crystals (see Appendix B5.2). Again, when DPE was used to replace DBE, more distinct absorbance shoulder at NIR wavelength range was observed (see Appendix B5, Figure B5.3).

Figure 5.5. Absorbance spectra of synthesized CISE nano-particles of sample A2 (290 °C + 260 °C) at different synthesis durations (solution samples in toluene).

5.3.3 Stoichiometric properties of CISE nano-particles

The stoichiometry of CISE nano-particles is especially important since it is known that it critically affects the functional properties of ternary (or even quaternary) chalcogenides. In this section, combined analysis of stoichiometry data was carried out based on (i) AAS: giving overall stoichiometry, since the CISE nano-particles are fully digested/dissolved inside the acidic solutions; and (b) XPS: giving surface stoichiometry, usually of several nm from surface. In this work, energy-dispersive X-ray spectroscopy (EDX) was not employed for stoichiometry determination due to its semi-quantitative nature. Previous works usually study the functional properties by assuming that the nano-crystals synthesized are of uniform overall stoichiometry; only a handful of reports mentioned the non-ideal conditions.

As shown in AAS results (Figure 5.6), overall stoichiometry of synthesized CuInSe₂ nano-particles was close to Cu:In:Se=1:1:2. This is consistent with the initial molar ratio of the Cu(acac)₂ and In(acac)₃ used for the precursors. However, the overall Cu atomic percentages of CISE nano-particles were observed to be slightly higher for all

the different combinations of hot injection temperature and growth temperature; indicating a favourable formation of Cu-rich intermediates. The values of the AAS results are provided in Appendix B6, Table 6.1.

Figure 5.6. The stoichiometric ratio of Cu:In:Se as measured by atomic absorption spectroscopy (AAS) of (a) sample A1 (290 °C+ 260 °C, with higher precursors concentrations (~3×)), (b) sample A2 (290 °C+ 260 °C), and (c) sample A3 (260 °C).

XPS was further carried out on sample A1 (290 °C+ 260 °C, high precursor concentrations) for identification of oxidation states and atomic percentage of the constituting elements. Surface stoichiometry of sample A1 shows a surprisingly very high indium and very low Cu content at the surface (see Table 5.2). The binding energy (BE) peak positions for In and Cu of the XPS spectra correspond to the theoretical values of CISE BE peaks. Oxidation of Se on the nano-particles surface was observed from the additional peak at ~59 eV inside Se BE spectra. However, the relative intensities are distinctly different from that of the standard CISE spectrum

[203]. This observation will be discussed by using the proposed mechanism in next chapter.

Due to the surface sensitive nature of XPS, the accuracy of measured stoichiometric ratio is believed to be able to be improved by removal of surface ligands. This objective was achieved by sonication of synthesized CISE nano-particles (of 30mins synthesis duration) inside ethanolic solution of hydrazine. Stronger photo-electron signal could be measured; and it gave slightly higher but still low Cu content. The XPS data had been summarized inside Table 5.3; additional detailed XPS spectra of individual elements are included in Appendix B7.

Table 5.2. The stoichiometric ratio of Cu:In:Se calculated from XPS data of synthesized nano-particles: sample A1 (290 °C+ 260°C, higher precursor concentrations).

Sample (A1), synthesis durations	Stoichiometric ratio		
	Cu	In	Se
6mins	~0	93.6	6.4
30mins	~0	91.7	8.3
30mins -HY*	3.1	85.5	11.4

* Samples sonicated inside ethanolic solution of hydrazine (for removal of organic ligands) before being prepared for XPS analysis

Table 5.3. Summary of theoretical and measured BE peaks for Cu, In, and Se of sample A1; corresponding to individual atomic orbital.

	Theoretical BE (eV)				Measured BE (eV)					
	elemental		For CuInSe ₂		6 mins		30 mins		30 mins -HY	
Cu	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$		$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$
	933	953	931.9	-	-	-	-	-	932.24	N.M. *
In	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$		$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
	444	452	444.7	-	444.2	451.7	444.66	452.08	445.13	452.7
					446.6	454.2				
Se	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$		$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
	56	57	54	-	53.8		54.19	-	54.06	
										58.9 #

Oxidation, SeO₂

As a short summary, results from AAS and XPS suggested that the synthesized nano-particles are of Cu-rich core and In-rich shell; this observation was never discussed in details inside literature for ternary chalcogenides; which is probably due to difference in size range of nano-particles and synthesis systems. Such unique stoichiometry is recognized to be important, considering the fact that the functional properties of ClSe are critically impacted by the stoichiometry.

5.4 Conclusion

In this chapter, the characterization results of ClSe nano-particles synthesized using hot-injection method are discussed, including their morphologies, crystal phase, absorption properties, and stoichiometry. Consistent with previous works, the results clearly show that the selection of suitable synthesis parameters including precursor concentration, hot injection temperature, and growth temperature is essential to obtain nano-particles with small size and size uniformity. One important non-intuitive

observation is that, despite the fact that the CISE nano-particles is only of several nano-meters in diameter, they possess a novel core-shell-like stoichiometric gradient: an increasing $\text{In}^{3+}:\text{Cu}^{2+}$ from core to shell. The stoichiometric gradient impacts the functional properties directly since CISE is p-type if Cu-rich and is n-type if In-rich. In next chapter, the formation mechanism of the CISE nano-particles with such stoichiometric gradient will be discussed; supported with further verification by further experimental results.

Chapter 6

Formation Mechanism of Core-shell-like CuInSe_2 Nano-particles

6.1 Introduction

6.1.1 Stoichiometry of CISE and its tailorability

Stoichiometry of CISE significantly impacts the functional properties such as n- or p-type semi-conducting properties, absorption band-edge, and charge mobility [225, 226]. There are many phenomena that can lead to stoichiometric changes. CISE employed in thin film photovoltaics is normally p-type (with an n-type CdS window); however, the issue on stoichiometry non-uniformity is commonly known. For instance, surface selenium atoms are replaceable by atmospheric oxygen and results in resistivity change [227]. Oxidation of indium atoms could also occur at grain boundaries [197] and indium rich CISE phase can form as CuIn_3Se_5 [228]. During multiple-step device fabrication, unavoidable atomic inter-diffusion within original CISE thin film could lead to stoichiometric gradient [229]. In fact, stoichiometry of

CISE thin film can be advantageously tailored through preparation parameters [230, 231]; this fact has provided a lot of research opportunities. Specifically for solution-based techniques, CISE stoichiometry is sensitive to synthesis parameters including types of precursors [199, 200, 218], types of ligand [222], injection temperatures [232], and selenization conditions [214, 233].

6.1.2 Formation mechanism of CISE nano-crystals

During hot-injection synthesis, the stoichiometric uniformity of CISE nano-crystals is critically dependent on the kinetics of different stages of nano-particle formation. The stages are generally accepted to consist of: (i) electron transfer reaction of $\text{Se} \rightarrow \text{Se}^{2-}$, (ii) conversion of precursors into monomers (e.g., $[\text{CuSe}]^x$, $[\text{InSe}]^x$); (iii) nucleation of binary intermediates (e.g., Cu_{2-x}Se , In_2Se_3), and (iv) reaction of binary intermediates to form ternary CuInSe_2 . Compared with binary chalcogenides, ternary chalcogenides involve precursors of two different metallic species; this complicates the formation mechanism because the difference of the precursor reactivities needs to be considered.

The formation mechanism of CISE was occasionally discussed in previous works. Wang et al. proposed that Cu_{2-x}Se seed crystals formed first (reaction between diphenyl diselenide and Cu-oleate complex) before incorporation of In^{3+} [203]. It is understood that high enough growth temperature was required for Cu_{2-x}Se and In_2Se_3 to react and produce CuInSe_2 with more uniform stoichiometry [234, 235]. Incomplete reaction as affected by different parameters (e.g., types of precursors and synthesis duration) could lead to formation of binary intermediates as by-products [221, 236, 237]. When organo-metallic compounds are employed as precursors in hot-injection syntheses; their decomposition before monomer formation is the crucial step that affects the subsequent nucleation phase. The specific coordination behaviour of

different organic ligated species towards the organo-metallic compounds indeed plays important role in determining the reaction pathway.

Utilizing nuclear magnetic resonance (NMR, including ^{31}P , ^{13}C , ^1H) to study binary chalcogenide systems (including PbSe, CdSe, CdS, and CdTe), nucleation was proposed to have proceeded through (TOPSe used in their works): (i) nucleophilic attack of TOPSe on ligated metallic species, (ii) weakening and breakage of P=Se bonding, and (iii) the formation of monomers [238, 239]. Yu et al. also conducted absorption spectroscopy and NMR investigation on ZnSe; and they proposed the formation of Zn-P complexes which possess higher reactivity leading to faster nucleation/growth (termed as ‘indirect route’) [240]. A similar concept which is ‘coordination polymer’ had been proposed by Owen et al.; they discussed the importance of Lewis acidity of cadmium octadecylphosphonate during the monomer formation [241].

6.1.3 Conducting polymer assisted synthesis of inorganic nano-crystals

Metallic nano-crystals have been synthesized inside non-conducting polymer (e.g., Au in PMMA) or conducting polymer (e.g., Ag [242], Pd [243], Au [243, 244], Cu or Cu_2O [245] in PANI). Of higher interest is the idea of synthesizing functional inorganic nano-crystals inside conducting polymers; creating hybrid nano-composites in one-step. This is due to the potential of achieving intimate interfacial contacts for good charge carrier dissociation and transport. Furthermore, the method potentially eliminates non-conducting ligands that impede charge carrier motion. Some examples demonstrated in literature include: CdSe in poly(3-hexylthiophene) (P3HT) [246], CdS in P3HT [93, 247], PbS in P3HT [248, 249], CdS in polyphenylene-b-poly(2-vinyl pyridine) (PPH-PVP) [80], and CdS in poly[2-methoxy-5-(2'-ethylhexyloxy)-p-

phenylene vinylene] (MEH-PPV) [76, 94, 250]. Good interfacial contacts [80] and longer charge carrier decay time [246] were experimentally evidenced.

Moreover, it is interesting when the conducting ligands act both as capping agent and templating agent for growth. Liao et al. proposed that coordination between ‘S on thiophene ring’ and Cd^{2+} took place when $[\text{Cd}^{2+}]$ is high enough; this phenomenon induced subsequent anisotropic growth and resulted in formation of CdS nanorods [93]. There remains a lot of research opportunities on the templating function of functional conducting polymers.

6.1.4 Scope and objectives

In this chapter, the 2nd part of CISE project will be discussed: the proposed formation mechanism of core-shell-like CISE nano-particles; supported by further characterization results obtained through the P3HT assisted synthesis of CISE nano-particles. The proposed mechanism builds up on relevant literatures which focused on binary chalcogenide systems. The effects of reactivity difference of organo-metallic precursors, leading to novel stoichiometric gradient, are discussed. Apart from achieving the objective of investigating on functional homopolymer assisted synthesis, this work highlights the feasibility of selection of polymeric coordination species for tailoring stoichiometric (thus functional) properties of nano-materials.

6.2 Experimental

The synthesis procedures and characterization techniques used are identical with what are included in Chapter 5. The exception is that conducting polymer assisted syntheses were carried out: additional poly(3-hexylthiophene) (P3HT) was added into the ‘precursor solution’ containing the $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_2$. The ‘precursor solution’

was put through same heating procedures; before the injection of TOP-Se. The steps of purification are also identical. The regioregular P3HT (Sigma-Aldrich) were used in syntheses without further purification. As shown in Table 6.1 is the summary of synthesis parameters employed.

Table 6.1. Reaction parameters used for P3HT assisted ClSe nano-particle synthesis.

Sample	Cu(acac) ₂ (mg)	In(acac) ₃ (mg)	Se (mg)	P3HT (mg)	DBE (ml)	TOP (ml)	Injection temp. (°C)	Growth temp. (°C)
B1 (290 °C +260 °C)	87.7	138.1	216	5	10	2	290	260
B2 (260 °C)	87.7	138.1	216	5	10	2	260	260
B3 (290 °C)	87.7	138.1	216	5	10	2	290	290

6.3 Results and Discussion

This result section consists of two major parts: (i) formation mechanism of core-shell-like ClSe nano-particles, and (ii) poly(3-hexylthiophene) (P3HT) assisted ClSe nano-particles synthesis.

6.3.1 Formation mechanism of core-shell-like ClSe nano-particles

This section aims to discuss the most plausible formation mechanism of ClSe nano-particles with indium-rich shell and copper-rich core as obtained in this work. It is understood that the proposed mechanism in following section requires more specific characterization results especially by NMR (including ¹H, ¹³C, ³¹P) for the verification; by looking at the organic species present during the synthesis. This type of data was not obtained; but instead the formation mechanism issue were herein approached indirectly by analysing the characterization results, at the same time based firmly on previously reported experimental studies. It is believed to be necessary to discuss the

formation mechanism in details, to better elucidate the characterization results; and at the same time highlighting the contributions of this work.

First of all, note that it is not un-reported that nano-particles with non-uniform stoichiometry could be prepared in one-pot or single-step synthesis. Some examples include ZnS(shell)@CdSe(core) [251], ZnS(shell)@InP(core) [252], and CdSeS nanorod with S-rich shell and Se-rich core [253]. The creation of non-uniform stoichiometry was attributed to the difference of: (i) precursor reactivities, and (ii) the affinities between precursor and coordination species. However, none of the works involves stoichiometry dependent transition of n- or p-type semiconducting properties. Furthermore, a lot of the time these works focused on the effects of the anionic species (e.g., Se^{2-} and S^{2-}) and the tailoring of their relative concentrations.

This CISE project is distinctive from previous works because: (i) it involves change of p- or n- type dependent on $\text{Cu}^{1+}:\text{In}^{3+}$ ratio; and (ii) it discusses kinetics of monomer formation following decomposition of organo-metallic compounds in ternary compound. Again, the difference between ‘intermediate’ and ‘monomer’ needs to be highlighted; in here, ‘intermediate’ is stable Cu- or In- based selenide compound (e.g., Cu_{2-x}Se , In_2Se_3), while ‘monomer’ could be $[\text{CuSe}]^{1-}$, $[\text{CuSe}]^0$, and $[\text{InSe}]^{1+}$ (only two atoms). Note that sometimes their definitions might be inconsistent across the literatures.

There are reported works on formation mechanism of CuInS_2 which is another widely studied ternary chalcogenide; there still lacks of works on CISE. It had been demonstrated that for CuInS_2 , the control of shape and alloyed compounds are possible through the tailoring of the reactivity of the organo-metallic precursors [254]. Norako et al. studied hot-injection synthesis of CuInS_2 by injecting di-tert-butyl-disulfide into

reactants containing $\text{In}(\text{acac})_3$ and CuCl [255]. They proposed that copper rich nuclei formed first, and stoichiometric uniformity was achieved within the later growth phase via Ostwald ripening and size focusing events.

Coming to the proposed formation mechanism in this work, main characterization results providing stoichiometric information are firstly summarized as followings:

- XPS (surface stoichiometry) showed very high indium atomic percentage and low copper atomic percentage.
- AAS (overall stoichiometry) showed slightly higher copper atomic percentage; and $\text{Cu}:\text{In}:\text{Se} \sim 1:1:2$.
- The stoichiometric gradient (combining AAS and XPS results) was less distinct when high injection temperature was used.
- UV-Vis absorption spectroscopy showed characteristic absorbance shoulder of Cu_{2-x}Se from synthesized products of shorter synthesis duration, higher precursor concentration, and inside less reducing solvent (i.e., DPE).
- TFXRD showed diffraction peaks of more reaction intermediate (e.g., CuSe and In_2Se_3) from synthesized products of lower synthesis temperature (both injection and growth temperature), higher precursor concentration, and less reducing solvent (i.e., DPE).

These above characterization results lead to one proposition: Cu-based monomers formed favourably compared to In-based monomers; within the synthesis parameters window in this work. This proposition could be directly related to the monomer formation kinetics and the degree of supersaturation (DS) of the monomer.

From a broad perspective, in this work, the formation of CISE nano-particles followed the generally accepted pathway: binary Cu-based and In-based intermediates formed firstly before they reacted to form the ternary CISE nano-particles (i.e., binary monomer $\rightarrow$ binary intermediate $\rightarrow$ ternary chalcogenide). The proposed formation mechanism is illustrated inside Figure 6.1; which involves two major phases: ‘nucleation phase’ and ‘growth and aggregation phase’. The discussion of the formation mechanism will focus on the ‘nucleation phase’; after that, the ‘growth and aggregation phase’ will be briefly discussed.

Figure 6.1. Proposed formation mechanism of CISE nano-particles with novel stoichiometric gradient; which includes: ‘nucleation phase’ and ‘growth and aggregation phase’. In ‘nucleation phase’, the decomposition of Cu- and In- based precursors are affected by the coordination of phosphine; leading to different monomer formation kinetics. During ‘growth and aggregation phase’, Ostwald ripening and cluster aggregation of Cu-based and In-based crystals of different sizes are responsible for the nano-particle growth.

In the reaction, TOPSe was reported to serve as homogenous medium bringing Se to close vicinity of the metallic species [256]. The formation of monomers ensures after the cleavage of P=Se took place after nucleophilic attack of organo-metallic complexes [239]. Different reaction kinetics of $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$ during monomer formation (following thermal decomposition of organo-metallic precursors) are believed to be responsible for creation of novel stoichiometric gradient. This is dependent on reactivity of the organo-metallic precursors; which further affects the DS of monomer at certain instance. The reactivity is not only related to the intrinsic molecular properties, but also to the specific coordination between the organic species and metallic species (note that these metallic species could be the species exist before or after organo-metallic compound decomposition).

Upon injection of TOP-Se, the DS of $[\text{CuSe}]^x$ monomer is higher as compared to that of $[\text{InSe}]^x$. The higher the DS, the smaller the size of stable embryo nucleus (r^*) is. The solubility of the monomer and the effect of hot injection temperature also need to be considered. With the same synthesis duration, the Cu-based intermediates formed are of larger size due to high DS and low solubility of $[\text{CuSe}]^x$ monomer. To prove this point, hot-injection syntheses using only individually $\text{Cu}(\text{acac})_2$ or $\text{In}(\text{acac})_3$ were carried out. The data on the morphologies and crystal phases of the nano-particles are included inside Appendix B8. Note that the results clearly indicate that the reactivity of the Cu-based precursors is higher. Of course, the results do not indicate that, in the syntheses with the presence of both $\text{Cu}(\text{acac})_2$ or $\text{In}(\text{acac})_3$, stable nuclei would possess only individual metallic element.

As the difference in monomer formation kinetics is established, the issue of interest is the reasons behind such difference. Extending from literatures discussing binary chalcogenide formation [238, 240], two different schemes during the formation of

ternary chalcogenide are proposed herein, which are dependent on the hot injection temperature (see Figure 6.2 for details):

- a) Lower hot injection temperature: $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$ had not completely thermally decomposed during TOP-Se injection. Coordination of TOP-Se affected their molecular integrity hence reactivity to form monomers. The favorable coordination between phosphine and Cu played a significant role in increasing the reactivity of the Cu-based precursors. The removal of ligated acetylacetonate side chains was also greatly affected. This resulted in more inhomogeneous overall formation kinetics.
- b) Higher hot injection temperature: The reaction solution contains decomposed metallic species (i.e., Cu^{2+} , Cu^{1+} and In^{3+}) during TOPSe injection. The decreased extent of favourable decomposition of Cu-based precursors (due to specific coordination with phosphine) resulted in more homogeneous overall formation kinetics.

Scheme 1

Scheme 2

Figure 6.2. Different schemes of the reaction pathways controlling the decomposition of organo-metallic precursors and the formation of monomers. Scheme 1 is predominant at low hot injection temperature and scheme 2 is predominant at high hot injection temperature.

Following scheme 1, high DS of Cu-based monomer (and its low solubility) resulted in larger Cu-based cluster for further nucleation. This non-symmetrical decomposition kinetics of Cu-based and In-based precursors could be moderated with higher injection temperature, under which condition the scheme 2 type of monomer formation is predominant. However, the reaction parameters employed in this work were not able to completely eliminate this asymmetry. Note that it is believed that under the synthesis conditions of this work, each of the two schemes could not be fully

eliminated at either lower (i.e., 260 °C) or higher (i.e., 290 °C) hot injection temperature. The proposed scheme 1 and scheme 2 are very similar to the concept as mentioned by Yu et al. [240]; which they termed as ‘indirect route’ and ‘direct route’ depending on whether the TOPSe (or DPPSe) or DPP (or DOP) are responsible for the complex formation.

Interestingly, the ease of decomposition of individual $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$ (based on theory and our experimental results) contradicted herein proposed favourable Cu-based intermediate formation. In term of the cleavage of ligated acetylacetonate side chains, $\text{Cu}(\text{acac})_2$ possesses larger equilibrium constant comparing to that of $\text{In}(\text{acac})_3$ [257]. Our thermogravimetric analysis also showed that $\text{In}(\text{acac})_3$ started decomposition at lower temperature (238 °C) comparing to $\text{Cu}(\text{acac})_2$ (263 °C) (see Appendix B9, Figure B9.1). These contradictory facts again highlighted the fact that the monomer formation was not solely dependent on the intrinsic molecular stability. The monomer formation, following thermal decomposition of organo-metallic precursors, is affected critically by coordination affinity between metallic species and nucleophilic species. Electronegativity of Cu ($\chi=1.9$) is larger than that of In ($\chi=1.7$); indicating that Cu-based nuclei formed easier due to stronger affinity with nucleophilic TOPSe. Based on ‘hard soft acid base’ (HSAB) principle, R_3P as a soft base prefers to coordinate with Cu^{2+} as a soft acid than with In^{3+} as a hard acid.

Formation of larger Cu-based clusters and smaller In-based clusters then led to solid state reaction involving Ostwald ripening and cluster aggregation (Figure 6.1). A combination of high injection temperature and low growth temperature should be used to obtain small size dispersity. As mentioned earlier, high enough growth temperature is still required to produce nano-particles with better stoichiometric uniformity. However, the growth temperature could not be too high, as it might induce not only

the concurrent nucleation at the growth phase, but also aggravate the Ostwald ripening causing widening of the nano-particles size. In fact, there remains no consensus on the formation mechanism in terms of role of TOP and the phenomena involved during nucleation. Therefore, more characterization results are required for study of the formation mechanism.

It is believed herein that the Ostwald ripening of In based intermediates onto the Cu based intermediate acts to control the nano-particles size. Similar discussion had been done on CoPt₃ which involves firstly the formation of Co nuclei before the addition of Pt(I) or Pt(II) (oxidation states were uncertain) to growing clusters; followed by alloying [258]. The fact that the obtained TFXRD spectra shows low detectable amount of In₂Se₃ (see Figure 5.4) (more noticeable when synthesized in DPE, see appendix B3, Figure B3.2) could be due to the small size and poorly crystallized In-based intermediates. Another possibility leading to such observation remained to be proven is the strong binding of the ligand to In-based monomers; restricting its nucleation.

6.3.2 P3HT assisted CISE nano-particle formation

The next stage of the CISE project is to employ conducting homopolymer to assist the synthesis of CISE nano-particles. This part of work, besides verifying the critical role of coordination species towards the monomer kinetics of different organo-metallic precursors, also creates hybrid nano-composites with intimate interfacial contact between CISE nano-particles and coordinated conducting polymers. At the same time, the employment of P3HT reduced amount of non-conducting TOP. Compared to the synthesis without employing P3HT, no investigation of precursor concentration was

done; instead, synthesis using 290 °C as both hot injection and growth temperature was carried out (sample B3).

6.3.2.1 Structural properties of CISe nano-particles synthesized with the presence of P3HT

As mentioned earlier, sulfur (S) in the repeating thiophene ring structure of P3HT was proposed to coordinate with Cd^{2+} and template the growth of CdS into nano-rod [93]. This coordination between S and Cu^{2+} (or Cu^{1+}) would also exist in this system, but no rod-like structure was observed in the samples. Preliminary proofs on the coordination between P3HT with Cu^{2+} , including UV-Vis and TFXRD results, can be found in Appendix B10. Figure 6.3 shows the morphologies of CISe nano-particles synthesized in situ P3HT as observed by TEM; while Figure 6.4 summarizes their measured size. The distinct differences of the CISe nano-particles as compared with the products obtained without using P3HT are: the increments of both the size and size dispersity. Furthermore, the shape of the CISe nano-particles synthesized with the presence of P3HT is more irregular. These observations are due to the weaker coordination of P3HT to metallic species as compared to that of TOP to metallic species. Besides that, P3HT does not help in dispersion as well as TOP, therefore, agglomeration of CISe nano-particles coordinated by P3HT was also more severe.

When low temperature (260 °C) was used for both injection and growth, CISe nano-particles capped with P3HT are clearly observed (see Figure 6.3(b)). At lower temperature, the polymer molecules are less mobile and coordinate better to the CISe nano-particles. Furthermore, this capping of P3HT, due to larger steric effect as compared with TOP, could inhibit the further growth of the CISe nano-particles as there was little size increment of nano-particles from 30 mins to 1 hour under such

conditions (sample B2, see Figure 6.3(b)). When high temperature (290 °C) was used for both injection and growth; much obvious increment in size and size dispersity were observed for sample synthesized from 30 mins till 1 hour (sample B3, see Figure 6.3(c)). The result highlights the fact that high temperature weakened the capping capability of P3HT and aggravated the Ostwald ripening effect. Note that TOP or TOPO could not be completely eliminated from the surface of CISe nano-particles; since excess TOP was used for the synthesis and they are very strong ligands to the CISe nano-particles.

Figure 6.3. Morphologies of ClSe nano-particles synthesized with the presence of P3HT using different synthesis parameters: (a) sample B1 (290 °C + 260 °C); (b) sample B2 (260 °C); (c) sample B3 (290 °C). The insets at each image are the SAED patterns and HRTEM images.

Figure 6.4. Sizes of CISE nano-particles synthesized with the presence of P3HT using different synthesis parameters: (a) sample B1 (290 °C+ 260 °C); (b) sample B2 (260 °C); (c) sample B3 (290 °C). At least 50 measurements are taken from TEM images of the samples at different conditions.

TFXRD spectra synthesized CISE nano-particles with the presence of P3HT are shown in Figure 6.5. It was found that P3HT has negligible effect on crystal phase (i.e., chalcopyrite phase is retained). As shown in Figure 6.5(b), 6 minutes was sufficient

for the formation of purer phase of CISE because no observable peaks belonging to intermediates were found. This is also true for sample B2 and B3; their XRD spectra are included in Appendix B3, Figure B3.1. However, it is important to highlight here that longer synthesis duration (>6 minutes) would be beneficial for good product yield. When high temperature (290 °C) was used as both hot-injection and growth, XRD peaks belonging to Cu_{2-x}Se intermediates were observed (Figure 6.5(a)). This was due to degraded capping capability of P3HT (i.e TOP still playing a predominant role) and is consistent with observations by TEM. The nano-particles size calculated using Scherrer's equation; together with the measured size from TEM images are summarized in Appendix B4, Table B4.1.

Figure 6.5. TFXRD spectra of synthesized ClSe nano-particles with the presence of P3HT; (a) of 6 minutes reaction duration using different synthesis parameters; (b) of sample B1 (290 °+260 °C) at different synthesis durations.

6.3.2.2 Absorption behaviour of ClSe nano-particles synthesized with the presence of P3HT

Figure 6.6 shows the absorption spectra of synthesized ClSe nano-particles with the presence of P3HT. Both the absorbance characteristics of ClSe and P3HT are observed

inside the spectra. Figure 6.6(a) showed that under different synthesis conditions, no detectable Cu_{2-x}Se could be observed (not broad absorbance shoulder at near-IR region); indicating purer CISE formed. One consideration is the stability of the P3HT during the synthesis. This consideration can be ascertained from the retainment of absorbance peak $\sim 452\text{nm}$ (attributed to P3HT) after thrice purification of synthesized products; indicating intimate interfacial contact between P3HT and the CISE nano-particles (instead of a simple blend). Also, as shown in absorption spectra of sample B1 (Figure 6.6(b)), the obvious increment of absorbance in the 600-1200nm wavelength range indicates a more complete reaction with longer synthesis duration. Additional absorbance spectra of sample B2 and B3 are included in Appendix B4, Figure B4.2. No observable characteristic absorbance shoulder attributed to Cu_{2-x}Se could be found in the absorption spectra of all three samples.

Figure 6.6. Absorption spectra of synthesized ClSe nano-particles with the presence of P3HT (solution samples in toluene); (a) of 6 minutes synthesis duration at different synthesis conditions; (b) of sample B1 (290 °C + 260 °C) at different synthesis durations.

6.3.2.3 Stoichiometric properties of ClSe nano-particles synthesized with the presence of P3HT

The overall stoichiometry of all three samples synthesized with the presence of P3HT was measured using AAS, and the results are included in Figure 6.7. The actual values of the AAS results are included in Appendix B6, Table B6.1. As shown in Figure 6.7(a), the overall stoichiometry of sample B1 was still copper-rich; but became

overall indium-rich when low and high temperatures were used for both the hot-injection and growth (sample B2 and B3). The weakening of the phosphine coordination effected asymmetrical monomer formation kinetics due to existence of P3HT is considered as the main reason. Based on HSAB principle, S as a soft Lewis base still prefers to coordinate to Cu^{1+} as a soft acid, than with In^{3+} as a hard acid. However, this effect was milder as compared to the case of R_3P . For sample B1, with the presence of P3HT, high temperature burst nucleation followed by low temperature growth is still required for achieving balanced stoichiometry. However, their size dispersity was not as uniform as those of samples synthesized without P3HT.

Figure 6.7. The stoichiometric ratio of Cu:In:Se as measured by atomic absorption spectroscopy (AAS) of (a) sample B1 (290 °C + 260 °C); (b) sample B2 (260 °C); (c) sample B3 (290 °C).

The reason that the overall stoichiometries for both samples B2 and B3 were slightly indium rich could not be fully understood at this stage. However, plausible

explanations can be proposed here. Firstly, the moderation effect of P3HT towards asymmetrical monomer formation kinetics still exists. The steric hindrance and dispersion capability of P3HT played important role during intermediate formation stage. Note that P3HT has a longer chain and also weaker dispersion capability as compared with TOP which is small organic ligands with strong dispersion capability.

For sample B2, during low temperature hot-injection, the DS of $[\text{CuSe}]^{x+}$ monomer was not only reduced due to weaker P3HT coordination to Cu^{2+} , the critical nucleus size was expected to have increased due to weaker dispersion capability. The steric hindrance hence took effect in the Ostwald ripening and cluster aggregation (limiting accessibility of Cu-based clusters more than that of In-based clusters) in later low temperature growth phase. This could in fact evidenced by the TEM images of sample B2 (see Figure 6.3) which showed that the P3HT capped around the entire ClSe nano-particles. While for sample B3, even higher indium atomic percentage (as compared with sample B1 and B2) could indicate the exacerbation of attachment of indium based clusters through Ostwald ripening during the low temperature growth phase. This added up to the diminished TOP caused asymmetrical monomer kinetics since the hot-injection was done at high temperature (Scheme 2 in Figure 6.2 was predominant). Of course, more characterization results would be required to verify these propositions. Nevertheless, the results again show the importance of selection of temperatures for hot-injection and growth phases.

The stoichiometry of sample B1 was also studied using XPS; the detailed XPS spectra of individual elements are included in Appendix B7. The elemental ratio of Cu:In:Se are shown in Table 6.2 and clearly indicates that the surface is still indium rich but the Cu atomic percentage is higher as compared to the samples synthesized without P3HT. Note that the AAS show overall indium rich stoichiometry; yet the surface $\text{In}^{3+}:\text{Cu}^{2+}$

atomic content in fact decreased. This is strong evidence that the original stoichiometric gradient is moderated; although not fully eliminated. The identification of the positions of various BE peaks belonging to different elements are further summarized in Table 6.3.

Table 6.2. The stoichiometric ratio of Cu:In:Se calculated from XPS data of synthesized nano-particles, sample B1 (290 °C+ 260°C).

Sample (B1), synthesis durations	Stoichiometric ratio		
	Cu	In	Se
6mins	10.1	65.2	24.6
30mins	6.8	71.2	22.1
30mins -HY*	15.4	45.2	39.4

* Samples sonicated inside ethanolic solution of hydrazine before being used for preparation of XPS

Table 6.3. Summary of theoretical and measured BE peaks for Cu, In, and Se of sample B1 (synthesized with the presence of P3HT) corresponding to individual atomic orbital.

	Theoretical BE (eV)				Measured BE (eV)					
	elemental		For CuInSe ₂		6 mins		30 mins		30 mins -HY	
Cu	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$		$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$
	933	953	931.9	-	930.9	950.9	930.57	950.8	932.69	N.M.
In	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$		$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
	444	452	444.7	-	444.6	451.9	444.63	452.02	445.23	452.8
Se	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$		$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
	56	57	54	-	53.4		53.4		54.47	
					58.2#		57.97#		59.15	#

Oxidation, SeO₂

6.4 Conclusion

This chapter discusses the proposed formation mechanism of the CISE nano-particles with core-shell-like stoichiometric gradient. The stoichiometric gradient resulted from different nucleation behaviours of Cu-based and In-based nuclei, dependent on affinity between the metallic species and nucleophilic ligands. This effect dominated over the intrinsic decomposition behaviour of the individual organo-metallic precursors. The degree of supersaturation and monomer solubility are critical parameters, affected by the hot injection and growth temperatures. Subsequent solid state reaction involving Ostwald ripening and cluster aggregation produced final CuInSe₂ nano-particles. This coordination induced stoichiometric gradient was verified as the effect was moderated with employment of P3HT; since the S group coordinated weaker with Cu¹⁺ as compared to R₃P group with Cu¹⁺. The synthesis also produced functional hybrid nano-composites in one-step. Based on the proposed mechanism, variable semiconducting properties (n- or p- type) at core-shell-like CISE nano-particles would be achievable by tailoring the stoichiometry. This presents the opportunity to achieve novel stoichiometry-related properties in other ternary or multi-components nanocrystals systems through selection of coordinating functionalities.

Chapter 7

Conclusion, Recommended Future Works and Outlook

7.1 Conclusion

Concise summary of major findings and key proposed mechanisms is given in this concluding section, accompanied with brief extended discussion. As defined clearly in Chapter 1, the project scope is on homopolymer assisted solution synthesis of inorganic nano-materials. Besides cost and scalability considerations, homopolymers are desirable, compared to block copolymers, because it is believed that structural directing and compositional regulating functions could potentially be found on homopolymers as well under controlled conditions. It is interesting from the perspective of materials science and related to the fundamentals of the material properties and physical/chemical behaviours of simple homologous structured polymer. Specific focus is given to representative synthesis systems i.e., (i) aqueous based synthesized metal oxide and (ii) organic solvent-based synthesized chalcogenides.

The contributions and novelties of this work are summarized as followings:

- In synthesis system involving poly(acrylic acid) (PAA) and Cu^{2+} counterions, the potential of utilizing the block copolymer-like self-assembly of homopolyelectrolyte/counterions has been demonstrated for the first time. This generated new insights, in terms of utilizing simple charged homopolymers and their interaction with counterions to achieve intelligent morphological control.
- For hot-injection synthesis of CuInSe_2 (CISe), the role of coordination species in affecting the monomer formation kinetics from individual organo-metallic precursor has been identified. This is the first time non-uniform stoichiometry of CISe nano-particles was studied. Hybrid nano-composite containing CISe nano-particles with core-shell-like stoichiometry coordinated with poly(3-hexyl thiophene) (P3HT) was prepared.

This work probed the molecular-level phenomena involved in the homopolymer assisted formation of inorganic nano-particles. From the starting nucleation phase, the dominant type of interaction (whether it is ionic or covalent) is critically dependent on the nature of the solvent environment. It is understood that completely different contexts should be considered for synthesis inside either aqueous or organic solvent media. The usually milder conditions in aqueous media enable thermodynamically favourable growth of complicated crystallite structures, such as meso-porous hierarchical structures. Inside organic solvent, the high degree of supersaturation of monomers in very short time frame helps capturing the growth kinetics of crystals. In both of the above scenarios, the roles of ligands or polymers such as stabilization or templating could not be emphasized more. Especially for polymers, its long-chain conformation and tailorable functionality/architecture profoundly influence the nano-crystal formation. These attributes has been studied and discussed in previous four

chapters and will only be briefly elaborated here. The functionalities of the polymers which are spatially confined on organic backbones can have effects not observable on small organic molecules (e.g., surfactant or oligomer). In aqueous environment, the polyelectrolytes which absorb metallic counterions can template the formation of novel nano-structures, based on the structural evolution of the polyelectrolyte-counterion complex and carefully controlled parameters including degree of deprotonation and binding ratio. In organic solvent, the coordinating functionalities affect the molecular integrity of the organo-metallic precursors; this changes the monomer formation kinetics significantly.

The concept and methodology developed in this work are adoptable for other relevant material systems. The limitations, which can be also viewed as further opportunities, arise due to the mere fact that there are different types of synthesis systems that could involve functional homopolymer. Despite the complexity, a general guiding principle can be established. Employing systematic approach, it is possible to reveal more effects of molecular level interactions contributed by the homopolymers (or other organic additives) towards the formation of inorganic nano-materials. The ultimate goal goes beyond the understanding but the utilization of these novel effects towards facile and well-controlled preparation method for hybrid functional nano-composites.

7.2 Recommended Future Works

The proposed future works here is meant to be concise and could not be exhaustive. Since this thesis work deals more with the fundamental material science associated with influence of homologous polymeric molecules towards inorganic nano-material formation, demonstration of the applications would be one major direction.

- Aqueous based PAA templated synthesis of CuO_x nano-materials

The effects of other parameters such as ionic strength, ionic species, temperature, PAA molecular weight, and so on towards the formation mechanism could be studied to establish a more complete understanding on PAA-Cu²⁺ system. In term of the PAA-Cu²⁺ interaction mechanism, more characterization results should be obtained through techniques including light-scattering, small angle x-ray or neutron scattering; as they will provide more specific evidence to the variation of chain conformation. Of course, other homo-PEL/counterions systems can also be studied. Examples of other PEL of interest are poly(acrylamide) and poly(ethyleneimine); it would be also interesting to study the roles played by positively charged PEL. Magnetic and transition metallic counterions (e.g., Fe²⁺, Co²⁺) would be of special interests as the incompletely filled d-shell would potentially lead to novel complexation phenomena.

In term of potential applications, the bio-toxicity of PAA based encapsulated CuO_x nano-materials could be done since the hybrid material combined both (i) exterior bio-compatible PAA and (ii) interior Cu-based materials that is known to possess certain toxicity. This means that the hybrid could be potentially introduced *in situ* or *in vivo* organisms for bio-related applications. Exploration of other applications e.g., catalytic and sensing could also be pursued, as nanotubular CuO_x possesses directional carrier properties.

The unique triblock copolymer-like self-assembly behaviour of homo-PEL remains to be explored as there are many gaps to be bridged. For instances, utilization and controlling the different extent of non-uniform charge distribution is challenging, whether the other novel nano-material morphologies could be produced, or applicable to other alkali, alkali earth metallic species, carbonates, phosphonates and so on.

- Hot-injection synthesis of CISE nano-crystals in situ conducting polymer:

Further study on the effects of the synthesis parameters, organo-metallic precursors, and ligands/polymers towards the formation mechanism can be done. Furthermore, the proposed mechanism could be extended to other ternary or even quaternary systems (e.g., $\text{Cu}_x\text{Zn}_y\text{Se}_z$, $\text{Cu}_w\text{In}_x\text{Ga}_y\text{Se}_z$). Other characterization techniques such as photoluminescence and NMR could be utilized to study monomer formation kinetics. Creation of nano-structured nano-materials (not only spherical) with controlled stoichiometric gradients or doped structures might be possible. Formation of charge transfer complex represents another important direction to be pursued, using technique such as transient absorption spectroscopy.

The electronic and opto-electronic properties of materials with such stoichiometric gradient could be studied based the principles of charge dissociation, charge transport, and bandgap alignment across the interfaces. The intimately diffused p-n interface offers high potential for highly sensitive light-sensor. Other potential applications could involve light emitting device and photovoltaic application; relying on controllable stoichiometric gradient.

7.3 Outlook: homopolymer assisted inorganic nano-materials synthesis

The research field of nano-materials synthesis has advanced greatly within past several decades, seeing both improved knowledge in materials science and constantly updated development of more cost-effective, reliable, and facile synthesis or fabrication techniques. From pragmatic perspective, it is desirable to develop a library of model-structured homopolymer assisted inorganic nano-materials synthesis. This is beneficial in terms of both the fundamental understanding and industrial/technological interests. Novel hybrid materials made up of homopolymers and inorganic nano-materials with tailorable structural, compositional, and functional properties can be prepared in facile

manner. Such hybrid materials can be chemically clean as the polymeric materials can act not only as template, but also as stabilization or coordination species; potentially able to be directly incorporated into functional devices. This goal however requires further exploration and utilization of other unique characteristics of homopolymer with simplistic molecular architecture and functionality; in controlling formation of inorganic nano-materials.

This concept goes beyond simple coordination or confinement functions; instead, it is the nucleation and growth phases that need to be intelligently perturbed. In-depth understanding on the specific coordination between long chain homologous structured organic molecules and nano-particles is particularly important. For instance, a conducting homopolymer not only directs the growth, but also coordinates to the photo-sensitive nano-materials; creating hybrid structure with intimate interface for charge transport. The study on the homopolymer functions can generate more insights on many novel phenomena such as biological mineralization or employment in new applications such as stimuli-responsive functional nano-composites or meta-materials. Again, homopolymer served as a model for studies of relevant synthesis systems. Based on solid understanding of homopolymer systems, imagine a tailorable polymeric structure, not restricted to homopolymer, that can be synthesized through selection of desirable functionality, chain length and architecture; intended to suit specific applications. It is believed that polymer-assisted synthesis is a research direction that bears many more possibilities.

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Appendix A

		P.g.
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Figure A3.3. The detailed solid light scattering (SLS) results used for R_g determination, the angle used for the measurement are: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140. The plots correspond to (a) sample A: pH 5, $[Cu^{2+}]:[COOH]_0 = 0.05$; (b) sample B: pH 5, $[Cu^{2+}]:[COOH]_0 = 0.075$; (c) sample C: pH 6.6, $[Cu^{2+}]:[COOH]_0 = 0.125$; at different heating duration at 55 °C ('1': 1.5h, '2': 3h; '3': 4.5h). 160

Figure A3.4. The definition of upper and strict binding limits of PAA at initial pH= 5. This slope change is more obvious at low pH and high ionic contents (weak electrostatic attraction). 163

A4 Supplementary TEM images

Figure A4.1. TEM images of (a) stained nano-tubular CuO_x obtained; the stained portion i.e. PAA was found to wrap the entire nano-crystals, after staining, the tubular structures appeared larger due to swelling and absorption of staining molecules; (b) whiskers-like morphology of Cu_2O (from SAED) formed without adding in any PAA (0.21875mM $CuCl_2 \cdot 2H_2O$ and 0.01M $NaNO_3$; hydrolyzed (5h) and heated at 55 °C (3h)); it is observed to be anisotropic aggregation of smaller crystals. 165

A5 Morphology of spherical Cu nano-crystals

Figure A5.1. Spherical Cu nano-crystals obtained in the PAA-templated synthesis. 166

A1. Construction of 3D diagram showing the relationship among pH, α , and $[\text{Cu}^{2+}]:[\text{COOH}]_0$

Figure A1.1. pH- α relationship of mixture of 1.25mM PAA and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with different $[\text{Cu}^{2+}]:[\text{COOH}]_0$ ratio, obtained in titration experiment B. Only the data within range of pH 4 to 7 was used in the 3D diagram construction.

Curve-fitting of the pH- α curves within region from pH 4 to pH 7 was done. After that, a regular array of data ('estimated α ' based on known pH and $[\text{Cu}^{2+}]:[\text{COOH}]_0$) can be generated using Matlab software (griddata function, linear estimation); as shown in Table A1.1. The construction of 3D diagram based on the data array can then be done, as shown in Figure A1.2.

Table A1.1. The degree of deprotonation (α) estimated using Matlab software.

	$[\text{Cu}^{2+}]:[\text{COOH}]_0$						
	0	0.05	0.075	0.125	0.175	0.25	0.375
pH	α						
4.1	-	-	-	-	0.011	0.077	0.004
4.2	-	-	-	0.013	0.065	0.119	0.054
4.3	-	0.020	0.038	0.061	0.117	0.154	0.098
4.4	0.018	0.019	0.078	0.101	0.159	0.185	0.137
4.5	0.044	0.033	0.112	0.134	0.191	0.212	0.174
4.6	0.070	0.063	0.107	0.162	0.218	0.236	0.206
4.7	0.095	0.092	0.134	0.198	0.241	0.257	0.235
4.8	0.120	0.128	0.153	0.215	0.246	0.275	0.260
4.9	0.145	0.166	0.183	0.227	0.258	0.292	0.282
5.0	0.169	0.202	0.218	0.246	0.288	0.308	0.301
5.1	0.193	0.236	0.250	0.276	0.293	0.321	0.319
5.2	0.217	0.252	0.281	0.302	0.319	0.334	0.336
5.3	0.242	0.268	0.294	0.305	0.321	0.345	0.352
5.4	0.267	0.283	0.292	0.326	0.350	0.355	0.368
5.6	0.292	0.304	0.315	0.341	0.357	0.365	0.383
5.7	0.318	0.336	0.345	0.361	0.386	0.374	0.397
5.8	0.344	0.367	0.370	0.391	0.404	0.383	0.411
5.9	0.369	0.396	0.401	0.406	0.423	0.393	0.425
6.0	0.395	0.424	0.447	0.426	0.418	0.402	0.438
6.1	0.421	0.445	0.472	0.454	0.451	0.413	0.450
6.2	0.447	0.469	0.497	0.484	0.477	0.423	0.462
6.3	0.474	0.494	0.492	0.488	0.504	0.435	0.473
6.4	0.501	0.519	0.527	0.510	0.525	0.446	0.484
6.5	0.529	0.546	0.561	0.531	0.536	0.457	0.493
6.6	0.556	0.574	0.581	0.561	0.538	0.469	0.502
6.7	0.582	0.595	0.587	0.576	0.545	0.480	0.510
6.8	0.608	0.620	0.619	0.603	0.585	0.491	0.518
6.9	0.634	0.639	0.642	0.621	0.585	-	-

Figure A1.2. 3D diagram showing the relationship among pH, α , and $[\text{Cu}^{2+}]:[\text{COOH}]_0$.

A2. Further analysis of ITC data

It is also meaningful to look at the enthalpy change (ΔH) with respect to $[\text{Cu}^{2+}]:[\text{COO}^-]$ during ITC experiments; and degree of deprotonation (α) is required for this purpose. To obtain α which was not measurable during ITC runs, firstly, separate titration experiments were carried out by titrating $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ into 1.25mM PAA solution; establishing relationship of pH vs. $[\text{Cu}^{2+}]_t$ (Figure A2.1). Secondly, using the 3D diagram plotting the relationship among pH, α , and $[\text{Cu}^{2+}]:[\text{COOH}]_0$ (Figure A1.2), the α could be estimated. Same sets of pH (i.e. 3.6, 4.4, 4.7, 5.0) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and PAA solutions of ITC samples were used for titrants and titrands. By assuming that the effect of dilution of PAA during ITC or titration experiments towards α was negligible, pH change during ITC runs can be estimated from pH- $[\text{Cu}^{2+}]_t$ graph (Figure A2.2). Due to the difference in working principles of ITC and titration, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (titrant) used for titration has a larger concentration than that used for ITC (20mM vs. 8mM).

Figure A2.1. Measured pH by titrating CuCl_2 solution into PAA solution (1.25mM); with different initial pH of both $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and PAA solutions.

Figure A2.2. Estimated pH of mixture of PAA and Cu^{2+} during ITC experiments.

As shown in Figure A2.3 are the estimated α (using 3D diagram) and ΔH plotted vs. $[\text{Cu}^{2+}]_t : [\text{COOH}]_0$ for initial pH 5 and pH 4.7 (Figure A2.3(a)); together with the re-plotted data with $[\text{Cu}^{2+}]_t : [\text{COO}^-]$ as y-axis (Figure A2.3(b)). Notice that for pH 4.4 and pH 3.6; the estimated α is too low for any meaningful interpretation. Besides that, despite the similarity in shape of both α curves in Figure A2.3(a), the value of α are very different.

For pH 5 curve, a drop in ΔH is observed at ratio ~ 0.6 . This is close to theoretical binding limit which is $[\text{Cu}^{2+}] : [\text{COO}^-] = 1:2$. At lower pH ($=4.7$), the binding ratio at where the ΔH drop happened is larger (~ 1.75) and more scattered. It is believed that during this ΔH drop (or α surge) in Figure A2.3(b), the PAA- Cu^{2+} complexes experienced structural collapse that was responsible this rapid event. Although chain collapse is intuitively expected, experimental proofs are lacking. The characterization results clearly verify such phenomenon taking place within a short time-frame. The difference as observed in Figure A2.3(b) for pH 5 and pH 4.7 ITC runs, shows the

significant role played by electrostatic interaction. Note that at low pH, the ionic background screens the weaker $\text{COO}^-/\text{Cu}^{2+}$ attraction more effectively. For pH 4.7 ITC run, with lower pH (lower α), its binding was delayed and the pH remain stable during the complexation; until higher $[\text{Cu}^{2+}]$ induce a greater extent of PAA deprotonation; which is believed to follow a chain collapse. The ΔH drop that appeared at larger $[\text{Cu}^{2+}]_t:[\text{COO}^-]$ ratio, which could be related to complexation involving bridging phenomenon that does not necessary restricted by 1:2 ratio for $[\text{Cu}^{2+}]_t:[\text{COO}^-]$.

Figure A2.3. Re-interpretations of the ITC data which show (a) α versus $[\text{Cu}^{2+}]_t:[\text{COOH}]_0$ and (b) α versus $[\text{Cu}^{2+}]_t:[\text{COO}^-]$ during ITC runs for initial pH of 4.7 and 5.

A3. Light Scattering studies on PAA-Cu²⁺ complexes after hydrolysis and heating

Dynamic light scattering (DLS) and static light scattering (SLS) studies were carried out using Brookhaven Instrument Corporation (model: BI-APD). The LS results revealed the influence of chain stiffness towards the morphologies of PAA-Cu²⁺ complexes after hydrolysis and heating. Notice that with the equipment used in this work, the simple mixture of PAA and Cu²⁺ (before hydrolysis step) could not provide high enough measurement intensity due to low scattering contrast. Three samples with different pH and [Cu²⁺]:[COOH]₀ had been studied (see table for sample conditions) and the results are shown in Figure A3.1. Included in Figure A3.2 and Figure A3.3 are the characteristic relaxation time distribution functions and dependence of decay rate Γ on q^2 plotted for R_h determination, as well as the detailed SLS results for R_g determination; respectively.

Sample	pH	[Cu ²⁺]:[COOH] ₀
A	5	0.05
B	5	0.075
C	6.6	0.125

Sample with pH=6.6 and [Cu²⁺]:[COOH]₀=0.175 was not able to be measured due to the difficulty of filtering through 45 μ m filter; as the products tended to aggregate. Nevertheless, LS studies provided important information on the PAA-Cu²⁺ interactions. R_h (obtained by DLS) is related to the stiffness of chain during shrinkage or stretching of PAA chain while R_g (obtained by SLS) is an indication of the distribution of Cu²⁺ (related to core compactness).

Notice that although the strict binding limit of pH=5 PAA is only 0.044, it is believed that the gentle slope going up during Cu²⁺ measurement (beyond

$[\text{Cu}^{2+}]:[\text{COOH}]=0.044$) indicates a screened interaction that involves further slowly progressing binding phenomena. As illustrated inside Figure A3.4, using two intersecting sloped lines, the ‘upper binding limit’ was estimated to be ~ 0.09 . This again highlights the importance of electrostatic attraction; which enable fast complexation especially at high pH.

Figure A3.1. Results of dynamic and static light scattering showing the hydrodynamic radius (R_h) and radius of gyration (R_g) of PAA- Cu^{2+} complexes at different conditions: (a) sample A: pH 5, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.05$; (b) sample B: pH 5, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.075$; (c) sample C: pH 6.6, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.125$; at different heating duration at 55 °C.

Figure A3.2. The characteristic relaxation time distribution functions and dependence of decay rate Γ on q^2 plotted for R_h determination; corresponding to (a) sample A: pH 5, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.05$; (b) sample B: pH 5, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.075$; (c) sample C: pH 6.6, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.125$; at different heating duration at 55 °C (‘1’: 1.5h, ‘2’: 3h, ‘3’: 4.5h).

Figure A3.3. The detailed solid light scattering (SLS) results used for R_g determination, the angle used for the measurement are: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140. The plots correspond to (a) sample A: pH 5, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.05$; (b) sample B: pH 5, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.075$; (c) sample C: pH 6.6, $[\text{Cu}^{2+}]:[\text{COOH}]_0 = 0.125$; at different heating duration at 55 °C ('1': 1.5h, '2': 3h; '3': 4.5h).

Figure A3.4. The definition of upper and strict binding limits of PAA at initial pH= 5. This slope change is more obvious at low pH and high ionic contents (weak electrostatic attraction).

At pH 5, R_h is smaller and R_g is larger for lower Cu^{2+} loading (sample A) as compared to higher loading (sample B). At lower Cu^{2+} loading (sample A), the PAA chain contracted more and had a more distributed Cu^{2+} cation. With higher Cu^{2+} loading (Sample B), the stiffness of the PAA chain increase and resulted in restricted contraction. Smaller R_g for sample B may indicate a more compact core. With heating, the R_h of sample B decreased clearly; which could be understood based on counterion induced shrinkage with increased chain flexibility and decreased solution viscosity. Eventually, the R_h of sample B is smaller than that of sample A at heating of 4.5 hours. As for sample A, the chain will stretch slightly at heating, thus giving a small increase of R_h . LS results showed that at higher pH (sample C), the R_h and R_g are more stable throughout the heating duration. This refers to the fact that the chain conformation does not vary much at higher pH and higher Cu^{2+} loading; as counterion ion induced collapse and chain stiffness effect can reach equilibrium very fast.

Looking at the values of R_g/R_h , sample A (pH 5, $[Cu^{2+}]:[COOH]_0 = 0.05$) adopted a near hard sphere structure (theoretical hard sphere has $R_g/R_h \sim 0.774$). For sample C (pH 6.6, $[Cu^{2+}]:[COOH]_0 = 0.125$), it appeared to possess a core-shell structure; i.e. inner core is Cu^{2+} concentrated with PAA chains interacting with external solvent environment (theoretical core-shell has $R_g/R_h < 0.6$). Interestingly, sample B (pH 5, $[Cu^{2+}]:[COOH]_0 = 0.075$) has an increased R_g/R_h with the time of heating. This is believed to be due to a transition to more core-shell structure to hard-sphere structure; indicating chain collapse throughout the heating. In fact, it is proposed that the chains of sample C when loaded with more Cu^{2+} was stiffer initially (comparing with sample B and C); only collapsed afterward with the extent of heating. Of course, more characterization results are required to verify this proposition.

The LS results support the proposition that block copolymer-like nature could be found on the PAA- Cu^{2+} since core-shell like micelle could be formed. This also showed that at high pH (i.e., high α), such block copolymer-like nature is more favored.

A4. Supplementary TEM images

Figure A4.1. TEM images of (a) stained nano-tubular CuO_x obtained; the stained portion i.e. PAA was found to wrap the entire nano-crystals, after staining, the tubular structures appeared larger due to swelling and absorption of staining molecules; (b) whiskers-like morphology of Cu_2O (from SAED) formed without adding in any PAA (0.21875mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.01M NaNO_3 ; hydrolyzed (5h) and heated at 55 °C (3h)); it is observed to be anisotropic aggregation of smaller crystals.

A5. Morphology of spherical Cu nano-crystals

Figure A5.1. Spherical Cu nano-crystals obtained in the PAA-templated synthesis.

Certain amount of spherical Cu nano-particles with diameter of 8(+/-3) nm was observed; as shown in Figure A4.1. The spatial amount of Cu^{2+} atoms was restricted by steric hindrance of the PAA chains; keeping the individual nano-particles separated. During hydrolysis step, further deprotonation of COOH into took place upon addition of NaOH. High charge density resulted in expansion of the PAA chain and more efficient repulsion among charged PAA- Cu^{2+} complexes. This effect further resulted in overall uniform diameters of spherical Cu nano-crystals. The SAED and lattice spacing showed that the nano-crystals were of Cu phase.

Appendix B

		P.g.
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B6 Detailed atomic absorption spectroscopy (AAS) of synthesized ClSe nano-particles

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B1. Phase diagram of CuInSe_2 **Figure B1.1.** Phase diagram of CuInSe_2 showing the phases at different Cu:In ratio.

(Extracted from reference: Journal of Applied Physics, 2000. 87(8): p. 3683-3690.)

B2. Absorbance spectra of ClSe samples synthesized at lower temperature

Figure B2.1. The UV-Vis absorbance spectra of ClSe nano-particles synthesized at lower growth temperature. The broad absorption shoulder at higher wavelength (>1000nm) is attributed to Cu_{2-x}Se ; indicating intermediates remained after extended synthesis time. (solution samples in toluene)

To study the effect of growth temperature required for Cu-based and In-based intermediate to react into ClSe, lower growth temperatures including 200 °C and 220 °C had been attempted (solvent is DPE). (Note: in the trial experiments, injection and growth temperatures were set as the same.) However, prolonged synthesis time up to 18h was insufficient for the reaction to reach completion. To ensure complete conversion to ClSe from intermediates, 260 °C was eventually selected.

B3. Detailed thin film XRD of synthesized CISE nano-particles

Figure B3.1. Thin film XRD spectra of synthesized CISE nano-particles using different synthesis parameters.

Figure B3.2. XRD spectra of CISE nano-crystals which were synthesized inside diphenyl ether (DPE) at low reaction temperatures and longer growth durations. Existence of Cu-based and In-based binary intermediates was more evident.

B4. Summary of measured of calculated size of CISE nano-crystals**Table B4.1.** Mean size of synthesized CISE nano-crystals (size in nm) measured from TEM images and calculated using Scherrer equation based on TFXRD results.

	6 mins			30 mins			1 h		
	TEM		Using Scherrer Eqn	TEM		Using Scherrer Eqn	TEM		Using Scherrer Eqn
	mean	stdev		mean	stdev		mean	stdev	
A1	5.9	1.3	19.7	9.2	2.3	22.2	8.0	1.7	20.0
A2	4.0	0.7	14.0	6.2	1.1	18.0	6.8	1.2	17.3
A3	3.9	0.5	14.9	8.7	1.5	19.0	7.7	1.7	22.8
B1	13.5	5.4	16.2	18.6	5.5	16.6	20.9	4.7	15.9
B2	12.4	2.7	10.5	17.8	4.4	10.1	14.0	2.2	8.5
B3	5.8	1.1	14.6	7.6	1.8	16.4	9.7	1.8	12.5

B5. Detailed UV-Vis absorption spectra of synthesized ClSe nano-particles

Figure B5.1. UV-Vis absorption spectra of synthesized ClSe nano-particles using different synthesis parameters (solution samples in toluene); (a-1) to (a-3) correspond to sample A1 to A3 synthesized without P3HT; while (b-1) to (b-3) correspond to sample B1 to B3 synthesized with P3HT.

Figure 5.2. The time dependent disappearance of absorbance shoulder ($>\sim 1000\text{nm}$); indicating the existence of Cu_{2-x}Se intermediate which converts to CISE with longer reaction time (solution samples in toluene).

Figure B5.3. Absorbance shoulders as observed in samples synthesized in DBE and DPE (solution samples in toluene), (a) without P3HT; (b) with P3HT. Both of the samples were prepared at hot-injection and growth temperature of 260 °C. The results clearly showed the importance of selection of solvent.

B6. Detailed atomic absorption spectroscopy (AAS) of synthesized ClSe nano-particles

Figure B6.1. AAS results of ClSe synthesized nano-crystals: (a) 6 minutes reactions without P3HT, at different synthesis conditions; (b) 6 minutes reactions with P3HT, at different synthesis conditions.

Table B6.1. Summary of AAS results of synthesized ClSe nano-particles

	6 mins			30 mins			1 h		
	Cu	In	Se	Cu	In	Se	Cu	In	Se
	(at%)	(at%)	(at%)	(at%)	(at%)	(at%)	(at%)	(at%)	(at%)
A1	29.27	21.78	48.95	23.47	22.77	53.76	24.25	25.07	50.67
A2	22.28	20.18	57.54	27.25	24.85	47.89	24.15	21.69	54.17
A3	21.05	21.38	57.57	18.91	16.83	62.89	20.98	17.94	61.07
B1	33.68	22.65	43.68	28.69	24.11	47.20	28.75	22.39	48.86
B2	19.67	26.37	53.96	17.79	19.62	62.60	17.88	16.94	65.19
B3	15.96	30.23	53.81	16.42	28.22	55.37	21.27	26.96	51.77

B7. Detailed XPS data of synthesized CISE nano-particles

Figure B7.1. XPS spectra showing binding energy peaks of different elements on surface of synthesized nano-crystals: (a) A1: without P3HT, 290+ 260 °C; for 30 minutes (b) B1: with P3HT, 290+ 260 °C; for 30 minutes. Hydrazine treatment was adopted to remove surface ligands to enhance the signals of inorganic elements.

The spectra of each of the main elements including Cu, In, Se, P, S will be shown in Figure B7.2.

Figure B7.2. XPS spectra of individual element of interests in samples A1 (290 °C+ 260 °C, higher concentration, without P3HT) and B1 (290 °C+ 260 °C, with P3HT): (a) Cu; (b) In; (c) Se; (d) P; (e) S.

B8. Synthesis experiments of binary chalcogenides: Cu_{2-x}Se and In_2Se_3 **Table B8.1.** Parameters used for synthesis of Cu_{2-x}Se or In_2Se_3

Sample	$\text{Cu}(\text{acac})_2$ (mg)	$\text{In}(\text{acac})_3$ (mg)	Se (mg)	DBE (mL)	TOP (mL)	P3HT (mg)	Reaction temp. ($^{\circ}\text{C}$)
A (Cu)	87.7	-	216	10	2	-	290+ 260 $^{\circ}\text{C}$
B (In)	-	138.1	216	10	2	-	290+ 260 $^{\circ}\text{C}$

Figure B8.1. Morphologies of synthesized Cu_{2-x}Se (A) and In_2Se_3 (B) nano-particles as observed by TEM, of two different reaction durations: 6 mins and 15 mins.

Figure B8.2. Size evolution of synthesized nano-crystals: (A) Cu_{2-x}Se nano-crystals and (B) In₂Se₃ nano-crystals; of two different reaction durations: 6 mins and 15 mins.

B9. Investigation of thermal decomposition of $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$
using TGA

Thermogravimetric analysis (TGA) was carried out in N_2 environment using TA Q500.

The heating rate used was $8\text{ }^\circ\text{C}/\text{min}$

Figure B9.1. TGA results showing the thermal decomposition behaviour of individually $\text{Cu}(\text{acac})_2$ and $\text{In}(\text{acac})_3$.

B10. Study on the interaction between P3HT and Cu^{2+} and In^{3+}

Two different techniques have been employed to study the coordination between P3HT with Cu^{2+} or In^{3+} : (i) solution UV-Vis, and (ii) thin film XRD (TFXRD). The interaction was studied based on the changes observed of characteristic P3HT absorbance peak and XRD peaks.

Mimicking the CISE synthesis procedures, P3HT with either $\text{Cu}(\text{Acac})_2$ or $\text{In}(\text{Acac})_3$ were heated up in DBE at 290+260 °C (i.e. heated to 290 °C and cooled to 260 °C). Note: no injection was done. The temperature profile was the same as actual CISE nano-particles synthesis.

As shown in Figure B10.1 is the absorbance spectra of five different samples.

Figure B10.1. Absorbance spectra of P3HT-based samples (in toluene) prepared by mimicking the actual CISE synthesis route; for the purpose of studying the coordination between P3HT and Cu^{2+} or In^{3+} .

The obvious shift of UV-Vis absorbance peak of pure P3HT (~452nm) to lower wavelength (~420nm) with the presence of $\text{Cu}(\text{acac})_2$; indicating formation of charge-transfer complex due to overlapping of electronic orbital. Interestingly, for $\text{In}(\text{acac})_3$, no shift of 452nm was observed, but additional small peak at ~610nm could be

observed. These changes when compared to the absorbance spectra of pure P3HT is very interesting and serves as preliminary evidence of coordination between the P3HT and Cu^{2+} (or In^{3+}) in solution phase.

For the TFXRD results, the (100) peak of P3HT at around 5.5° shifted to smaller 2θ in presence of both Cu^{2+} or In^{3+} ; indicating disruption of intrinsic P3HT crystallinity. Another obvious observation is the emergence of strong peak at $\sim 7.6^\circ$; as compared to that of pure P3HT. The possible reason is the insertion/intercalation of Cu^{2+} or In^{3+} in between the P3HT crystal; in the thin film form. Nevertheless, when comparing the XRD spectra of P3HT- Cu^{2+} and P3HT- In^{3+} , no obvious differences could be observed.

Figure B10.2. TFXRD spectra of P3HT-based samples (casted on silicon wafer) prepared by mimicking the actual CISE synthesis route. The shifting of (100) peak of P3HT to smaller 2θ suggests the larger spacing between P3HT chain, which could be due to the insertion of metallic species.

Both of the UV-Vis absorption and TFXRD results suggested strongly that, qualitatively, there exist coordination or interaction between P3HT with Cu^{2+} or In^{3+} ; more detailed study needs to be carried out for quantitative analysis of the

coordination strength difference for Cu^{2+} and In^{3+} . The chemistry of the interaction also requires much intensive study, before a well-controlled synthesis system based on coordination species could be developed.

List of Publications

1. Y.N. Liang, J. Hu, M.K.C. Tam, and X. Hu, *CuO_x nanotubes via an unusual complexation induced block copolymer-like self-assembly of poly(acrylic acid)*. RSC Advances, 2012. 2(25): p. 9531-9537.
2. Y.N. Liang, K. Yu, Q. Yan, X. Hu, *Colloidal CuInSe₂ Nanocrystals from Gradient towards Homogeneous Alloyed Structure Moderated by Conducting Polymer P3HT*. ACS Applied Materials & Interfaces, Accepted with minor correction
3. A. Chaurasia, L. Wang, L.H. Gan, T. Mei, Y. Li, Y.N. Liang, and X. Hu, *Polymerothermal Synthesis – A Facile and Versatile Method towards Functional Nanocomposites*. European Polymer Journal, 2013. 49(3): p. 630-636.
4. Y.N. Liang, B.K. Lok, L. Wang, C. Feng, A.C.W. Lu, T. Mei, and X. Hu, *Effects of the morphology of inkjet printed zinc oxide (ZnO) on thin film transistor performance and seeded ZnO nanorod growth*. Thin Solid Films, 2013. 10.1016/j.tsf.2013.01.032.
5. T.R.B. Foong, Y.N. Liang, X. Hu, *Anodic Aluminum Oxide (AAO) Templates on Transparent Conducting Oxide Coated Glass: New Prospects for a Mature Nano-Fabrication Tool*, Nanoscience and Nanotechnology Letters, 2012, 4(5): p. 494-504.
6. S. W. Zeng, Y.N. Liang, H.F. Lu, L. Wang, X.Q. Dinh, X. Yu, H.P. Ho, X. Hu, K.T. Yong, *Synthesis of symmetrical hexagonal-shape PbO nanosheets using gold nanoparticles*, Materials Letters, 2012, 67(1): p. 74-77.
7. B.K. Lok, Y.M. Ng, Y.N. Liang, X. Hu, *Inkjet Printing of Multi-Walled Carbon Nanotube/Polymer Composite Thin Film for Interconnection*, Journal of Nanoscience and Nanotechnology, 2010, 10(7): p. 4711-4715.