(Micro)spectroscopy investigations of the properties of soft colloidal particles and perovskite materials

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(Micro)spectroscopy investigations of the properties of soft colloidal particles and perovskite materials

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SUMMARY

This thesis utilizes (micro)spectroscopy techniques to investigate crystallization behavior of soft colloidal particles, properties of perovskite quantum dots and interactions between perovskite microrods and upconversion nanoparticles. Our aim is to investigate the phase transition behavior of colloidal particles, fine-tuning PL emission of perovskite quantum dots with high quantum efficiency and excitation of upconversion nanomaterials by perovskite microrods.

Chapter 1 provides general introduction of on synthesis and characterization of poly(N-isopropylacrylamide) (pNIPAm) microgel particles. Particular attention will be given to the recent studies on the stimuli-responsive volume transitions and crystalline behavior of pNIPAm-based soft colloidal particles. Fabrication of hybrid metal halide perovskite materials both in bulky and nano scaled will be summarized, along with the applications of perovskite materials investigated in this decades.

In Chapter 2, monodisperse microgel colloids were synthesized via free radical precipitation using pNIPAm and 2-aminoethyl methacrylate hydrochloride (AEMA) as monomers. In this poly(NIPAm-co-AEMA) suspension, single particle tracking at the fluid-to-crystal phase transition were investigated via wide-field microscopy (WFM). Based on the mean square displacement (MSD) analysis on trajectories of colloidal particles, two types of particle motions were investigated, along with the influence of pH on phase transition.

In Chapter 3, pure cubic phase perovskite quantum dots (PK QDs) composed by

$\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ alloy were successfully prepared via a facile ligand-assisted reprecipitation (LARP) method at room temperature. Substitution of organic cations and halide anions achieved fine tuning of photoluminescence emission of the PK QDs. The as-synthesized PK QDs have high quantum efficiencies peaking at 84%, which could even rise to 96% after 12 h of resting time.

In Chapter 4, we have synthesized $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ perovskite microrods in a two-step solution based method, in which the perovskite microrods are converted from pre-synthesized PbI_2 microrods by a fast in situ solid-liquid interfacial conversion reaction. Two morphologies of Er-Nd doped nanomaterials were synthesized, where nanorods with hundreds of nanometers lengths and aspect ratio around 10; nanoparticles with tens of nanometers diameters, both of the nanomaterials exhibit monodispersion in size. The photoluminescence and lifetime trajectories were recorded to investigate the interaction between perovskite and upconversion materials.

Chapter 1 General Introduction

1.1 Introduction of pNIPAm-based microgel

Microgel suspensions of assembled soft colloidal particles have been studied for decades for their stimuli-sensitive properties, unique softness in particle behavior and their utility in numerous applications. Since the first published account of thermo-sensitive poly(*N*-isopropylacrylamide) microgels in 1986¹², pNIPAm-based microgels have attracted increasing amounts of attentions from scientists due to their potential use in both academic and industrial fields. The multi-sensitive properties of pNIPAm make it possible to tune their size by changing the ionic strength¹³, pH¹⁴, temperature¹⁵, ultrasound¹⁶ and solvent composition¹⁷, which enriches the particle behaviors during phase transition.

In addition to their significance in theoretical component of materials science, microgel suspensions have extensive applications in nano-imprint¹⁸, food, cosmetics, drug delivery¹⁹ and optical devices²⁰. In the context of pNIPAm-based microgel's multi-responsive properties, increasing number of studies has focused on the fabrication of pNIPAm-based soft colloidal suspensions as novel materials. Microlenses composed of pNIPAm-based particles offer a new method of device miniaturization, where dried microgels with plano-convex shapes on a substrate have the ability to project patterns in an ordered array²¹. Two dimensional arrayed pNIPAm-base crystal undergoes swelling on exposure to gradient concentrations of

surfactant solvent, which induces changes of crystal lattice accompanying changes in crystal color²². Within photolithograph technology, polymer crystal containing NIPAm can form photonic paper with thermo-tunable color read by water as ink²³. Thin microgel films with iridescent colors have the potential application as ink without

Figure 1.1. Photograph of test letters written from colorless microgel particle dispersions on a polystyrene substrate. Reprinted with permission from Langmuir⁶ copyright (2015) American Chemical Society.

pigments⁶ (Figure 1.1).

1.1.1 Synthesis and Characterization of pNIPAm-based microgel

The most commonly used method to synthesis pNIPAm-based colloidal particles is via emulsion polymerization¹ in aqueous solution and atom-transfer radical polymerization²⁴. The colloidal particles are basically composed of three parts: NIPAm is the main building block of thermo-sensitive microgel colloids,

Methylene-bis-acrylamide (BA) is commonly used as a cross-linker to co-polymerize with NIPAm, and functional co-monomers like 2-aminoethyl methacrylate (AEMA) and acrylic acid (AAc) can provide pH sensitivity to the microgels (Figure 1.2).

Figure 1.2. Monomers used in pNIPAm microgel synthesis.

The surfactant-free emulsion polymerization (SFEP) is ideally suited for the preparation of pNIPAm-based microgel particles²⁵, for it yields colloidal particles in a narrow size range, generally with a polydispersity below 10%, and simplifies the preparation procedure without the need for surfactant removal. The water-soluble initiator, such as ammonium persulfate (APS)²⁶ or potassium persulfate (KPS), undergoes thermal decomposition at $\sim 70^{\circ}\text{C}$ and releases free radicals which induces the NIPAm monomers to grow into polymer chains. When the surface activated oligomers

(negative charged by the sulfate groups) grow beyond a soluble length, the oligomers will form nuclei and the particle size increases in precipitation polymerization. When the surface charge of the particles reaches an electrostatic stabilization, the aggregation is reduced and eventually terminated by another radical species²⁷. The crosslinker monomer, BA, consumes much faster than NIPAm²⁸, thus the crosslinking density is decreasing from the surface to the center of a particle. The size and distribution of the microgel particles can be characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) in the dry state, and dynamic light scattering (DLS)^{1, 29}, small-angle neutron scattering (SANS)³⁰, and laser diffraction particle distribution instrument¹⁶ in the hydrated state.

Besides pure pNIPAm microgel, adding functional co-monomer has evidently expanded its application. The most commonly used modified method is to enable the pH responsiveness of the microgel by copolymerizing with ionic monomers, such as acrylic acid^{14, 16, 20c} (AAc) with negative charge at high pH and 2-aminoethylmethacrylate hydrochloride (AEMA) with positive charge at low pH. The amine group of AEMA can further functionalize the microgel particle by linking to fluorescent dyes via a variety of amine reactive dyes containing succinimidyl, NHS esters or carboxylic acid, such as commonly used succinimidyl ester (TAMRA)³¹ and Atto 647N-NHS ester. Methacrylic acid used as co-monomer can be fluorescently labeled by Rhodamine B³².

1.1.2 Stimuli-responsive Volume Transitions

The stimuli-responsive volume transitions of pNIPAm materials are briefly summarized in Table 1.1.

Table 1.1. Summary of stimuli-responsive volume transitions of pNIPAm microgel particles

Number	Inducements	Volume Transition
1	Temperature	Radius reduces with increasing temperature
2	pH	When functionalized with $-\text{COOH}$ groups, the radius increases with increasing pH value; when functionalized with $-\text{NH}_2$ groups, the radius changes in opposite trend
3	Ultrasound	When exposed to ultrasound, the radius increases

1.1.2.1 Thermal-induced Volume Transition

The most unique property of pNIPAm-based microgel is their thermal sensitivity correlation. The first correlation of particles sizes as a function of temperature was

plotted by Pelton et al.³³, which quantitatively indicates the sensitive response of microgel to temperature.

Figure 1.3 DLS data of hydrodynamic radius plotted as a function of temperature for pNIPAm particles in water. Reprinted with permission from The Journal of Physical Chemistry B³.

At low temperature, the hydrophilic amide residues of pNIPAm microgel are hydrogen bonded to water molecules. The microgel particles are well swollen containing around 90 vol% of water. When the temperature is elevated gradually, water molecules inside the polymer network are compelled out due to the breaking of the hydrogen bonds. As the microgel particles become insoluble in water, the suspension becomes turbid with reducing transmission of light. The lower critical solution temperature (LCST) is thus defined when 90% of the light transmission is not allowed³⁴. Around the LCST, ~32°C for pure pNIPAm microgel, the particles undergo a hydrophobic collapse with a coil-to-globule transition (Figure 1.3). Even in the collapsed state, the amide residues are engaged in hydrogen bonding to water

molecules other than interamide hydrogen bonding²⁹. The crosslinker BA is not involved in the hydrogen bonds, but it can confine the size changes by tuning the crosslinking density³⁵. In addition, the critical temperature can be tuned in the range of 32~50°C by copolymerizing with different ratios of acrylamide (AAm)³⁶, thus the microgel can be applicable *in vivo*.

1.1.2.2 pH-reduced volume transition

The pNIPAm-based microgel is sensitive to pH changes mainly due to the functional co-monomers. For the frequently used p(NIPAm-co-AAc) microgel particles, interactions between particles can be tuned from weak attractive, at low pH, to pure repulsive, at neutral and high pH.

Figure 1.4. Hydrodynamic radius of p(NIPAm-co-AAc) particles on the dependence of pH. Reprinted with permission from Journal of Physical Chemistry B³⁷ copyright (2008), American Chemical Society.

The hydrodynamic radius R_h of the microgel is sensitive to the changes of pH²⁶.

The pH response of particle sizes mainly originates from the electrostatic interactions between the ionic groups. For AAc incorporated microgel particles, R_h increases with increasing pH (Figure 1.4) and has a shape change near $pK_a = 4.25$ due to the electrostatic repulsion between the deprotonated AAc groups. Introduction of high ionic strength medium and inert electrolytes can efficiently screen the ionic groups and

Figure 1.5. Variation of the hydrodynamic diameter as a function of temperature of poly(NIPAm) microgel dispersions at different ionic strengths of electrolyte (NaCl). The concentrations of NaCl used were 0 (●), 10^{-4} (○), 10^{-3} (△), 10^{-2} (■), 10^{-1} (□), and 0.5 M (▲). Reprinted with permission from Langmuir copyright⁷ (2000).

thus limit the sensitivity of particle swelling to pH³⁸. As shown in Figure 1.5, with the addition of NaCl, the value of the hydrodynamic diameter of poly(NIPAm) decreases⁷.

1.1.2.3 Sono-reduced volume transition

Apart from the traditional stimulations, ultrasound exposure has recently been found to efficiently break the internal hydrogen bond and elevate the phase transition temperature of pNIPAm-co-AAc microgel (Figure 1.6)¹⁶.

Figure 1.6. Thermo-sensitive effect of hydrodynamic diameters of PNAM microgel irradiated with (○) 83 kHz US, (Δ) 48 kHz US, (□) 24 kHz US and (◆) without US. Reprinted with permission from Polymer Journal¹⁶ (US is ultra-sound).

The first shrinkage of the microgel is induced by the intermolecule hydrogen bond between amine groups and carboxylic acid and the second step is the desolvation of water. On exposure to higher frequency ultrasound, the diameters of the microgel are

shifted toward larger values.

1.1.3 Microgel Crystal Structure

As the pNIPAm-based microgel particles contain ~90% of water and their size is in the micron range, they can be observed via optical microscopy, such as bright-field microscopy and confocal microscopy¹ if they are labeled with fluorescent dyes. The crystal structure data can thus be extracted from optical images.

Figure 1.7. Left) Face-centered cubic unit cell; Right) paralleled 111 planes (A,B,C) shown in FCC unit cell².

The closest packed hard spheres assemble in a face-centered crystal structure with a volume fraction of 0.74 as shown in Figure 1.7.

The 3D radial distribution function (RDF) of pNIPAm-based crystal via confocal microscope indicates that the structure of the crystals of soft colloidal particles is also face-centered cubic (FCC), which is independent of the number concentration,

Figure 1.8. Radial distribution functions for various samples at different concentrations, monomer ratios and pH values show agreement with FCC crystal structure throughout. Reprinted with permission from Physical Review E⁵.

monomer ratio and pH⁵ (Figure 1.8). Besides, the crystal could retain its structure when subjected to external stress, resulting from the softness of the colloids.

In the context of loosely cross-linked pNIPAm particles at concentrations above the overlap concentration, as shown in Figure 1.9, hexagonal, trigonal and body-centered orthogonal crystals⁴ are found besides the FCC structure.

Figure 1.9. The phase diagram of ionic microgels with diameter $\sigma=100$ nm.

Reprinted with permission from Physical Review Letters ⁴.

The softness of microgel particles also enables particles with different diameters to form long-range ordered crystals. When large soft particles are added into small stiff particles, the former shows self-healing behavior and deforms to conform to the crystal lattice³⁹.

1.1.4 Crystalline Behavior

Crystallization is generally a phase transition from fluid state to long range ordered solid state. Understanding the mechanisms of crystallization is important for designing academic experiments and preparation of high quality crystals free of defects. The challenge of this study is that, during the crystallization process, atoms move too fast to be tracked and due to the small size of atoms, the phase transition process is unobservable under traditional optical microscopy. One alternative approach is to explore the crystallization process to model the typical atomic system. In the last few decades, poly(*N*-isopropylacrylamide)-based microgels emerged to be soft colloidal models due to their multi-stimuli sensitivities and intrinsic softness, which confer to the microgels richer phase behaviors than hard sphere dispersions.

In 1940s, The interactions between charged particles in aqueous dispersions were originally described by Derjaguin and Landau⁴⁰ and Verwey and Overbeek⁴¹ (DLVO theory) based on Debye-Huckel theory⁴². The calculation of particle interactions combines the electrostatic repulsion and the van der Waals attraction. In these theories, colloidal particles are classified into hard spheres, sticky hard spheres and soft spheres according to the shapes of their interparticle pair potential curves. The sterically stabilized poly(methyl methacrylate) (PMMA), polystyrene (PS) and silica spheres have been used as models for hard sphere systems and sticky hard sphere systems to

prove theoretical prediction and computer simulations of colloidal phase behaviors and particle interactions.

The crystallization process is mainly affected by effective volume fraction⁸, temperature and pH. Comparing to hard sphere assemblies, the microgel crystal structures is observed in a broader range of effective volume fraction⁸. The effective volume fraction is tunable in situ by changing the temperature^{20a}, thus crystallization behavior at different volume fraction can be studies by using only one batch of sample. When pNIPAm-based microgel particles are copolymerized with pH-sensitive monomers, like acrylic acid (AAc), interactions between colloidal particles can be tuned by changing pH value⁴.

1.1.4.1 Effect of volume fraction

For hard spheres, the crystalline behavior is only controlled by volume fraction Φ , whereas for soft repulsive colloidal particles, both Φ and their softness can influence the phase behavior.

Figure 1.10. Phase diagram of hard sphere system. Reprint with permission from Physical Chemistry B. ⁸

According to Figure 1.10, the volume fraction Φ in the range from 0.49 to 0.74 covers phases containing fluid (F), crystal (C) and glass (G) states⁴³. For Φ below 0.49, particles exhibit fluid state with no long-range correlation. Crystal state appears from $\Phi=0.49$, which is defined as the freezing point and dominates the system at Φ above 0.55, which is defined as the melting point, whereas between these two points, there exhibits the coexistence of fluid state and crystal state. Although the thermodynamic preferred state at Φ above 0.55 is crystalline conformation, glass state appears from 0.58 to 0.64 due to kinetic confinement. The highest volume fraction for hard sphere is $\Phi_{cp} = 0.74$ with a close-packed face-centered crystal structure.

In contrast, crystal state in soft colloidal system has a broader range of effective volume fraction Φ_{eff} compared to the hard sphere system. In the context of softness from pNIPAm-based colloidal particles, the particles maximize particle-particle contact by extending their sizes, which induces the existence of crystal state at Φ_{eff} below the freezing point. Again, for Φ_{eff} above 0.74, the soft particles are over-packed due to high osmotic pressure and maintain crystal structure at Φ_{eff} as high as 1.10, which in turn demonstrates the distinct compression⁸. Transitions from fluid to crystal, crystal to glass and fluid to glass have been thoroughly studied via RDF or pair-correlation function $g(r)$, which means the number density of particles varies as a function of distance from a reference particle. The range of crystalline assembly can be tuned even broader by adding the AAc component, which enhances particle-particle attraction due to AAc dimerization and/or AAc-amide interaction (Figure1.11).

Figure 1.11. Differential interference contrast microscopy images of pNIPAm-AAC colloidal crystals ($R_h = 410$ nm). The polymer concentrations in weight percent are indicated on each image, along with the hard sphere (Φ_{HS}) and effective (Φ_{eff}) particle volume fractions. Scale bars = 1 μ m. Reprint with permission from Physical Chemistry B ⁸

Figure 1.12. Pair-correlation functions $g(r)$ with increasing Φ_{eff} . Inset: magnified view of the second peak. Reprint with permission from Soft Matter¹.

Transitions from fluid to crystal, crystal to glass and fluid to glass have been thoroughly studied via RDF or pair-correlation function $g(r)$, which means the number density of particles varies as a function of distance from a reference particle. For a wide range of Φ between $0.52 < \Phi < 0.74$, evidences for both fluid-crystal and fluid-glass transitions have been observed. The split second peak in the $g(r)$ plot is a characteristic structure signature for 2D hexagonal crystals. With increasing $\Phi_{eff} > \Phi_{cp}$,

the split of the second peak disperses and become smooth¹ at the same time the height of the first peak passes a maximum value and decreases (Figure 1.12). Changes of the configuration in $g(r)$ figures indicate the shrinking and interpenetration of soft colloidal particles, which can reduce the free energy induced by high Φ_{eff} .

1.1.4.2 Effect of pH

For p(NIPAm-co-AAc) microgel, at low pH (< 6), hydrogen bonds existing among the carboxylic acid groups and water give rise to a weak attraction between particles. Therefore, the crystallization is the result of attraction-induced nucleation¹⁴. In contrast, at neutral and high pH, the carboxyl groups are deprotonated with negative charge, which induces electrostatic repulsion, and crystallization is thus driven by entropic force²⁶.

Muluneh *et al.* followed the evaluation of the soft colloidal system after quenching from liquid state¹⁴. At low pH and low concentration, crystallization driven by the attractive interaction occurs throughout the sample, while at high concentration, the microgel evolves into a disordered solid. At neutral pH, phase behavior is only determined by particle number density with glassy state at high concentration. At the glass state, microgel particle possesses the features of glass formation in molecule materials, phase behavior containing glass state also drew considerable attentions from researchers⁴⁴.

1.1.4.3 Particle behavior in microgel crystallization

In the last decade, the movements of colloidal particles were monitored via normal optical microscopes. Their relatively slow motions make real-time single particle tracking possible and hence reveal details in crystallization transition as well as melting process.

Figure 1.13. (a) Schematic of linear growth colloidal clusters. A and B are two positions near the cluster. The thin lines are the contour lines of screened coulomb potential. (b) At strong short-range attractions, the rearrangement forms string-like structures at attraction strength $U = -20.1k_bT$ and colloidal volume fraction $\Phi_c = 0.07$. Reprint with permission from Soft Matter⁵⁵

In the beginning of crystallization, small clusters form at low volume fraction. Zhang *et al.*⁴⁵ observed the shape and microstructure of the clusters changes depends on the strength of short-range attraction: from compact clusters at weak attractions to quasi-linear clusters at strong attractions. When the interactions between particles are long-range repulsions, the kinetic barrier at position A is about 2 times of that at position B. Hence, incoming particles are easier to reach position B, a linear growth is

Figure 1.14. Steering effect resulting from the long-range attraction. (a) Step peaks (pyramidal protrusions) on the growing front. (b, c) Incorporation process of particles A. (d) Trajectory of particle A. (e) Two-dimensional diffusion coefficient of colloidal particles on the glass substrate. Reprint with permission from Journal of Physical Chemistry C.⁵⁶

kinetically preferred (Figure 1.13).

In the study of two-dimensional crystallization of colloidal particles on glass substrate (Figure 1. 14), an incoming particle A moving towards the growing peak. Its motion changes from Brownian motion when it is 5 μm away from the cluster, then it moves directly towards the step peak. Compared to its diameter 1 μm, the distance 5

μm can be defined a long distance, within which exists an long-range attraction induced by the steering effect⁴⁶.

1.2 Introduction of Hybrid metal halide perovskite materials

1.2.1 Development of hybrid metal halide perovskite material

Hybrid metal halide perovskite (PK) materials have been attracting wide attention from the scientific community since their impressive optoelectronic properties were discovered by Tsutomu Miyasaka *et al.*⁴⁷ in 2009. Most notably, the world solar-power-conversion efficiency record based on lead halide perovskites has been dramatically improved from 3.8%⁴⁷ to 22.1%⁴⁸ in a remarkably short time span (2009-2017). Additionally, perovskite materials also exhibit potential applications in the fields of solid-state light-emitting devices such as lasers and light-emitting diodes (LEDs) due to their outstanding features of optical, photovoltaic and optoelectronic properties. Perovskites show many interesting properties such as large absorption coefficients⁴⁷, long life time, high charge mobilities⁴⁹, long-range balanced charge diffusion⁵⁰, and they can be prepared using low-cost solution-processable and facile deposition techniques. Strong photoluminescence and high absorption coefficients make metal halide perovskite a promising active material in LEDs (PeLEDs)⁵¹, sensitive photodetector⁵², laser diodes⁵³ and high-performance piezoelectric nanogenerator⁵⁴.

1.2.2 Compositions of hybrid metal halide perovskite material

The general formulation of lead halide perovskite is ABX_3 , where A is a monovalent organic cation such as methylammonium ($CH_3NH_3^+ = MA^+$) and

formamidinium ($\text{CH}(\text{NH}_2)_2^+ = \text{FA}^+$), or atomic cation Cs^+ ; B is Pb^{2+} or Sn^{2+} ; and X is often a halide anion Cl^- , Br^- or I^- .

The unit cell three-dimensional (3D) structure framework, perovskite is depicted in Figure 1.15. Each metal cation is surrounded by six halide anions to form an octahedron. The cation A is encapsulated in the voids of eight BX_6 octahedra in 3D structure, or sandwiched between corner-sharing BX_6 octahedral layers for 2D layered perovskite. For perovskite quantum dots (known as 0D material), they have longer alkyl chain cations that act as capping ligands at the periphery of the BX_6 octahedral. The long chains dangle outside the particles, therefore preventing the array from extending in three dimensions.

Figure 1.15. Illustration of unit structure of ABX_3 perovskite crystal

The bandgap of perovskite materials can be tuned to cover a wider range facilely by changing the chemical identities of A and X. For single crystals, MAPbCl_3 has a

band gap of 2.88 eV^{52b}, while the bromide and iodide counterparts have larger band gaps of 2.18 eV and 1.51 eV⁵⁵, respectively.

1.2.3 Synthesis methods for bulky perovskite materials

Various methods and approaches have been reported to synthesize lead halide perovskite with diverse morphologies including thin films, single crystals and fibers. For the ease of reading, the following chemicals are written in abbreviation.

Table 1.1 Abbreviations of mentioned chemicals

Abbreviation	Chemical	Abbreviation	Chemical
DMF	N,N-Dimethylformamide	DMSO	Dimethyl Sulphoxide
ACN	Acetonitrile	CB	Chlorobenzene
GBL	γ -butyrolactone	OA	Oleic acid
OAm	Oleylamine		

1.2.3.1. Thin films

Up to now there have been several methods to prepare organic-based lead halide perovskite films (Figure 1.16), wherein the general approach to prepare APbX₃ (A= MA⁺, FA⁺ or Cs⁺ and X= Cl⁻, Br⁻ or I⁻) polycrystalline perovskite films is to spin coat the precursor solution on a substrate followed by an one-step (conventional method) or two-step (intramolecular exchange process, IEP) procedure to convert PbX₂ to APbX₃^{10b, 10c, 56}. In some cases heating is needed to evaporate the precursor solvent

(DMF or DMSO).

Figure 1.16. The comparison of FESEM surface images of FAPbI₃-based layer formed on mp-TiO₂ by IEP and conventional method. Reprint with permission from Science⁵⁷.

Thin film fabrication is the most commonly used method to prepare hybrid lead-halide perovskite based solar cells (PSCs). The morphology and uniformity play crucial role in the performance of PSCs, so the manipulation of perovskite crystallization has attracted researchers to dedicate efforts to enhance the power-conversion efficiency⁵⁸.

1.2.3.2 Single crystal

High quality single crystals of hybrid perovskites are shown to possess low trap density and long carrier diffusion lengths, which are key factors for the utilization of perovskite materials in optoelectronic devices⁴⁹.

Figure 1.17 (a) Continuous growth of an MAPbBr_3 crystal by moving the crystal into a larger vial with a fresh growth solution. (b) Shape-controlled crystals of MAPbBr_3 (orange) and MAPbI_3 (black) by varying the geometry of the confining vessel. From left to right—crystals grown in a round-bottom test tube and a 2-mm cuvette. Reprint with permission from Nature Communication⁵⁵.

Osma M. Bakr group^{52b, 55, 59} utilized a fast way to synthesize single crystals of hybrid perovskites and is called inverse temperature crystallization (ITC). Due to the retrograde solubility behavior of organo-lead halide perovskites in certain solvents (DMF, DMSO or GBL), sizeable single crystals were easily produced with a remarkably low trap-state density (Figure 1.17). In application practice, the high quality of the single crystal along with suitable optical band gap renders MAPbCl_3 as an efficient visible-blind UV-photodetector^{52b}.

1.2.3.3 Microrods and nanowires

The applications of perovskite nanowires in photodetector and solar cells have several advantages over thin films morphology: (i) a smoother charge flow from the reduced grain boundary, (ii) the morphological anisotropy leads to sensitivity in detecting polarized light and (iii) band gap tuning properties^{52c, 60}. Both one step (Figure 1.18)⁶¹ and two step^{60c} methods are utilized in the synthesis of perovskite nanowires (PK NWs), which exhibit a low lasing threshold and better photostability.

Figure 1.18. SEM images and fluorescence images of single nanowires below and above lasing threshold. Reprinted with permission from Nano Letter.⁶¹

1.2.3.4 Microcrystal

Solution processing of perovskite films may form microcrystals by increasing the

precursor concentration to sub-saturated degree and subsequently removing the polar solvent under thermal annealing. The cubic crystal size ranges from 100 μm to 400 μm depending on the spin-coating velocities (Figure 1.19). The as-synthesized highly pure perovskite microcrystals exhibit low threshold values, faster amplified spontaneous emission (ASE) lifetime and strong light-absorption intensity.

Figure 1.19. Top-view scanning electron microscopy (SEM) images of micron-sized $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite cubic crystals with sizes at 400 (a), 200 (b) and 100 μm (c), respectively. The scale bar is 500 μm . Reprinted with permission from Physical Chemistry⁶².

1.3 Introduction of hybrid metal halide perovskite nanomaterials

Recently, synthetic capabilities have been developed to achieve perovskite nanocrystals (NC) with controllable morphologies with one or more reduced dimensions. Schmidt *et al.*⁶³ first synthesized free, non-template, nanometer-sized MAPbBr_3 perovskite nanoparticles. Since then, synthetic recipes for preparing

nanocrystals have emerged as an important research topic. In contrast to bulk states, nanoscale perovskites exhibit remarkable enhanced radiative recombination and superior excitonic properties⁶⁴. As such, the prominent potential of perovskite nanoparticles (PK NCs) as a new class of photoactive materials has been demonstrated in photo detectors, light-emitting diodes (LEDs) and solar cells.

1.3.1 Synthesis methods

The general procedure to prepare perovskite material is to first dissolve precursor salts (in the form of AX and BX₂) and organic ligands in proper ratio in polar solvents (e.g. DMF, DMSO or pyridine). Some of the salts are commercially available but others need to be synthesized *in situ* where prepared halide acid reacts with specific amine followed by purification via recrystallization. By inducing the crystallization of the precursor solution via different techniques, perovskite materials with various morphologies can be achieved.

1.3.1.1 Spin coating

A typical method to produce perovskite 2D materials is to deposit a DMF solution containing lead halide salts and the corresponding organic ligands by spin coating to induce the self-organization of perovskite crystals. In this context, the hybrid perovskites organize into a material with chemical formula (R-NH₃)₂BX₄, where X is an organic group and R is an alkyl group. K. Gauthron et al. demonstrated the synthesis of self-organized perovskite structures with strong 2D quantum confinement,

consisting of alternating inorganic and organic layers with thicknesses ranging from 3 nm to 100 nm⁶⁵.

1.3.1.2 Mechanical Exfoliation

The basic idea of exfoliation is to intercalate organic ligands and solvent in the bulky perovskite crystals to form 2D perovskite sheets⁶⁶. Hintermayr *et al.* first fabricated colloidal 2D MAPbI₃ perovskite nanoplatelets (PK NPLs) and controlled the crystal thicknesses by the tuning centrifugation speed¹¹.

Figure 1.20. Schematic of the synthesis for perovskite nanocrystals by mechanical exfoliation. Reprint with permission from Advanced Materials¹¹.

Solid precursors PbX₂ and AX are grounded with a pestle and mortar while monitoring under UV-light until fluorescent emission occurs. The obtained powder is suspended in a nonpolar solvent with organic ligands under tip sonication. After several minutes, the bulk crystals are fractured to quasi-2D perovskite sheets which are then

collected by centrifugation. Nevertheless, the resulting perovskite crystals are polydisperse both in size and morphology as shown in Figure 1.20¹¹. In this method, the crystal structure is alternating layers of inorganic part B_nX_{3n+1} (B is Pb^{2+} or Sn^{2+} , X is Cl^- , Br^- or I^- , n is the number of layers) and organic ligands.

1.3.1.3 Solid state crystallization

Figure 1.21 (A) Structural illustration of a single layer 2D $(C_4H_9NH_3)_2PbBr_4$ crystals. (blue balls, lead atoms; large orange balls, bromine atoms; red balls, nitrogen atoms; small orange balls, carbon atoms; H atoms were removed for clarity). (B) Optical image of the 2D square sheets. Scale bar 10 μm . Reprint with permission from Science⁶⁷.

The solid state crystallization method is commonly used to form layered-perovskite as reported previously^{57-58, 58d}. Dou et al. modified the procedure to produce square shaped nanoplatelets directly on the substrate with average edge length of 4.2 μm and

mono- or double-layered thicknesses⁶⁷ (Figure 1.21). They used a ternary co-solvent (composed of DMF, ACN and CB) to dissolve the precursor salts. The perovskite nanoplatelets then grow as the solvent evaporating under mild heating. With faster evaporation of ACN, the ultrathin 2D PK sheets are generated and the addition of CB into DMF further reduces the solubility of the ions. In contrast with the bulky crystal made from the same components, the atomically thin 2D nanoplatelets exhibit new features such as PL blue shift and structural relaxation⁶⁷.

The direct growth of atomically thin sheets using this method overcomes the limitations of conventional spin coating and exfoliation methods, which normally produce relatively thick perovskite plates with random shapes.

1.3.1.4 Hot injection (HI)

Hot injection is the method in which lead halide salt is dissolved in 1-octadecene at high temperature and a coordinating solvent, such as OA or OAm, is added as ligand to stabilize the formed colloidal nanocrystals⁶³. Crystallization of perovskite nanoplatelets occurs when the cation oleate dissolved in polar solvents injected into the above mixture. Additionally, antisolvent acetone helps to precipitate the perovskite nanoplatelets (PK NPLs), which is collected by centrifugation.

PK NPLs produced using this method is uniformed in square shape with lateral sizes ranging from 10 to 100 nm. Due to the poor solubility of CsX₂ salts in DMSO at room temperature, the synthesis of Cs based PK NPLs is usually carried out using hot

injection method. Although PK NPLs produced using this method have good crystal quality and monodisperse morphology, the procedure is tediously time consuming and in some cases byproducts may emerge in high temperature reaction. Especially for FA-based perovskite, $\text{NH}_4\text{Pb}_2\text{X}_5$ can be detected as impurity from the thermal decomposition of FA^+ .

1.3.1.5 Ultrasonic irradiation (UI)

Recently, ultrasonic method as a simpler and much efficient route has been used to assist the crystallization of perovskite materials^{52a, 68} compared to similar route without activation by ultrasound⁶⁹. Transient hot spots induced by ultrasound provide local areas for precursors to dissolve, supersaturate, nucleate and subsequently crystallize^{52a}.

Figure 1.22. (a) HRTEM image of monodisperse 10 nm CsPbBr_3 NCs. Lattice-resolved and FFT images (scale bar = 2 nm) of cubic-phase (b) CsPbBr_3 and (c) FAPbBr_3 NCs, showing $d_{200} = 2.9$ and $3.0 \text{ \AA}$, respectively. Reprint with permission from Journal of Physical Chemistry Letters^{52a}.

Precursors composed of AX, PbX₂ and coordinating ligands are dispersed in nonpolar solution, like toluene, forming a suspension. The produced PK NPLs have rectangle shape with side length of around 10 nm and thickness of 5 nm as shown in Figure 1.22.

1.3.1.6 Ligand-assisted re-precipitation

In contrast to the above methods, ligand-assited re-precipitation (LARP) stands out as being easy and relatively fast to implement at room temperature, resulting in highly pure and uniform perovskite products especially for PK quantum dots (QDs) and NPLs^{64a, 70}.

Figure 1.23. (a) TEM image of colloidal CH₃NH₃PbBr₃ QDs. (b) Analysis of size distribution for the sample shown in panel a. Reprint with permission from ACS nano^{64a}.

A typical procedure to synthesis PK NCs is by first dissolving PbX_2 and AX in polar solvent, such as DMF and DMSO. Additionally, coordinating solvent, like OA and OAm, is added as a stabilizer. The mixture is injected dropwise into nonpolar solvent, typically chloroform, toluene or hexane, under vigorous stirring. The polar solvent and the aprotic nonpolar solvent are mutually soluble, whereas the halide salts have poor solubility in the latter, therefore PK NCs are formed instantaneously upon solvent blending. As crystallization completes within several seconds, the morphology disperses from QDs^{64a, 70a, 70d, 70f} to NPLs^{70b, 70c} as shown in Figure 1.23 and Figure 1.24 respectively. The mixture can be separated by centrifugation, and for some cases, a mixture of ACN and toluene is used to precipitate the PK NCs^{70b}.

Figure 1.24. Bright-field TEM characterization of the ligand-assisted layer control of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NPLs. Lateral particle size and thickness determination are derived from

the upper and lower images, respectively, of (a) blue (447 nm), (b) cyan (488 nm) and (c) green (514 nm) emitting NPLs. Insets: selected standing nanoplatelets and their corresponding photoluminescence color. Reprint with permission from Chemical Communication^{70c}.

In conclusion, for spinning coating, exfoliation and solid-state crystallization methods, the achieved perovskite materials grow in two dimensions, forming monolayers of corner-sharing PbI_6^{2-} octahedra sandwiched between organic alkyl ammonium layers. In contrast, synthetic routes like HI, UI and LARP are capable of producing PK NCs in 3D or 0D structures with uniform morphology and significant quantum confinement. Above all, LARP is superior due to the relatively easy and fast route to fabricate PK NCs with good quality.

1.3.2 Controlling factors in PK NCs synthesis

1.3.2.1 Compositional mixing

Facile emission adjustability is one of the most superior features of perovskite materials. In many cases, emission tuning is achieved by substituting the halide element, for instance, from chloride to bromide or from bromide to iodide, which covers the whole visible spectrum from blue to red (400 to 700 nm) as shown in Figure 1.25.

The PL peaks change linearly to the content of halide elements, however, gradually phase separation occurs under intense photo radiation; splitting the single

emission peak⁷¹. Additionally the mixing of cations, such as FA^+ , MA^+ and Cs^+ could also realize the fine tuning of their optical emission, however the controlling range is narrower than for halide mixtures. Apart from the above routes, the replacement of lead by tin shifts the emission from red to near infrared range (700-1000 nm)⁴⁹.

Figure 1.25. Tuning the PL emission of perovskite NCs through composition. a)

By selecting a specific ratio of halides during the synthesis, the color of the PL emission can be tuned through the visible range. b) PL and UV–vis spectra of mixed halide perovskite NC dispersions. Each sample only shows a single PL peak, whose position is determined by the halide composition in the precursors. c) Positions of the (100) peak and (110) peak for cubic and tetragonal perovskite crystal structures, respectively, dependent on halide composition. Reprinted with permission from Advanced Materials¹¹.

1.3.2.2 Organic ligands

Organic ligands (commonly OA and OAm) are located at the periphery of the octahedra with their chains dangling outside. Thus, these ammonium ions or long chain acid act as the capping ligands of the nanoparticle, limiting the growth of the array extending in three dimensions. This strategy produces intrinsic PK NPs stabilized by the alkyl chains^{63, 72}. The length of the ligands affects the growth of PK NCs to different degrees, resulting in smaller particle sizes with longer alkyl chains^{64a, 70c}. Additionally, the concentration of organic ligands added in the precursor solution plays an important role to precisely control the thickness of PK NPLs, which decreases from several layers to bilayer or even single layer and at the same time, increasing the band gap⁷⁸.

1.3.2.3 Temperature

In LARP synthesis, the precipitation temperature dramatically affects the quality and size dispersion of PK NCs. Huang *et al.*^{70a} discovered that by varying the precipitation temperature from 0 °C to 60 °C the emission shifts from 475 nm to 520 nm with increasing absolute emission quantum yield (QY) up to 93%. The QY improvement comes from the contribution of good crystallization at high temperature with low defects.

1.3.3 Quantum confinement on PK NCs

Due to the low dimensionality, comparable or even smaller to the Bohr radius of

excitons, PK NCs have shown new quantum phenomena in optical, electronic, mechanical and thermal properties, which in turn renders them applications in various fields. One of the most obvious phenomenon of confinement effect is the blue shifting of 0.75 eV in the bandgap of PK NCs compared to the 3D bulk analogues⁶⁷. As the degree of quantum confinement is determined by a single dimension, PK NCs with similar thickness share same optical absorption and emission, despite differences in lateral sizes. Furthermore, enhanced binding energy, reduced dielectric screening effects and higher quantum yield along with the quantum confinement render perovskite nanomaterials superior properties not found in their bulky counterparts.

1.3.4 Applications of PK NCs materials

Colloidal perovskite nanocrystals, as a new class of colloidal semiconductor nanomaterials have attracted considerable attentions in both the optoelectronic and photovoltaic applications. This is due to the ease of bandgap tunability and promising properties such as enhanced optical properties, high quantum yield and quantum size effect.

1.3.4.1 Detect photons

Solar cells

Perovskite nanomaterials have their dominant position in the field of photovoltaic applications, especially working as light harvesting materials in solar cells. Owing to the resistance to air/water provided by the inorganic layers, the stability of 2D PK NPLs

based photovoltaics have been effectively increased⁷³.

Photodetectors

Solution processed perovskite nanomaterials have extraordinary low recombination loss so perovskite-based photosensors response fast and have high sensitivity. The morphology of the perovskite also has impact on the properties of photodetectors. Gao *et al.* first discover the linear dichroic photodetection on MAPbI₃ nanowire as photodetector^{70b}.

1.3.4.2 Generate photons

Perovskite Light emitting diodes (PeLEDs)

Apart from solar cell devices, PK NCs are an exceptional active material for light emitting devices due to the facile synthetic route, low cost, fine tuning of emission wavelength, high quantum efficiency and high color purity with full width half maximum (FWHM) of approximately 10-30 nm in photoluminescence. The small grain size of PK NCs renders them limited exciton diffusion, resulting in enhanced radiative recombination. Organic-inorganic hybrid PK NPLs⁷⁴ and QDs⁷⁵ both have been used to fabricate PeLEDs, among which the latter nanostructures exhibit significant high device performance. To overcome the stability issue, all inorganic Cs⁺-based PeLEDs⁷⁶ are developed, however, their performance is inferior to their hybrid counterparts.

Optical lasing

The amplified spontaneous emission (ASE) is discovered not only in bulky perovskite but also in the nanoscaled counterparts. As a naturally formed cavity, PK NPLs perform in whispering-gallery mode⁷⁷ and PK NWs in Fabry-Pérot mode^{60a, 60b}, emitting with exceptionally low threshold and carrier density, which make PK NCs a potential nanoscale optoelectronic material in electrically driven lasing.

Chapter 2 Visualizing the Crystallization of Soft Colloids in Real Time

Abstract: We used monodispersed poly(NIPAm-co-AAm) microgel as soft colloids for crystallization study. The thermo- and pH-responsive particle size are characterized by dynamic light scattering (DLS). The 2D crystal structure is measured by confocal laser scanning microscopy (CLSM) and results in long-range ordered face-centered cubic (FCC) structure. The fluid-to-crystal phase transition behavior and the effective volume fractions at low pH (3.50) and high pH (11.01) are observed via wide-field microscopy (WFM), from which two types of motions, the Brownian motion and directed motion, are found prior to crystallization. Based on the diffusion coefficient D , drift velocity V , transitional distance and the effective volume fraction data, we propose that the effective volume fraction is the main parameter to manipulate the crystallization behavior of soft colloidal system.

2.1 Introduction

Microgel suspension assembly of colloidal particles has attracted tremendous attention in the past decades due to their similar phase transition behavior to atomic systems⁷⁸. The micron sized colloidal particles move relatively slowly which enable studies on their phase behavior via optical microscopy and light scattering methods to be conducted. Apart from hard sphere colloidal particles, soft colloidal suspensions exhibit large potentials in achieving a better understanding of phase transitions, among which poly(N-isopropylacrylamide) (pNIPAm) microgel stands out as a classic soft material to study.

The applications of pNIPAm colloids, are greatly expanded due to their superior features, such as thermal and pH sensitivity when copolymerized with acid/base functional groups, softness in particle behaviors and refractive index being close to water. Since the first published account of thermo-sensitive poly(N-isopropylacrylamide) microgel in 1986¹², pNIPAm-based microgels have been utilized in fields like nano-imprint¹⁸, biosensors⁷⁹, drug delivery¹⁹, catalysts⁸⁰ and optical devices²⁰. Poly-NIPAm materials also have great potential in a wide range of industrial applications like the breakage of emulsions and on-demand⁸¹ stabilization⁸².

As the size of pNIPAm particles can be tuned by external conditions such as pH¹⁴, temperature¹⁵ and ultrasound¹⁶, the suspension exhibits flexible and controllable behaviors during phase transitions. Pelton *et al.*¹² were the first to report on the formation of ordered loosely packed two-dimensional (2D) colloidal crystals based on

pNIPAm microgels with a constant interparticle distance⁸⁰. When a tiny diluted solution of microgel suspension is placed on a solid substrate, the spheres will form several levels of 2D arrays as 2D crystal. In contrast to the close-packed hard spheres, hairy pNIPAm nanoparticles form crystals in a loosely packed array^{6, 83}. The formation mechanism of colloidal crystals has been studied upon self-organization when dried in air, so two-dimensional (2D) crystals can be facily achieved by dip-coating or spin-coating¹². The process is driven by capillary interaction between the pNIPAm particles and their coalescence is prevented by steric hindrance from the hairy colloidal particles⁸⁴. Controlling the distance of the crystal lattice is realized by modifying the electrostatic interaction⁸⁵, thickness of the pNIPAm particles¹², colloidal concentration and deposition techniques¹³. Emulsion polymerized pNIPAm microgel particles are not homogenous in density and has a denser core composed of cross-linked polymer and a corona containing dangling polymer chains. As the swollen microgel particles contain about 90% water, their refractive index and density are close to those of water which effectively reduce the light scattering induced by optical artifacts and sedimentation. This means that the phase behavior of pNIPAm microgel particles could be recorded by microscopy with high resolution, for instance, wide-field microscopy (WFM).

Confocal microscopy has been used to detect crystal structures in both 2D crystal and three-dimension (3D) crystal, but the real-time observation of crystallization is not possible because the scan rate is slower than the crystalline growth rate. To this

end, wide-field microscopy with a high-speed electron multiplying CCD (EMCCD) camera is utilized to track in real-time the 2D crystallization process at the single-particle level. The detailed motions of single particles during fluid-to-crystal phase transitions in soft materials are still not well understood. Further understanding of the kinetic information of single particles during crystallization yields a deeper insight into the driving force behind the growth of soft colloidal crystal.

In this study, we use monodisperse poly(NIPAm-co-AAm) microgel as soft colloids for crystallization study. The thermo- and pH-responsive features of particle size are characterized by dynamic light scattering (DLS). The 2D crystal structure is measured by confocal laser scanning microscopy (CLSM) which results in long-range ordered face-centered cubic (FCC) structure. The fluid-to-crystal phase transition behavior and the effective volume fractions at low pH (3.50) and high pH (11.01) are investigated and observed via wide-field microscopy (WFM), from which two types of motions, the Brownian motion and directed motion, are found to occur prior to the formation crystalline state. Based on the diffusion coefficient D , drift velocity V , transitional distance and the effective volume fraction data, we gain a conclusion that the effective volume fraction is a main parameter to manage the crystallization behavior of soft colloidal systems.

2.2 Experimental Section

2.2.1 Materials

N-Isopropylacrylamide 2-Aminoethyl methacrylate hydrochloride (NIPAm), *N,N'*-Methylenebisacrylamide (BIS), 2-Aminoethyl methacrylate hydrochloride (AEMA) and Potassium peroxydisulfate (KPS) were purchased from Sigma-aldrich. These chemicals were not further purified for synthesis of soft colloidal particles. Acetic acid was purchased from Schedelco. Atto 647N NHS-ester dye were obtained from Polymer Atto-Tec GmbH. Dimethylsulfoxide (DMSO, 99.9%, spectrophotometric grade, Aldrich) was used as received.

2.2.2 Synthesis of colloidal polymer particles

A 250 ml of three-neck round-bottom flask equipped with a reflux condenser and a suitable size of stirring bar (500 rpm) was used for synthesis of soft colloidal particles. In the reaction, argon was used as a protected gas. 3.2 g of NIPAm, 0.06 g of AEMA and 0.0985 g of BIS were dissolved into approximately 150 ml of DI water. The pH of resulting solution was adjusted to 3.30 by adding acetic acid and measured by pH meter (Sartorius). The prepolymerization of the aqueous suspension was performed at 73°C under nitrogen for 1 h. The free radical precipitation copolymerization was initiated by 0.0364 g KPS, which was added into the suspension after the prepolymerization. The reaction was stopped after 6 hrs and cooled down to room temperature (Scheme 2.1). The hydrodynamic diameters of the microgel particles were measured by dynamic light

scattering (DLS) (Brookhaven 90 Plus), which showed that the resulting colloidal suspension is monodispersed (polydispersity <10%) with an effective diameter of about 726 ± 24 nm.

2.2.3 Labeling of colloidal particles

Atto 647N NHS-ester dye was dissolved into 40 μ l of DMSO and dispersed into 1 ml of the resulting colloidal particles above. The pH of solution was kept at 7.0. The reaction was carried out at 40 °C for 2 h under stirring and then kept at room temperature for overnight. The colloidal particles with 647N dye solution was centrifuged (140,00 rpm) for 10 min and the supernatant liquid was removed. The labeled colloidal particles obtained was re-suspended into DI water and centrifuged again. The labeled colloidal particles were collected and stored at 4 °C for further use.

Scheme 2.1. Synthesis route of p(NIPAm-co-AEMA) colloidal particles

2.2.4 Characterization Methods

Confocal laser scanning microscope (CLSM) (LSM510 Car Zeiss Inc.) equipped with laser at wavelength 633 nm was used to measure the crystal structure of microgel fully labeled particles. A software ImageJ is used to extract the positions of the particles from each frame. The algorithm comes from Sbalzarini *et al.*⁸⁶ from MOSAIC Group. The radius of the particle and cutoff are set manually based on the quality of the video. The position of the particle means the central position. Estimating the feature point is done by finding local intensity maxima in the filtered image. We extracted the positions of particles via confocal microscopy images and calculated the 2D radial distribution function $g(r)$ in order to characterize the crystal structure, which measures the probability of finding a particle at distance of r away from the reference particle.

$$g(r) = 4\pi r^2 \rho dr \quad (1)$$

where ρ is the number density, $g(r)$ is the RDF, r is the distance of a particle away from a given reference particle.

Scheme 2.2. Sample geometry in this experiment. Three coverslips form a sealed chamber by stacking together. The coverslip in the middle have a hole (8 mm in diameter). A drop of microgel solution is placed at the center of the chamber.

A droplet of 1.2 μL microgel suspension was sandwiched into a sealed chamber consisting of two coverslips and one coverslip with an 8 mm diameter of hole that formed a quasi-cylindrical shape connecting two coverslips. The thickness of a coverslip with hole is 0.13~0.16 mm (Scheme 2.2). Wide-field microscope (WFM) (Olympus IX71, Camera Cascade II 512 Photometric) with an oil immersion objective lens (100 $\times$, N.A. 1.3, Olympus) was used to observe the growth of crystal of soft colloidal particles in real time at room temperature. The 2D field of view for WFM image stacks is 512 $\times$ 512 pixel², which equals to 24.22 $\times$ 24.22 μm^2 . The objective was tuned to focus on crystal planes about 5 crystalline layers upon the bottom coverslip to minimize wall effects. The integration time of the CCD camera is 33.3 ms per frame.

The trajectories of labeled particles were extracted from a sequence of WFM images by Image J, developed by MOSAIC group⁸⁷. In statistic analysis, the mean

square displacement (MSD) is generally used to quantify the motions of particles⁸⁸:

$$\text{MSD}(\tau) = \frac{1}{j-n} \sum_{i=1}^{j-n} r_{i,i+n}^2 \quad (2)$$

where n is the number of frames, $r_{i,i+n}$ is the distance moved from frames i to frames $i+n$ and j is the total frame numbers.

Although the suspensions are in three dimensions, the movies acquired via WFM can only provide the projections of the colloidal particles on the focused plain, which means the analysis was based on two-dimensional movements. We can use the equation:

$$\text{MSD}(\tau) = 4D_{2D}\tau \quad (3)$$

where D_{2D} is the self-diffusion coefficient.

$$\text{MSD}(\tau) \propto \tau^\beta \quad (4)$$

where β is the scaling parameter.

In double-logarithmic profile of MSD versus τ (Equation 4), the slop β sorts different kinds of particle motions. For $\beta=1$ indicates the free Brownian motion, $\beta=2$ denotes the ballistic motion, while the value of β between 0 and 1 means the sub-diffusive motion.

As a result of the deformability of the soft colloidal particles, traditional methods to calculate the volume fractions for hard sphere system are not available here. Thus we define the effective volume fraction as $\Phi_{eff} = V_o n$, where n is the number density of particles and V_o is the effective volume of single particle calculated with the

corresponding hydrodynamic diameters D_H . For 2D images, we extract the number of particles from 512×512 pixel scaled area and assume the volume of the box is $L \times L \times D_H$, which only induces 5% of error compared to that of 3D system. We find a reference concentration at which the system can form large range of crystals with no fluid state and lower defective percentage and get the effective volume fractions refer to the dilute or concentrate ratio of the reference concentration.

2.3 Results and Discussion

2.3.1 Colloidal particle size analysis

Figure 2.1. Dynamic light scattering data as a function of temperature for pNIPAm-AEMA microgel particles at pH 3.5, 7.0, 11.0, respectively.

Both the thermal response and pH sensitivity of the microgel particles are

measured by DLS. As shown in Figure 2.1, pH has an obvious influence on the degree of swelling. The particle hydrodynamic diameter at 25°C increases from ~630 nm at pH 11.01 to ~840 nm at pH 3.50, indicating the protonation of the AEMA ($pK_b = 11$) groups at low pH. The increasing positive charge on the surface of the microgel particles from high pH to low pH values below the pK_b increases osmotic pressure and the Donnan potential inside the particles⁸⁹. At pH 3.50 the largely protonated AEMA groups introduce Coulombic repulsion between the polymer chains in the microgel network, which changes the random coil chain conformation to a rodlike conformation with resultant increase in particle size. There is no obvious difference between the temperature-dependent curves at pH 3.5 and pH 7 as the result of the protonation of amino residues at pH below pK_b 11. Microgels at different pH possess remarkable reduction in particle size with the rise of temperature. The volume phase transition occurs around the lower critical solution temperature (LCST) of pNIPAm. With increasing temperature, the particle size decreases slowly and when the temperature is near LCST, the particles suddenly collapse. In Figure 2.1, the LCST is at the equivalence point at the steepest part. The shape shifts at ~30°C LCST for each curve at different pH values. The variations of the hydrodynamic diameters close to the LCST at low (pH 3.5) and neutral (pH 7) are broader than that at high pH (pH 11), which indicates that the electrostatic repulsion has confined the thermo-sensitivity of the charged particles. This hypothesis is further demonstrated by measurement of the Zeta potential in each condition. According to Table 2.1, there is no obvious charge on the

particle surface at pH near the AEMA pK_b value (pH = 11), however, with the decrease of pH, zeta potential increases as a result of more amino groups of AEMA being protonated.

Table 2.1. Zeta potential values of microgel suspension at different pH

pH	4.08	8.37	10.83
Zeta Potential (mV)	12.67 ± 0.78	5.07 ± 0.76	-1.94 ± 1.88

2.3.2 Crystal structure

The crystal structure of microgel particles is consistent with the FCC structure, except for ultra-soft microgel above the overpacked concentration⁴. The confocal microscope images in Figure 2.2 provide the position distributions of the particles in crystalline assembly, where the radial distribution functions (RDF) are plotted for crystals at different pH. The theoretical RDF peaks of ideal FCC structure have values of 1, $\sqrt{3}$, $\sqrt{4}$

Figure 2.2. Radial correlation functions (RDF) and the corresponding confocal images of pNIPAm-based microgel particles observed by CLSM Top) pH = 3.5, 5.57 wt%; Bottom) pH = 11.0, 5.22 wt%. The dashed lines represent the theoretical values of ideal 2D FCC RDF peaks.

Here we minimize the particle size influence on the peak position by calculating the r_i/r_l ratios, in which r_l is the nearest distance between two particles. In Figure 2.2, for the microgel crystals both at pH 3.5 and pH 11.0, the (111) faces are parallel to the

coverslip wall with RDF peaks well matching the theoretical peak values of ideal 2D FCC RDF. The split of second peak is a characteristic feature of 2D FCC structure.

2.3.3 Experimental method to track phase transition behavior

It is difficult to track single particle motions via bright-field microscopy because single particles are not distinguishable from the microgel dispersion, especially in fluid state. However, for confocal microscope, although particle positions can be captured clearly when they are at the crystal state, it is challenging to observe the fluid-to-crystal transition of colloidal particles due to problems associated with high concentration and the intrinsic drawback of low camera speed. Confocal laser scanning microscope (CLSM) is normally used to characterize the structure and stacking of pNIPAm crystal structure because it can scan materials in three dimensions. The scan speed of CLSM is specified as 200, 400, 800 and 1000 Hz. The highest speed is at 1000 Hz. It takes 1.28s to scan a 512-line image. The disadvantage is high speed means short pixel sampling time, which reduce the quality of the image. While for wide field microscope (WFM), a frame is taken at every 33.3 ms. Hence, WFM can detect more details of particle motion than CLSM.

For the purpose of tracking clear single particle motions during fluid-to-crystal transition, we first labeled pNIPAm colloidal particles with fluorescent dye, Atto 647N NHS ester. As shown in Scheme 2.2, Atto 647N NHS ester is a cationic fluorescent dye

with bulky aromatic group, which brings a net electrical charge of +1 after coupling to an amino group. The heterogeneous surface between fluorescently labeled and unlabeled particles may introduced an additional effect in the crystallization process. The alkyl tail of dye could enhance the hydrophobicity property on the particle surface and the surface heterogeneity may influence the interaction between normal particles and labeled particles, thus affecting the crystallization. However, the effects induced by fluorescent dye may not play an important factor.

Scheme 2.2. Chemical structure of Atto 647N NHS ester

To track the motions of single particles, a microgel suspension is prepared by mixing the as-synthesized pNIPAm colloidal particles with 2 mol % fluorescently labeled pNIPAm colloidal particles. A droplet of 1.2 μL microgel suspension is then sandwiched in a sealed chamber consisting of two coverslips and one coverslip with an 8 mm diameter of hole that formed a quasi-cylindrical shape connecting the two coverslips. The sample is first observed under bright light via WFM (Figure 2.3a). When a focused colloidal area is observed to have both a crystal-state region and fluid-state region the light source is switched from bright light to laser light (633 nm)

(Movie 1). As shown in Figure 2.3b, single fluorescent colloid particles are distinguishable as white dots. In this way, the motions of single particles can be tracked efficiently. After all the labeled particles have stopped moving (trapped in crystal state), the bright light is switched back and a view of the sequential crystal layer is observed. The trajectories of labeled particles are extracted from sequenced frames in Figure 2.3b. Only the particles going through the fluid-to-crystal phase transition with good resolution were chosen for MSD analysis.

Figure 2.3. WFM images of crystal formation (a) Under white light, fluid state and crystal state coexist (b) Under 633 nm laser, the crystallization process of labeled single particle is observed. (c) Under white light, crystallization is completed. The labeled region on the images indicates the initial crystal and fluid areas.

As all the experiments were performed at room temperature, the main factor affecting crystallization behavior is the concentration of the colloidal suspension. Different concentrations of microgel suspension have been tested to find the proper concentration at which the crystallization process can be detected in real time under wide field microscope. Given the pH of the as-synthesized pNIPAm colloidal

suspension is at 3.5, the ideal concentration that enables the crystallization to be observed in real time is 3.57 wt%. If concentration is higher than 3.57 wt%, crystallization completes too fast after the colloidal solution is deposited on the substrates. If concentration is lower than 3.57 wt%, the colloids will stay in fluid state for a long time and the crystallization is too slow to be analyzed.

According to Figure 2.1, the pNIPAm particles in our system are sensitive to pH. In this case, the single particle trajectories of pNIPAm colloids both at pH 3.5 and at pH 11.01 are recorded for comparison. To determine the appropriate concentration of colloidal particles to crystallized in real time for observation, preliminary assays were carried out. As mentioned above, for pH = 3.50, the ideal concentration is 3.57 wt%, while for pH = 11.0, it is increased to 5.22 wt%. The lower concentration needed at pH = 3.50 is due to the repulsive force between particles at low pH which can stabilize the crystal structure with long particle to particle distance.

2.3.4 MSD studies on particle motions in different states

To get a better understanding of particle motions prior to crystallization, the trajectories of single particles at pH = 3.50 undergoing fluid-to-crystal phase transition have been analyzed. Surprisingly, the motions can be classified into two classes: Brownian diffusive motion and directed motion which have not been observed in previous works.

Figure 2.4. Two typical motions prior to attachment to the growing front at pH = 3.5, 3.57 wt% a) Brownian diffusive motion $D = 1.34 \times 10^{-14} \text{ m}^2\text{s}^{-1}$, fitting function $\langle r^2(t) \rangle = 4Dt$; b) Directed motion $D = 2.52 \times 10^{-14} \text{ m}^2\text{s}^{-1}$, $V = 6.26 \times 10^{-7} \text{ ms}^{-1}$, fitting function $\langle r^2(t) \rangle = 4Dt + (Vt)^2$.

As shown in Figure 2.4a, the MSD plot of the Brownian diffusive motion of a typical particle has a linear dependence on lag time and is fitted with the function $\langle r^2(t) \rangle = 4Dt$ for 2D Brownian motion (Movie 2). In contrast, the MSD plot of another typical particle with directed motion deviates from linearity (Figure 2.4b) and forms a smooth curve with fitting function $\langle r^2(t) \rangle = 4Dt + (Vt)^2$, where V represents a drift velocity (Movie 3).

Figure 2.5. Distribution histograms of diffusion coefficient D , drift velocity V and transition distance at pH=3.50 and pH=11.01, respectively a) D of Brownian motion b) & c) D and V of directed motions. d) Transitional distances of Brownian motion. e) Transitional distances of directed motions

One hundred particles at both pH = 3.50 and pH = 11.0 were analyzed (Figure 2.5). At pH = 3.50, the suspension was observed to evolve into a crystal at low

concentration (3.57 wt%) with directed motion accounting for 50% of the particles. For pH = 11.01, crystallization was observed at a higher concentration (5.22 wt%) with 61% of particles displaying directed motion. The diffusion coefficients of Brownian motion (averaged $D = 1.9 \times 10^{-14}$ and $2.3 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ for pH = 11 and 3.5, respectively) are similar to those with directed motion ($D = 1.5 \times 10^{-14}$ and $1.2 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ for pH = 11 and 3.5, respectively), in which the drift velocity dominates the dynamic motions (averaged $V = 0.38$ and 0.042 ms^{-1} for pH = 11 and 3.5, respectively). The transitional distances, or the distances for which particles move from fluid state to crystal state, are about 1 particle-diameter length, i.e. $\sim 500 - 700 \text{ nm}$. The presence of the drift velocity indicates a long-range attraction between the crystal front and the incoming particles. A possible reason is that when the fluid state particles move close to the crystal-growth front, they are attracted by the water capillary force³². In addition, the convective water flow pushes the particles to the crystal front, thus there is a small acceleration in the motion. There are no clear differences between D , V and transitional distance at pH = 3.50 and pH = 11.01, which is surprising due to the stronger electrostatic repulsion at low pH compared to uncharged microgel at high pH. For the sake of explaining this problem, we measured the effective volume fraction along different densities and pH values.

pH 3.50

pH 11.02

Figure 2.6. Bright-field images of p(NIPAm-co-AEMA) microgel crystal at different concentrations and pH. At pH = 3.50: a) 3.57 wt%, Φ_{eff} = 0.69; b) 3.88 wt%, Φ_{eff} = 0.75; c) 4.24 wt%, Φ_{eff} = 0.82; d) 5.90 wt%, Φ_{eff} = 1.13. At pH = 11.02; e) 5.22 wt%, Φ_{eff} = 0.67; f) 5.90 wt%, Φ_{eff} = 0.76. Scale bar = 2 μ m.

As shown in Figure 2.6, Φ_{eff} increases with the increase in weight concentrations. For both pH and at the same weight percentage (5.9 wt%), Φ_{eff} = 1.13 at pH = 3.5 is easily attainable, which denotes a large compression in particle size. For microgel crystals with the same weight percentage but at pH = 11.01, Φ_{eff} is smaller (0.76) which is close to the close-pack fraction for hard sphere (0.74). The difference in effective volume fractions at different pH but same weight concentration is a result of the electrostatic repulsion arising at low pH. The Φ_{eff} values of the suspensions at pH = 3.50

(3.57 wt%) and pH = 11.01 (5.22 wt%) (i.e., the conditions used in our crystallization experiments) are remarkably close (0.69 for pH 3.6 and 0.67 for pH = 11, see Figure 2.5) and is possibly the reason for the similar diffusion dynamics observed.

There are two extreme states during the crystallization process: fluid state, which is observed before crystal is formed, and crystalline state. For fluid state (Figure 2.7a blue curves), the time evolution of the MSD profile reveals a linear shape for the first 30 steps (first 1 s). Subsequently, it begins to deviate from linearity, so the MSD curve is unpredictable for a long-time trajectory (see Figure 2.7a).

Figure 2.7. MSD profiles of pNIPAm-AMEA colloidal suspensions with 3.57 wt% at pH = 3.5, in fluid state and in crystal state. (a) MSD against t plots for 100 steps of 50 fluid particles (blue curves) and 50 crystal particles (pink curves), respectively. (b) Log-log time evaluation for crystal state and fluid state.

For the fluid state (averaged diffusion coefficient $D_{ave} = 2.10 \times 10^{-14} \text{ m}^2\text{s}^{-1}$, Figure 2.7a blue curves), the colloidal particles move much faster than those in the crystal

state ($D_{ave} = 8.76 \times 10^{-16} \text{ m}^2\text{s}^{-1}$, Figure 2.7b pink curves). The scaling parameter β of fluid state is 0.76, which shows the particles are at sub-diffusive motion. The plausible reason for β under 1 is that colloidal particles are in a concentrated environment, which suggests the particle-to-particle and substrate-to-particle interactions are not negligible. In the case of crystal state ($\beta = 0.12$), the particles only vibrates around a small region.

Figure 2.8. MSD analysis for crystallization process at pH = 3.50, 3.57 wt% (a) 100 steps before attachment to the crystal-growth front for 60 particles (b) 100 steps after attachment to the crystal-growth front for 60 corresponding particles (c) 200 steps after attachment and (d) 300 steps after attachment.

To further investigate the evolution of particle motions from fluid state to crystal

state, MSD analysis for the fluid-to-crystal phase transition is given in Figure 2.7. By analyzing the trajectories of 60 colloidal particles, their phase behavior evolutions are divided into four parts: 100 steps before crystallization, and 100, 200 and 300 steps after particles are attached to the crystal-growth front (Figure 2.8).

The following average diffusion coefficients D_{ave} are obtained from the average fitting curves of 60 colloidal particles. For particles prior to crystallization (Figure 2.8a), the diffusion coefficient $D_{ave} = 2.04 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ is similar to that of the fluid state, which indicates a sub-diffusive type of motion. When crystallization begins, particles deposited on the crystal front display diffusion coefficient D_{ave} that decreases in the order $3.64 \times 10^{-15} \text{ m}^2\text{s}^{-1}$ (Figure 2.8b) $< 3.01 \times 10^{-15} \text{ m}^2\text{s}^{-1}$ (Figure 2.8c) $< 2.49 \times 10^{-15} \text{ m}^2\text{s}^{-1}$ (Figure 2.8d) for 100, 200 and 300 steps after the particles are attached to the growing front, respectively. The difference between motions after crystallization indicates that the crystal state has a gradient of diffusion speed. The stability of crystal structure and interaction among particles increase with time till a final stable crystal state ($D_{ave} = 8.76 \times 10^{-16} \text{ m}^2\text{s}^{-1}$ Figure 2.4a pink curves) is achieved.

2.4 Conclusion

In contrast to hard sphere, where phase behaviors are mainly controlled by volume fraction, the parameter managing phase transitions in soft colloidal system is the effective volume fraction. The pH induced influences on phase behaviors can be eliminated by bringing in the hydrodynamic diameter, which is affected by pH in the

same way. As the softness enables microgel system to possess a broader range of possible crystal state than that of hard sphere, we may speculate that microgels with same softness and effective volume fraction could exhibit similar phase behavior, from crystallization to motions of single particles, even under different external conditions, which needs to be further proven by future work.

Chapter 3: Fine-Tuning From Near-infrared to Visible Emission of Cation Mixed $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ ($0 \leq x \leq 1$, $\text{X}=\text{Cl, Br, I}$) Quantum Dots

Abstract: High quality pure cubic phase perovskite quantum dots (PK QDs) composed of $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ ($0 \leq x \leq 1$, $\text{X}=\text{Cl, Br, I}$) alloy were successfully prepared via a facile ligand-assisted reprecipitation (LARP) method at room temperature, in which a precursor solution containing AX , PbX_2 ($\text{A}=\text{FA}^+$ or MA^+) and organic ligands dissolved in DMF/DMSO are mixed with aprotic solvent to precipitate PK QDs. Substitution of organic cations and halide anions achieve fine tuning of the photoluminescence emission of the PK QDs. The as-synthesized PK QDs have high quantum efficiencies peaking at 84%, which could even rise to 96% with 12h resting time.

3.1 Introduction

Since 2009⁴⁷, hybrid lead halide perovskite materials have led to a breakthrough performance in photovoltaic applications, especially when used as a light harvesting film in solar cells^{10b, 56}. When arrays extending in one or more dimensions are confined to the Bohr radii of perovskite materials, they function as both the principal light absorber and also as the transporter of electrons/holes⁹⁰, resulting in enhanced efficiency solar cells⁹¹. Nanoscale perovskite particles are prepared initially by depositing precursors on metal oxide^{91a} until Schmidt *et al.*⁶³ first introduced the nontemplate synthesis of CH₃NH₃PbBr₃ perovskite nanoparticles (PK NPs) via a hot injection method. After that, many approaches have been developed to synthesize perovskite nanomaterials, like ligand assisted reprecipitation (LARP)^{64a, 70b, 70c}, ultrasound irradiation^{52a, 68b} and mechanical exfoliation⁶⁶, within which LARP performs a facile route and produces high quality perovskite quantum dots (PK QDs) or perovskite nanoplatelets (PK NPLs).

Perovskite nanomaterials exhibit unique properties that distinguish them from their bulk counterparts and make them promising candidates in electroluminescent devices^{70b}. For LED applications, a smaller grain size of PK NPs is preferred because it limits the exciton diffusion which in turn increases the possibility of radiative recombination. The ease of coating PK NPs on deformable materials extends their application in flexible LED film⁹². The versatile structure-tunable optical properties render PK NPs the application as sensors and probes⁹³.

One of the most remarkable features of organic-inorganic hybrid lead halide perovskite materials is the ease of tuning their bandgaps as well as the photoluminescence (PL) properties¹¹. In the case of bulky perovskite materials, the commonly used method is by gradually substituting a small halide ion with a larger ion, for instance halide mixing from bromide to iodide, so that the bandgap becomes narrower and the corresponding emission peak undergoes redshift. In addition to compositional substitution, especially for perovskite nanoparticles, when one or more dimensions are reduced by long chain amines, quantum confinement effect arises and results in reduced bandgap⁶⁷. Apart from extensive research on size control and halide substitution to modulate the optical and excitonic properties of PK QDs, little attention has been paid to cation substitution. With the replacement of inorganic cation Cs^+ for MA^+ or FA^+ based organic perovskite, the material stability is enhanced, however the quantum efficiency of this organic-inorganic mixed cation perovskite is lower than that of the organic cation perovskite, and even more the synthesis method is always more time consuming. Chen *et al.*⁹⁴ achieved $\text{Cs}_m\text{FA}_{1-m}\text{PbX}_3$ perovskite via a facile LARP route, but the low solubility of Cs-halide salts limits the tunable spectrum range of this method.

In the present work, we demonstrate the synthesis of $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ hybrid lead halide PK QDs, which to our knowledge has not been reported. Compared to the commonly used elaborate hot injection method, LARP could produce high quality perovskite nanomaterials at room temperature in ambient conditions without the

protection of inert gas or generation of byproduct at high temperature ($\sim 250\text{ }^{\circ}\text{C}^{95}$).

3.2 Experimental Section

3.2.1 Materials

Dimethylformamide (DMF, anhydrous, HPLC grade) and dimethyl sulfoxide (DMSO, anhydrous, HPLC grade) were obtained from Tedia. Lead (II) iodide (PbI_2 , 98%), lead (II) bromide (PbBr_2 , 98%) and lead (II) chloride (PbCl_2 , 98%) were obtained from Sigma-Aldrich. Methylamine (41% w/w aqueous solution) and formamidine acetate were obtained from Sinopharm Chemical Reagent Co. Ltd. Hydroiodic acid (HI, 57% w/w aqueous solution), hydrobromic acid (HBr, 48% w/w aqueous solution) and hydrogen chloride (HCl, 37% w/w aqueous solution) were obtained from Alfa Aesar. Oleylamine (OAm, approximate C18-content 80-90%) was purchased from Acros Organics. Oleic acid (OA, 97%) was purchased from VWR Chemicals. All chemicals were used as received.

3.2.2 Sample preparation

Methylammonium halide (MAX) synthesis. Typically, methylamine (8.439 mL, 0.1 mol, 11.85 M, 41% w/w in H_2O) dissolved in 15 mL ethanol and hydrochloric acid (8.354 mL, 0.1 mol, 11.97 M, 37% w/w) diluted in 15 mL ethanol are mixed in 250 mL round-bottom flask under stirring for 2h in 0°C ice bath. Upon drying at 60°C in rotary evaporation, methylammonium chloride (MACl) crystals are precipitated as white

powder. After washing with diethyl ether, the as-synthesized crude MACl crystal is re-dissolved in ethanol and recrystallized by diethyl ether. Subsequently, the final product is dried in a vacuum oven for further use. For methylammonium bromide (MABr) and methylammonium iodide (MAI), the corresponding acids are hydrobromic acid (11.321 mL, 0.1 mol, 8.84 M, 48% w/w) and hydroiodic acid (13.193 mL, 0.1 mol, 7.58 M, 57% w/w), respectively.

Formamidinium halide (FAX) synthesis. FAX powders are synthesized using similar processes as MAX, in which the organic starting material is replaced by formamidine acetate (10.411 g, 0.1 mol, 104.11 g/mol) dissolved in 15 mL ethanol.

ABX₃ Perovskite Quantum Dots (PK QDs) synthesis. All the synthesis were carried at room temperature in air with average room humidity ~50%. Halide stock solutions were first prepared at 100 mg/mL in DMF (for bromide and iodide salts) or DMSO (for chloride salts). AX solution was mixed with PbX₂ solution with same stoichiometry at a final volume of 1 mL DMF (or DMSO) forming 0.1 mM solution as shown in Table 4.1. Additionally, the mixture was added 200 μ L OA and 100 μ L OAm under stirring for 15 min to form the precursor solution. Subsequently, 100 μ L of the precursor solution is added dropwise by using Harvard Apparatus 11 plus syringe pump with a fixed speed (60 μ L/min) into 3 mL chloroform under vigorous stirring. To purify the resulting solution, large clusters are discarded by centrifuging at 3000 g for 10 min.

Table 3.1. Parameters of synthesis ABX₃ PK QDs with mixed cations

FAMAPbI ₃	FA content/%	FAI/ μ L	MAI/ μ L	DMF/ μ L	PbI ₂ / μ L
	100	172	0	367	461
	80	138	32	369	
	60	103	64	372	
	40	69	95	375	
	20	35	127	377	
	0	0	159	380	
FAMAPbBr ₃	FA content/%	FABr/ μ L	MABr/ μ L	DMF/ μ L	PbBr ₂ / μ L
	100	125	0	507	369
	80	100	23	509	
	60	75	45	512	
	40	50	67	515	
	20	25	90	517	
	0	0	112	520	
FAMAPbCl ₃	FA content/%	FACl/ μ L	MACl/ μ L	DMSO/ μ L	PbCl ₂ / μ L
	100	81	0	641	278
	80	64	14	624	
	60	48	27	607	
	40	32	41	589	
	20	16	54	572	
	0	0	68	554	

3.2.3 Characterization Methods

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction pattern was obtained using an X-ray diffractometer (D8 Advance, Bruker) and Cu-K α radiation source with a conventional cobalt target X-ray tube set to 40kV and 40mA. The chloroform suspension of perovskite quantum dots was centrifuged at 60k rpm for 30 min, then the concentrated solution was drop casted onto a silica wafer and dried in vacuum oven at room temperature for further measurements. The samples were scanned from $10^\circ < 2\theta$

$< 50^\circ$ at an increment of $3\text{s}/0.02^\circ$.

Transmission electron microscopy (TEM). TEM images were recorded using a JEOL JEM 1400 TEM (100 kV acceleration voltage). Samples for TEM were prepared by casting 20 μL of the PK QDs solution in chloroform or cyclohexane onto a standard copper grid coated with a continuous amorphous carbon film. The size distribution and thicknesses of NCs were obtained from the TEM image with ImageJ software.

Optical measurements. Steady-state absorption and fluorescence spectra of PK QDs solutions were recorded by using an UV/Vis absorption spectrometer (Cary 100, Varian) and fluorescence spectrometer (Eclipse, Varian), respectively.

Lifetime measurements. The time-resolved fluorescence lifetimes of PK QDs dispersed in chloroform were measured using a time-correlated single-photon counting (TCSPC) spectrofluorimeter (FluoroCube, Horiba Jobin Yvon). The samples were excited at 375 nm by using a pulsed diode laser (NanoLED-635 L, Horiba Jobin Yvon). The fluorescence decay profiles were analyzed using the Horiba Jobin Yvon DataStation software and the goodness of fit was assessed by considering the reduced chi-square (χ^2) value and the randomness of the weighted residuals. All measurements were performed at ambient conditions.

Absolute fluorescent quantum efficiency. The PK QDs solutions were mounted in an integrating hemisphere, which was excited with a monochromatic light emitter from a

monochromator combined with an Xenon lamp. The QE-2000 system is equipped with Otsuka Electronics' multichannel spectrometer.

3.4 Results & Discussions

3.4.1 Synthesis of Perovskite quantum dots

In a typical LARP synthesis, perovskite nanoparticles are prepared when a mixture of organic halide salt and lead halide salt in the presence of organic ligands dissolved in DMF/DMSO is added to nonpolar organic solvents under vigorous stirring.

In the precursor preparation, DMF is an ideal solvent to dissolve the organic halide salts (FABr/FAI and MABr/MAI) and lead halide salts (PbBr_2 or PbI_2) together with the organic ligands Oleic acid (OA) and Oleylamine (OAm), while for the chloride analogues, DMSO is used instead of DMF due to a higher polarity. In the case of CsPbX_3 , all the cesium halide salts can only be dissolved in DMSO. The poor solubility of Cs-based salts in organic polar solvents make them more suitable to be synthesized at high temperature with the hot injection method rather than at room temperature via the LARP method.

Organic capping ligands play a key role in the formation of perovskite nanoparticles. For instance, OA and OAm are commonly used to limit the perovskite crystal lattice extending in three dimensions by coordinating at the periphery of PK NPs surface, and, rendering them good solubility in aprotic solvents. To determine the best molar ratio between OAm and lead halide salts, preliminary assays were carried

out. It has been reported that when the stoichiometry of OA is fixed, with increasing amount of OAm, the size of perovskite nanoparticles is reduced along with the PL shifting towards a lower wavelength^{70b, 70c}. In order to prepare zero dimensional perovskite nanomaterials, the volume ratio of OA/OAm is fixed at 2 throughout this work.

Another important factor in the LARP method is the choice of the anti-solvent. For instance, in the synthesis of MAPbBr₃ PK QDs, aprotic organic solvent like chloroform, dichloromethane, chlorobenzene, toluene, ethyl acetate, diethyl ether and tetrahydrofuran can precipitate out perovskite particles when mixed with the precursor solutions, however, in the case of pyridine and isopropyl alcohol, no precipitate is observed. For FAPbBr₃ PK QDs, precipitation will appear only in chloroform, dichloromethane and chlorobenzene. Taking the quality of the resulting PK QDs into consideration, chloroform is used as the antisolvent throughout the experiment.

A typical manner to add precursor solution into antisolvent is by direct injection of the mixture under vigorous stirring, resulting in NCs with a broad size distribution. In particular, we use syringe pump with a fixed rate (60 μ L/min) to add the precursor solution dropwise, so as to prepare monodispersed PK QDs.

3.4.2 Structural Properties

In ABX₃ perovskite materials, the structural properties and stability of perovskite materials can be assessed by an empirical index, Goldschmidt tolerance factor (t)⁹⁶:

Figure 3.1 (a) Cubic perovskite structure of ABX_3 . (b) Structural map of ABX_3 compounds.

$$t = \frac{r_A + r_B}{\sqrt{2}(r_B + r_X)} \quad (1)$$

where r_A , r_B and r_X are the ionic radii of the A and B site cations and the X site anion, respectively. In an ABX_3 perovskite framework, A site cation locates within the cuboctahedral cavity formed by BX_6 octahedra, which arrays into a cubic structure with corner sharing connection in three dimensions as shown in Figure 3.1a. Tolerance factor t assesses the suitability of A site cation's fit in the cavity with $t = 1$ indicating a perfect fit (generally $0.9 < t < 1.0$ forms an ideal cubic structure). For the inorganic-organic hybrid halide perovskite material, for t in the range of $t > 1$ and $t < 0.8$, A site cation is too large or too small for BX_6 octahedra and results in a non-perovskite array (hexagonal phase and orthorhombic phase, respectively)⁹⁷.

Figure 3.2. Summary of the effective tolerance factors of different mixed $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ perovskite alloys.

Alternatively, another consideration is the octahedral factor (μ) as shown in equation (2), which assesses the fit of B site cation in the X_6 octahedron as well as the AX_3 array:

$$\mu = \frac{r_B}{r_X} \quad (2)$$

When the six halide anions are packed closely, $\mu=0.41$. As all the ABX_3 compounds shown in Figure 3.1b are in the range $\mu>0.41$, perovskite structures are formed. According to previous studies, the best device absorption performance possesses t in the range 0.94-0.98⁹⁷⁻⁹⁸. By proper tuning of the effective tolerance factor (t_{eff}), the alloyed material $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ can fall in the desired range, whilst enhancing the material stability as shown in Figure 3.2.

$$r_{\text{eff}} = x r_{\text{FA}^+} + (1 - x) r_{\text{MA}^+} \quad (3)$$

$$t_{eff} = \frac{r_{eff} + r_{X^-}}{\sqrt{2}(r_{Pb^{2+}} + r_{X^-})} \quad (4)$$

Table 3.2. Bohr radii a_B and binding energies E_b of several perovskite compounds

	MAPbBr ₃ ^a	MAPbI ₃ ^a	FAPbBr ₃ ^b	FAPbI ₃ ^b
a_B/nm	2.0	2.2	3.5	6.35
E_b/meV	76	50	24	10

^a Kenichiro et al.⁹ ^b Krzysztof et al.¹⁰

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Perovskite nanomaterials produced in our study using the LARP method have a zero-dimension morphology, (i.e. quantum dots). According to the size distribution histograms and TEM images of FA_xMA_{1-x}PbBr₃ PK QDs shown in Figure 3.3, the replacement of FA⁺ by MA⁺ does not lead to an obvious change in size, from 3.4 ± 0.7 nm for FAPbBr₃ to 2.7 ± 0.5 nm for MAPbBr₃. Notably, all the diameters are comparable or even smaller than the Bohr radii a_B of pure FAPbBr₃ (3.5 nm) and MAPbBr₃ (2.5 nm) in Table 3.2. Similar PK QDs morphologies are also observed in FA_xMA_{1-x}PbCl₃ as shown in Figure 3.5.

Figure 3.3. TEM images and sized distributions of $\text{FA}_x\text{MA}_{1-x}\text{PbBr}_3$ PK QDs. Scale

Bar=20 nm

As shown in Figure 3.4, the iodide PK QDs have comparable sizes to the bromide counterpart, however, the former is less stable when observed by TEM. Under electron beam irradiation at 100 kV, some of the materials started to decompose from QDs to powders and disappear in view due to the fragile component of Pb and I in energy deposition⁹⁹. It is suggested that the presence of the methylammonium ion that contains relatively lighter elements helps to dissipate the

electron energy, so that PK QDs with higher content of MA^+ are more stable under electron beam irradiation⁹⁹, so this can help to explain the presents of large QDs in

Figure 3.4. TEM images and size distributions of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ PK QDs.

Scale bar= 20 nm.

higher content MA^+ samples in Figure 3.4. The small QDs present in high content of FA^+ might be the result of decomposition of large QDs. While for chloride PK QDs, the size of QDs significantly increased compare to the bromide and iodide QDs.

The reason is due to the increased in polarity from Cl component in PK QDs, so the solubility of chloride PK QDs is lower in chloroform than bromide QDs and iodide QDs.

Figure 3.5 TEM images of $\text{FA}_x\text{MA}_{1-x}\text{PbCl}_3$ PK QDs. Scale bar= 20 nm.

Figure 3.6 XRD patterns of typical PK QDs. (a) $FA_bMA_{1-b}PbBr_3$. (b) $FA_aMA_{1-a}PbCl_3$. (c) $FA_cMA_{1-c}PbI_3$. (d) Magnified XRD diffraction peaks at [100] plane of PK QDs.

To get more insight into the crystal structures of the as-synthesized PK QDs, their XRD patterns are recorded. As shown in Figure 3.6.a, b and c, all the XRD patterns of the PK QDs match well with those of the cubic perovskite phase, which indicates the purity of the crystalline without any detectable impurity phase. Interestingly, with increasing content of FA^+ , the diffraction peak gradually shifts to a low angle due to the larger ion radius of FA^+ compared to MA^+ (Figure 3.6d). Similarly, when the halide component changes from chloride to bromide and from bromide to chloride, the XRD diffraction patterns move towards small angles with increasing ion radii. In conclusion, mixed cation $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ PK QDs with different FA/MA ratio will not alter the cubic phase of the pure FAPbX_3 or MAPbX_3 .

3.4.3 Optical Properties

The optical properties of $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ PK QDs are investigated here. The UV-visible absorption spectra of the PK QDs solutions exhibit broad absorptions (Figure 3.7a, Figure 3.9a and Figure 3.10a), which makes large Stoke shifts possible in this system. As a result, intense fluorescence emission is collected under 375 nm excitation without autoabsorption occurring. The photoluminescence (PL) spectra of the perovskite colloidal solutions show single PL peaks near the band edges with a full width at the half-maximum (FWHM) at around 20-35 nm for bromide and chloride PK QDs and around 50 nm for iodide PK QDs (Figure 3.11). With increasing amount of MA^+ substituted by FA^+ , the fluorescent emission gradually redshifts from pure

MAPbBr₃ at 478 nm to pure FAPbBr₃ at 522 nm with the color changing from blue to cyan and then to green (Figure 3.6b) at 365 nm UV light irradiation.

Figure 3.7. Optical properties of the FA_xMA_{1-x}PbBr₃ alloy PK QDs in chloroform.

(a) Representative optical absorption (dashed lines) and PL spectra (solid lines). (b)

Digital picture of FA_xMA_{1-x}PbBr₃ PK QD solution in chloroform taken under white

light and 365 nm UV-light. (c) PL decay dynamics of the pure and mixed-cation PK

QDs. (d) Average lifetime of PK QDs with different content of FA⁺. (e) Absolute

PLQY for PK QDs with different content of FA⁺. (λ_{ex} =375 nm)

As shown in Figure 3.8b, the PL peak position could be tuned linearly with respect

to the FA content x in $\text{FA}_x\text{MA}_{1-x}\text{PbBr}_3$. Given that the size distributions of $\text{FA}_x\text{MA}_{1-x}\text{PbBr}_3$ QDs are all at around 3 nm (Figure 3.3), the shifting of perovskite PL peak positions could be attributed to the ratio between FA^+ and MA^+ , which indicates the capability of fine tuning PL emission in our cation substitution method.

Figure 3.8. Photoluminescence peak of $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ as a function of FA content x . a) $\text{X} = \text{Cl}^-$, b) $\text{X} = \text{Br}^-$ and c) $\text{X} = \text{I}^-$.

The trend of PL spectra and UV absorption moving towards longer wavelength with increasing ratio of FA^+/MA^+ in $\text{FA}_x\text{MA}_{1-x}\text{PbBr}_3$ is attributed to the change in exciton binding energy as well as the band gap, from 2.594 eV ($x=0$) to 2.375 eV ($x=1$) obtained from the PL emission. The electronic structures of perovskite materials are determined by the Pb-Br bond lengths as well as the angles in PbBr_6^{4-} octahedron. In the gradual replacement of MA^+ (2.17 Å) with FA^+ (2.53 Å), the effective radius of the A site cation is increased, which alters the structure parameters of the PbBr_6^{4-} octahedron and result in decreasing band gap. From Figure 3.7a, Figure 3.9a and Figure 3.10a, the spectral tuning range with the increase in FA^+/MA^+ ratio is in the order of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3 > \text{FA}_x\text{MA}_{1-x}\text{PbBr}_3 > \text{FA}_x\text{MA}_{1-x}\text{PbCl}_3$, due to the energy gap decreasing in the sequence $\text{Cl}^- > \text{Br}^- > \text{I}^-$. Similar trends are also observed in the iodide PK QDs, in

which the PL and UV-vis absorption band edge move toward a longer wavelength with increasing replacement of MA⁺ by FA⁺, from red (705 nm) for MAPbI₃ to near-infrared region (778 nm) for FAPbI₃ in Figure 3.9a. On the other hand, the chloride PK QDs show a reverse trend compared to the bromide and iodide ones. One assumption might be related to the synthesis part in which the precursor solvent is DMSO rather than DMF. However more work is needed to understand the exact mechanism behind the difference in PL behaviors.

In order to study the changes in the exciton recombination dynamics of the cation substituted PK QDs, their time-resolved PL decay profiles are measured, as shown in Figure 3.7c and d for bromide PK QDs and Figure 3.9c and d for iodide PK QDs. The average PL lifetime is gradually enhanced with increasing content of MA⁺ replaced by FA⁺, which indicates an increase in the exciton binding energy. The relative radiative decay rate (k_{rad}) and non-radiative decay rate ($k_{non-rad}$) can be determined by the following formulae:

$$\tau_{PL} = \frac{1}{(k_{rad}+k_{non-rad})} \quad (5)$$

$$PLQY = \frac{k_{rad}}{k_{rad}+k_{non-rad}} \quad (6)$$

where τ_{PL} is the average lifetime and PLQY is the photoluminescence quantum yield as summarized in Table 3.3.

Table 3.3. Optical parameters of FA_xMA_{1-x}PbX₃ PK QDs

PK QDs	<i>x</i>	PL Peak,nm	PLQY,%	τ_{PL} , ns	k_{rad} , s ⁻¹	$k_{non-rad}$, s ⁻¹
FA_xMA_{1-x}PbCl₃	1.0	398	<1	0.2	-	-
	0.8	402	<1	1.1	-	-
	0.6	407	<1	2.2	-	-
	0.4	407	<1	2.6	-	-
	0.2	406	<1	2.1	-	-
	0.0	401	<1	2.3	-	-
FA_xMA_{1-x}PbBr₃	1.0	522	83.0	34.7	2.4×10^7	0.5×10^7
	0.8	516	59.4	29.5	2.0×10^7	1.4×10^7
	0.6	506	51.3	28.3	1.8×10^7	1.7×10^7
	0.4	498	43.1	20.4	2.1×10^7	2.8×10^7
	0.2	484	39.0	7.0	5.5×10^7	8.7×10^7
	0.0	478	41.0	6.8	6.1×10^7	8.7×10^7
FA_xMA_{1-x}PbI₃	1.0	778	44.2	160.7	0.3×10^7	0.3×10^7
	0.8	761	23.6	91.3	0.3×10^7	0.8×10^7
	0.6	753	14.8	50.4	0.3×10^7	1.7×10^7
	0.4	741	10.6	26.3	0.4×10^7	3.4×10^7
	0.2	717	8.7	15.7	0.6×10^7	5.8×10^7
	0.0	705	9.6	13.8	0.7×10^7	6.6×10^7

As in FA_xMA_{1-x}PbBr₃ alloys, the large Stoke shift between PL (478 nm ~522 nm) and the excitation wavelength (375 nm) considerably hinders autoabsorption, hence the determination of absolute PLQY is feasible. The PLQY of the PK QDs is up to 85% (Figure 3.7e), which is significantly higher than the bulk counterpart. High PLQY is attributable to the increase in exciton binding energy as a result of the size quantum confinement. In bulk perovskite material, the excitons exhibit the Wannier type, producing a strong delocalization with weak binding energy. However, for the reduced dimensional materials, the exciton binding energy is significantly increased, preventing dissociation of the exciton prior to its radiative decay. Interestingly, with increasing content of MA⁺ replaced by FA⁺, the PLQY is monotonically enhanced. A plausible

reason is the increased structural stability due to the addition of FA^+ in MAPbBr_3 . Given the tolerance factor t of an idea symmetry cubic structure of APX_3 is 1, according to Figure 3.2, the effective tolerance factor t_{eff} increases from 0.927 ($x=0$) to 1.008 ($x=1$) in $\text{FA}_x\text{MA}_{1-x}\text{PbBr}_3$, indicating the enhancement in crystal structure. Whereas, for $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ PK QDs with I^- (2.20 Å) larger than Br^- (1.96 Å), t_{eff} is drawn below 1 (Figure 3.2). For any particular x , the t_{eff} for $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ is smaller than that for $\text{FA}_x\text{MA}_{1-x}\text{PbBr}_3$, hence reduces the structural stability and gives rise to the lower PLQY (10%~45%) compared to the bromide counterpart (Figure 3.9e). As shown in Table 3.3, the decrease in quantum yield is accompanied by the reduction of the PL decay lifetimes. As a rule, while the radiative decay rate remains almost unchanged, the replacement of MA^+ by FA^+ shows a significant reduction in nonradiative rate, which leads to the enhanced PLQY. For instance, in $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ PK QD, from $x=0$ to $x=1$, the nonradiative rate reduces 22 times. In general, the sensitivity to moisture and air leads to the lower PLQY of iodide QDs as compared to that of the bromide QDs, In the case of chloride PK QDs (Figure 3.10), their PLQY is quite low, even below 1%. Despite that for any particular x (Figure 3.2), t_{eff} of chloride PK QDs is closest to 1 when compared to the other halide counterparts, however the PLQY is the lowest. This could be due to the intrinsic property of chloride PK QDs¹⁰⁰.

All the above data suggest the success of preparing cation substituted $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ QDs and the fine-tuning of PL emission is realized in the range from near-infrared to visible region.

Figure 3.9. Optical properties of the $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ alloy PK QDs in chloroform. (a) Representative optical absorption and PL spectra. (b) Digital picture of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ PK QD solution in chloroform taken under white light and 365 nm UV-light. (c) PL decay dynamics of the pure and mixed-cation PK QDs. (d) Average lifetime of PK QDs with different content of FA^+ . (e) Absolute PLQY for PK QDs with different content of FA^+ . ($\lambda_{\text{ex}}=375$ nm)

Figure 3.10 Optical properties of the FA_xMA_{1-x}PbCl₃ alloy PK QDs in chloroform.

(a) Representative optical absorption and PL spectra. (b) PL decay dynamics of the pure and mixed-cation PK QDs. (c) Average lifetime of PK QDs with different content of FA⁺ (λ_{ex} =375 nm).

Figure 3.11. Full width at half maximum (FWHM) of FA_xMA_{1-x}PbX₃ ($0 \leq x \leq 1$, X = Cl⁻, Br⁻, I⁻) as a function of FA content x

3.4.4 Stability of PK QDs

The stability of FAPbBr₃ and MAPbBr₃ PK QDs is also investigated. The motivation of this examination originates from the discovery of increasing PL intensity of the colloidal perovskite solutions with resting time. Three samples from each materials are prepared, one is the as-synthesized raw product solution without post-treatment, one is the colloidal PK QDs solution obtained by discarding large precipitates after centrifugation, and one is the solution of redissolved precipitates. As demonstrated in

Figure 3.12. Stability properties of FAPbBr₃ perovskite colloidal solutions. (a) Average lifetime as a function of time. (b) Absolute PLQY as a function of time (c), (d) and (e) are the PL spectra of the raw solution, supernatant solution and redissolved precipitate solution for the duration of 30h, respectively.

Figure 3.12, within a resting time of 30 h, the PL intensity of the raw solution kept increasing, while the supernatant solution increases in 12 h then decreased to zero, with white precipitates forming from the yellow solution. On the other hand, for the redissolved precipitate solution, the intensity as well as the PLQY and lifetime kept decreasing. The unreacted starting materials remaining in the raw solution and supernatant solution keep growing on the surface of the as-synthesize QDs and at the same time, sufficient quantity of capping ligands passivate the newly formed surfaces. This is similar aggregation-induced enhanced emission^{93b}, and is confirmed by the redshift in the PL peak (Figure 3.12 c and d).

For the redissolved precipitate solution, there is no residue organic capping ligands in the solution, and the sample is diluted in the redissolved procedure. Exfoliation can be induced by dilution and new surfaces are formed with the fracturing of the as-synthesized perovskite particles. The lack of protection from additional organic ligands leads to an increase in non-radiative decay rate, blue shift in PL peak, and decrease in PL intensity, lifetime and PLQY.

The influence of air is also investigated in the colloidal perovskite raw solutions (Figure 3.13). To remove air, especially oxygen, the antisolvent chloroform is pretreated by degassing for 1h in argon flow. Consistent with Figure 3.12, both the FAPbBr₃ and MAPbBr₃ display an increase in the PL intensity as well as a redshift towards longer wavelength, which indicates the increase in particle sizes. This phenomenon is more obvious in FAPbBr₃ samples. Initially, the PL intensity of the

degassed samples are lower than those without degassing treatment, but with the increase of the resting time, the degassed MAPbBr₃ solution exhibits stronger PL than the untreated sample. For FAPbBr₃ solution, although the untreated solution have higher PL than degassed solution, the former is less stable than the latter (Figure 3.13c). As reported, oxygen plays a role in the enhancement of PL emission so that the untreated solutions have brighter PL than the degassed ones¹⁰¹. Nevertheless, oxygen is

a double-edge sword in enhancing the PL emission and inducing the decomposition of perovskite nanomaterials at the same time. Meanwhile FAPbBr₃ samples decompose faster compared to MAPbBr₃ samples due to their high sensitivity to air and moisture¹⁰².

3.5 Conclusion

Figure 3.13. Aging optical behavior of MAPbBr₃ and FAPbBr₃, in comparison with the degassed samples. (a) Changing of wavelength as a function of resting time. (b) and (c) changing in PL intensity of MAPbBr₃ and FAPbBr₃ colloidal solution.

In summary, $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ alloy PK QDs with pure cubic phase were successfully prepared via a facile LARP method at room temperature, in which a precursor solution containing AX, PbX_2 and organic ligands dissolved in DMF/DMSO are mixed with aprotic solvent to precipitate PK QDs. The as-synthesized PK QDs have high quantum efficiencies peaking at 84%, which could even rise to 96% in 12 h resting time. Gradual substitution of MA^+ by FA^+ enhances the structural stability and realized a fine tuning from near-infrared region to visible region in the spectrum.

Chapter 4: The Interaction between Perovskite Microrods and Upconversion Nanomaterials

Abstract: In this study, perovskite microrods were prepared in a two-step method.

First PbI_2 microrods were formed by drop-casting PbI_2/DMF solution on coverslip and gradual evaporation of solvent, then perovskite microrods were converted to perovskites by immersing the PbI_2 microrods in organic halide solution in isopropyl alcohol (IPA). By adjusting the cation ratio in the IPA solution, the photoluminescence (PL) emission of the synthesized perovskite microrods was tuned to 794 nm, which is the most intense absorption wavelength of Nd^{3+} -doped upconversion nanomaterials. Upconversion nanomaterials were prepared using both the hydrothermal method and thermal decomposition method. Nd^{3+} -doped core-shell upconversion nanorods (UCNRs) and nanoparticles (UCNPs) were prepared in monodispersion. When UCNRs or UCNPs were spin coated on the surface of perovskite microrods, their interactions with perovskite microrods were studied using time resolved fluorescence spectroscopy.

4.1 Introduction

Lanthanide-doped up-converting nanoparticles (UCNPs) have a special capability of NIR-to-visible upconversion emission, which attracts increasing interest in various fields spanning from bio-imaging technology¹⁰³ to chemical probes¹⁰⁴. Generally, photoluminescent occurs when an electron goes through single-photon excitation from ground state to excited state by absorbing high-energy light, and then low-energy light is emitted when it relaxes to its ground state. Given a very high photon density, multiphoton luminescent may occur in quantum dots and dyes. While for lanthanide ions, multiphoton process can be realized using low power densities by absorbing low-energy light and emitting high-energy light. This anti-Stokes luminescence is known as upconversion¹⁰⁵. In this complex nonlinear optical process, a lanthanide ion is first excited under a single-photon excitation. Owing to the intermediate long lived excited states, the lanthanide ion sequentially absorbs a second photon and reaches a higher excited state. When the ion relaxes to its ground state, the output radiation has shorter wavelength than the pump one¹⁰⁶.

In contrast to commonly used Stokes-shifted luminescent materials like quantum dots, organic dyes and semiconductor polymer materials, UCNPs are nontoxic, stable and have narrow optical absorption and emission bands, high emission efficiency and long lifetime¹⁰⁷. This is due to the superior features of the complex energy level structure of rare-earth ions (REs).

Table 4.1 Commonly used rear earth ions

Rear earth ion	f-f transition	Emission wavelength/nm
Er^{3+}	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	520 ¹⁰⁸
	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	540
	$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$	655 (630~680 dominant)
Tm^{3+}	$^1\text{G}_4 \rightarrow ^3\text{H}_6$	450.5, 475 ^{107b} (main)
	$^1\text{G}_4 \rightarrow ^3\text{F}_4$	630-680 (weak)
	$^3\text{H}_4 \rightarrow ^3\text{H}_6$	750-850
Eu^{3+}	$^5\text{D}_0 \rightarrow ^7\text{F}_1$	593 ¹⁰⁹
	$^5\text{D}_0 \rightarrow ^7\text{F}_2$	617

UCNPs have high flexibility in assigning the dopant species and host material in order to establish the NaYF_4 matrix with trivalent lanthanide ions. For example, Yb^{3+} ions act as sensitizers that absorb 980-nm NIR excitation light without any visible up-converted emission while the other RE^{3+} ions (Table 4.1) act as activators that emit visible up-converted luminescence characteristic of their atomic transitions.

There are two commonly used methods to produce upconversion nanomaterials, hydrothermal method¹¹⁰ and thermal decomposition method¹¹¹. Different from

thermo-decomposition method which produces quasi sphere or sometimes hexagon nanoparticles below 100 nm, by adjusting the synthetic conditions, various morphologies ranging from nanowire to tube, rod, particle and disk can be obtained in micron range via hydrothermal synthesis.

UCNP based materials have extraordinary advantages in biological field because of their minimal spectral overlap with cellular autofluorescence, deeper penetrability excitation using near-infrared laser and exceptional photostability, which exhibit no loss of intensity following hours of continuous excitation¹¹². One of the most commonly used applications of UCNPs is biosensor which works in tandem with the Forster resonant energy transfer (FRET). Recently, the 800 nm excited Nd³⁺-doped UCNP instead of those 980 nm excited Yb-doped UCNP, due to the over-heating effect of water in biosystems under 980 nm irradiation¹¹³.

The PL emissions of iodide perovskite materials are in the range of 760 nm to 810 nm, which make them a potential material to excite Nd³⁺-doped UCNP. Although there are previous works that examine the enhancement of efficiency by UCNP in perovskite based solar cells^{10a}, research on UCNP excited by perovskite materials has not been investigated yet. For this purpose, we studied the interaction between Nd³⁺-doped UCNP or UCNRs and perovskite materials in this work.

We are trying to use the strong PL emission at 790 nm from the excited perovskite microrods to excite upconversion nanomaterials. We assume that by using UCNP on

the surface of perovskite microrods, UCNPs can quench the PL emission of perovskite microrods, which is under Forster resonance energy transfer. The key instrument in this study to detect the PL change is the time-resolved confocal microscope. This instrument can sensitively record the PL intensity and lifetime simultaneously at the interface between two materials. For instance, the quenching behavior between spiro-OMeTAD and $\text{CH}_3\text{NH}_3\text{PbI}_3$ ^{60c}. It also can effectively detect energy transfer between single molecules¹¹⁴. By using NaYF_4 as the host material, the core particle is triply doped with Yb^{3+} (as sensitizer), Nd^{3+} (as light harvest to absorb light at 800 nm) and Er^{3+} (as activator). The concentrations of Nd^{3+} doped in the core and shell play a crucial role in the photoluminescence efficiency of upconversion nanoparticles¹¹⁵. In the shell, for the purpose of effectively harvesting light at around 800 nm, mol 20% Nd^{3+} is used. In comparison, a relative small amount of Nd^{3+} (mol 1%) is doped in the core to minimize concentration quenching. Because of the abundant energy level structures and Laporte-forbidden f–f electronic transitions of REs, the sharp emission peaks of upconversion nanomaterials can be easily distinguished compared to the broad emission of semiconductor. The NIR-to-visible upconversion is based on sequential energy transfers between lanthanide dopants or excited-state absorption involving their real metastable-excited states with lifetimes as long as several milliseconds. In this study, we used perovskite material in microrod morphology. For perovskite microrod, the proper size makes it easy to be detected and focused under time-resolved confocal microscope compared to perovskite nanocrystals. It is more flexible and fast to tune the

PL emission position by adjusting the FA/MA ratio in precursor solution for perovskite microrods compared to bulky perovskite films. Besides, perovskite microrods exhibits advantages over thin films by improved strain relaxation and reduced reflection¹¹⁶.

For the ease of reading, the following chemicals are written in abbreviation.

UCNPs	Upconversion nanoparticles
UCNRs	Upconversion nanorods
Er-UCNPs	NaYF ₄ :Yb/Nd/Er@NaYF ₄ :Y/Nd core-shell UCNPs
Er-UCNRs	NaYF ₄ :Yb/Gd/Nd/Er@NaYF ₄ :Y/Nd core-shell UCNRs

4.2 Experimental Section

4.2.1 Materials

Dimethylformamide (DMF, anhydrous, HPLC grade) and isopropanol (IPA, HPLC grade) were obtained from Tedia. Lead (II) iodide (PbI₂, 98%), Y(CH₃CO₂)₃, Yb(CH₃CO₂)₃, Er(CH₃CO₂)₃, Nd(CH₃CO₂)₃, Y(NO₃)₃, Yb(NO₃)₃, Er(NO₃)₃, Nd(NO₃)₃, Gd(NO₃)₃ and Tm(NO₃)₃ were purchased from Sigma-Aldrich. Methylamine (41% w/w aqueous solution) and formamidine acetate were obtained from Sinopharm Chemical Reagent Co. Ltd. Hydroiodic acid (HI, 57% w/w aqueous solution) was obtained from Alfa Aesar. Oleic acid (97%) was purchased from VWR Chemicals. Absolute ethanol (AR grade) was obtained from Fisher Scientific UK. All chemicals were used as received.

4.2.2 Sample preparation

Inorganic/organic halide materials, methylammonium iodide (MAI) and formamidinium iodide (FAI), were synthesized according to the method described in Chapter 3. Section 3.2.2

4.2.2.1 Preparation of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ ($0 \leq x \leq 1$) perovskite rods.

Glass coverslips and silicon wafers ($20 \times 20 \text{ mm}^2$) were ultrasonic cleaned in acetone, detergent and DI water, then UV/Ozone cleaned for 15 min. In this two-step synthesis, PbI_2 rods on the precleaned substrates were obtained by drop-casting and evaporating a droplet (10 μL) of DMF solution of PbI_2 (concentration 5 wt %) on the substrate surface at ambient conditions for overnight. The PbI_2 rods were subsequently annealed at 75 °C for 15 min in an oven to remove any residual solvents. $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ perovskite rods were formed by immersing PbI_2 rods into an IPA solution of MAI (15 mg/mL) and FAI (5 mg/mL) for 15 min, then the product was annealed at 75 °C in oven for another 15 min.

4.2.2.2 Preparation of Upconversion nanoparticles (UCNPs)

The core-shell UCNPs were synthesized in a typical two-step thermal decomposition method.

Synthesis of $\text{NaYF}_4\text{:Yb/Er/Nd}(30/0.5/1\%)$ UCNPs. The UCNPs were prepared according to the references published before¹¹⁷. To a 50-mL three-necked flask with

oleic acid (3 mL) and 1-octadecene (7 mL) was added 2 mL of $\text{RE}(\text{CH}_3\text{CO}_2)_3$ (0.2 M, RE=Y, Yb, Er and Nd) in methanol and the solution was heated to 150 °C for 1 h with magnetic stirring and then cooled down to 50 °C, all under N_2 protection. Subsequently, a methanol solution (6 mL) containing NH_4F (1.6 mmol) and NaOH (1 mmol) was added and stirred at 50 °C for 30 min. Then the temperature was increased to 100 °C to remove any residual methanol (pumped three times). Finally, the solution was heated at 300 °C under a nitrogen flow for 2 h and then cooled to room temperature. The resulting nanoparticles were precipitated by ethanol (10 mL), collected by centrifugation (5000 rpm for 10 min) and redispersed in cyclohexane (4 mL). The sample is used as cores in the synthesis of core-shell UCNP.

Synthesis of $\text{NaYF}_4\text{:Yb/Er/Nd}(30/0.5/1\%)\text{@NaYF}_4\text{:Y/Nd}(80/20\%)$ core-shell UCNP. The core-shell UCNP were prepared in the similar way as the synthesis of cores, only with a few adjustments. In the first step, instead of $\text{RE}(\text{CH}_3\text{CO}_2)_3$ methanol solution, the as-synthesized core UCNP solution was added in the 50 mL three-necked flask with oleic acid (3 mL) and 1-octadecene (7 mL). The rest steps are all the same. After washed in ethanol and collected by centrifugation, the core-shell UCNP were dispersed in 4 mL chlorobenzene for further use.

4.2.2.3 Preparation of Upconversion nanorods (UCNRs)

The core-shell UCNRs were synthesized in a combination of a hydrothermal synthesis for core and a thermal decomposition method for the core-shell structure.

Synthesis of NaYF₄:Yb/Gd/Nd/Er (18/30/1/1%) core UCNRs. Basically, 0.3g of NaOH was dissolved in 1.5 mL DI water, then it was mixed with ethanol (5 mL) and oleic acid (5 mL) under stirring¹¹⁸. To the resulting mixture were added 2 ml of RE(NO₃)₃ (0.2 M, RE = Y, Yb, Tm, Er, Nd and Gd) and 1 ml of NH₄F (2 M). Then the mixture was transferred into a Teflon-lined autoclave (20 mL) and heated at 210 °C for 3 h in oven, finally cooled down to room temperature. The obtained nanorods were collected by centrifugation (3000 rpm for 10 min), washed with ethanol and redispersed in 4 mL chlorobenzene.

Synthesis of NaYF₄:Yb/Gd/Nd/Er(18/30/1/1%)@NaYF₄:Y/Nd(80/20%) core shell UCNRs. The core-shell UCNRs were prepared in the same way as the core-shell UCNPs.

4.2.2.4 Preparation the mixture of FA_xMA_{1-x}PbI₃ (0 ≤ x ≤ 1) perovskite samples and upconversion nanomaterials.

Upconversion nanomaterials (UCNRs or UCNPs) dispersed in chlorobenzene (1mg/mL) were covered evenly on the surface of as-prepared FA_xMA_{1-x}PbI₃ perovskite rods by spin coating.

4.2.3 Characterization Methods

Powder X-ray Diffraction (PXRD). XRD patterns were obtained using an X-ray diffractometer (D8 Advance, Bruker) with Cu-Kα radiation source. PbI₂ rods were

prepared on silicon wafers ($20 \times 20 \text{ mm}^2$) and converted to perovskite rods by immersing in IPA solution (15 mg/mL MAI and 5 mg/mL FAI). The samples were scanned from $10^\circ < 2\theta < 50^\circ$ at an increment of $1\text{s}/0.02^\circ$.

Transmission electron microscopy (TEM). TEM were recorded using a JEOL JEM 1400 TEM (100 kV acceleration voltage). Samples for TEM were prepared by drop casting 20 μL of the 10 times diluted UCNPs (or UCNRs) solutions in cyclohexane onto a standard copper grid coated with a continuous amorphous carbon film. The size distribution and thicknesses of UCNPs (or UCNRs) were obtained from the TEM image with ImageJ software.

Filed emission scanning electron microscopy (FESEM). The morphologies of the PbI_2 rods and perovskite rods were characterized by FESEM (JEOL JSM 7600F)

Optical measurements. Steady-state absorption the UCNPs and UCNRs solutions were recorded by using a NIR/Vis absorption spectrometer (Cary 100, Varian). The upconversion luminescence spectra of UCNPs and UCNRs chlorobenzene solutions were measured at an angle of 90° to the excitation laser (808 nm) and an optical SEC-2000 spectrometer coupled 2048 pixels CCD assay (ALS Co., Ltd, Japan). A filter with short pass 750 nm was placed before the spectrometer to minimize scattering from the excitation laser beam.

Time-resolved confocal microscope. The fluorescence lifetime and intensity of $\text{FA}_x\text{MA}_{1-x}\text{PbI}_3$ perovskite microrods and those covered with UCNPs or UCNRs samples were obtained by an time-resolved confocal microscope (MicroTime 200,

PicoQuant), which is equipped with a scanning stage (P-733.2CL, Physik Instruments), an air objective lens (20×, N.A. 0.4, Olympus) and an inverted microscope (IX71, Olympus). Perovskite rods were excited by a 635 nm pulsed laser diode (LDH-P-C-635B, PicoQuant) at 2.5MHz. Half-wave and quarter-wave plates are used to provide circular polarized excitation light. Circular polarized excitation light passed through an excitation filter (Z636/10, Chroma) before being focused through an air objective lens (20×, N.A. 0.4, Olympus) which was also used to collect the fluorescence. The fluorescence was then passed through a dichroic mirror (Z638rpc, Chroma) and an emission filter (FGL715, Thorlabs) before being detected by a single-photon avalanche diode (SPAD, SPCM-AQR-15, PerkinElmer).

4.3 Results & Discussions

4.3.2 Synthesis of NaYF₄:Yb/Nd/Er@NaYF₄:Y/Nd core-shell UCNPs (Er-UCNPs).

The morphologies of the core UCNPs and the core-shell UCNPs are characterized by TEM (Figure 4.1). The difference of 15.2 nm (39.4-24.2 nm) in diameter between NaYF₄:Yb/Nd/Er core NPs (Figure 4.1a) and NaYF₄ NPs (Figure 4.1c) indicates the influence of dopants on the particle size. In the synthesis of core-shell UCNPs (Figure 4.1b), the shell deposits on the core surface with directional preference, resulting in the growth of length 22.7 nm (62.1-39.4 nm) and width of 15 nm (44.4-39.4 nm).

Figure 4.1. TEM images and the corresponding size distribution histograms of the as-synthesized nanoparticles. (a) NaYF₄:Yb/Nd/Er core NPs, (b) NaYF₄:Yb/Nd/Er@NaYF₄:Y/Nd core-shell UCNPs and (c) NaYF₄ NPs

The optical properties of the core-shell UCNPs are recorded as shown in Figure 4.2. Nd³⁺-doped UCNPs obviously have two absorption peaks in the near-IR absorption spectrum (Figure 4.2a), at 794 nm and 804 nm respectively, among which the latter exhibits more intense absorption than the former. However, the commonly used commercial lasers to excite Nd³⁺-doped UCNPs are mostly centered at 808 nm, which leads to a low PL efficiency.

Because of the abundant energy level structures and Laporte-forbidden f–f electronic transitions of REs, these sharp emission peaks can be easily distinguished compared to the broad semiconductor emission. The NIR-to-visible upconversion is based on

sequential energy transfers between lanthanide dopants or excited-state absorption involving their real metastable-excited states with lifetimes as long as several milliseconds, a process orders of magnitude more efficient than the 2-photon absorption process typically used in multiphoton microscopy¹¹². For Er³⁺-doped UCNPs (dispersed in chlorobenzene solution), the up-converted luminescent spectrum is shown in Figure 4.2b. The luminescence peaks at 525 nm, 544 nm and 655 nm originate from the f-f transitions of $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$, respectively, among which the peak at 655 nm is the dominant emission

Figure 4.2. Optical spectra of NaYF₄:Yb/Nd/Er@NaYF₄:Yb/Nd core-shell UCNPs in chlorobenzene.(a) Near-IR Absorption spectrum (b) Upconverted Emission spectrum ($\lambda_{exc}=808$ nm).

4.3.1 Synthesis of NaYF₄:Yb/Gd/Nd/Er@NaYF₄:Yb/Nd core-shell UCNRs (Er-UCNRs).

In this synthesis of core-shell UCNRs, the rod-shape core was synthesized using

hydrothermal method and the shell was synthesized using thermal decomposition method. In the synthesis of core particles, the resultant nanorod morphology is attributed to the dopant Gd^{3+} . On doping with Gd^{3+} , cubic phased nanoparticles are transformed to hexagonal phase, due to the substitution of Y^{3+} ions by larger Gd^{3+} ions in the host lattice¹¹⁰. As shown in Figure 4.3a, the UCNRs are monodispersed with an aspect ratio of 14. It is noted that the thermal decomposition method successfully coat an Nd-NaYF_4 shell on the surface of the as-synthesized core UCNRs with little effects on the overall shape.

The combination of hydrothermal synthesis and thermal decomposition method could be further used to achieve micron-sized core shell upconversion nanomaterials with various morphologies with excitation wavelength at ~ 800 nm.

Figure 4.3. TEM images and the corresponding size distribution histograms of the as-synthesized nanorods. (a) NaYF₄:Yb/Gd/Nd/Er core NRs.

4.3.3 Two-step synthesis of FA_{0.24}MA_{0.76}PbI₃ perovskite microrods.

Due to the most intense absorption at 794 nm of upconversion materials doped with Nd (Figure 4.2a), the PL position of the perovskite was adjusted to 794 nm by mixed cation method, which is a commonly used approach to control the bandgap of perovskite materials^{98c}. As shown in Figure 4.4, with increasing content of FA⁺, PL redshifts from 767 nm (MAPbI₃) to 809 nm (FAPbI₃). The ratio of FA⁺/MA⁺ at

FA_{0.24}MA_{0.76}PbI₃ (15 mg/mL MAI and 5 mg/mL FAI) exhibits PL at 794 nm.

Figure 4.4 Photoluminescence images of different perovskite microrods. MAPbI₃ (black line), FA_{0.24}MA_{0.76}PbI₃ (red line) and FAPbI₃ (blue line).

The preparation of ultralong FA_{0.24}MA_{0.76}PbI₃ perovskite microrods begins with the synthesis of PbI₂ microrods. Initially, 10 μ L of 5 wt% PbI₂ in DMF is drop casted on a precleaned glass coverslip or silicon wafer. It should be noted that the cleaning procedure under UV/Ozone is a crucial treatment in forming ultralong PbI₂ microrods. By removing the organic contaminants, the surface of the substrate becomes hydrophilic, which enables the 10 μ L droplet of PbI₂ solution to form a thin film, fully covering the 20 $\times$ 20 mm² substrate surface. With increasing rest time, DMF is evaporated slowly and the concentration of the PbI₂ solution is gradually increased till the emergence of PbI₂ nuclei. Continuous DMF evaporation stabilized the nuclei, and the crystal growth evolution exhibits a preferential crystallization along the (001) plane,

which shows up as the most intense diffraction peak in the PXRD spectrum Figure 4.5 (black line) and results in ultralong PbI_2 microrods.

Figure 4.5 PXRD patterns of PbI_2 microrods (black) and $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ microrods (red). The lattice planes are labeled on top of each reflection peaks.

The aspect ratio of the PbI_2 microrods can be controlled by adjusting the concentration of PbI_2 solution. Based on the classical crystallization theory^{58e}, from low to high supersaturation levels, the initial amount of nuclei increases and leads to a faster consumption of free monomers, which gives rise to microrods with a lower aspect ratio^{60c}. The morphology of the PbI_2 microrods is characterized using field emission scanning electron microscopy (FESEM). As shown in the SEM image (Figure 4.6a) the distribution of 110 PbI_2 microrods have an average length of $30.2 \pm 7.2 \mu\text{m}$ and an average diameter of $3.0 \pm 0.8 \mu\text{m}$ obtained from a Gaussian fit to their respective distributions (Figure 4.6b). The aspect ratio is 10.

In order to completely convert PbI_2 to perovskite, the substrates were immersed in an IPA solution containing 15 mg/mL FAI and 5mg/mL MAI for 10 min. The yellow PbI_2

Figure 4.6. SEM images of PbI_2 microrods prepared from the evaporation of 5 wt% PbI_2/DMF solution (a). SEM images of the surface of PbI_2 microrods (c) and the converted perovskite microrods (d). The scale bars are 100 μm for (a) and 1 μm for (c-d).

microrods immediately turned to black, demonstrating a fast conversion to perovskite structure. Yang *et al.* have investigated this in situ solid-liquid interfacial conversion dynamic¹¹⁹. When PbI_2 molecules is exposed to rich I^- in IPA solution, they tend to

dissolve in IPA with the formation of PbI_4^{2-} . Increasing amount of PbI_4^{2-} monomers leads to a recrystallization on the interface, along with encapsulating FA^+ and MA^+ cations in the perovskite structure and releasing I^- ions back to the solution. Due to this dissolution and recrystallization process, compared to the relatively smooth surface of PbI_2 microrods (Figure 4.5c), the converted perovskite microrods have tough surface with small cubic crystals observed on the surface. Furthermore, long immersion times of PbI_2 molecules in FAI/MAI/IPA solutions can corrode the microrods to smaller pieces. Nevertheless, in this study, 10 min of immersion would retain the shape of the microrods as well as achieve a thoroughly conversion to PbI_2 perovskite. PXRD patterns are collected in order to further investigate the crystal structure of $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ microrod. As shown in Figure 4.5 (red line), all the PXRD diffraction peaks are coincident with the cubic perovskite phase, which indicates the complete conversion from PbI_2 microrods to $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ microrods.

The PL lifetime image of a single $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ perovskite microrods is shown in Figure 4.7a. In order to protect the microrods from air and moisture, the glass coverslip with perovskite microrods deposited on the surface was put in a sealed coverslip with a quartz bottom for observation under microscope. A randomly chosen point on a typical perovskite microrod shows increasing PL intensity under continues irradiation at 635 nm (0.05 W) for 10 min with the initial PL intensity of 40.18 counts/ms enhanced by 4.8 times under continues irradiation (Figure 4.7b). Up to ~95% of 200 randomly chosen points on perovskite microrods displayed PL enhancement to different degrees.

This phenomenon could be attributed to the reported light soaking effect, in which free electrons generated under laser irradiation gradually passivate the electronic traps of the perovskite microrods¹²⁰.

Figure 4.7 (a) PL lifetime image (size $80 \times 80 \mu\text{m}^2$) of single perovskite microrods. (b) PL intensity trajectory of a randomly selected point on a $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ perovskite microrod. (c) PL lifetime decays and corresponding monoexponential fits for profiles constructed at times A (0~1.5s), B (300~301.5s) and C (597.5~600

s)

The time-resolved PL lifetime decay profiles of $\text{FA}_{0.24}\text{MA}_{0.76}\text{PbI}_3$ perovskite microrods were extracted from the PL intensity trajectory (Figure 4.7b). Three separate times were studied, point A, B and C are 1.5 s time steps corresponding to 0, 300 and 598 s respectively (Figure 4.7c). Described using a monoexponential decay function, the lifetime at point A, B and C increases gradually from $\tau = 85.3$ ns, 135.3 ns to 144.5 ns, which indicates the increasing in lifetime τ illumination time. The rate of increasing in τ decreases at the later state of irradiation. This is due to the decrease in trap density. The surface defects in perovskite crystal structure and vacancies arise from the loss of iodine, which limits the PL performance of the perovskite microrods¹²¹. Upon light irradiation, the trap density of perovskite microrods is relatively high and photogenerated electrons are captured by the traps, which leads to the reduction of radiative recombination between free electrons and free holes (point A). With increasing amount of traps filled by photogenerated electrons, the enhanced radiative recombination renders an intensified PL emission as well as longer lifetimes (point B and C)^{60c}.

4.3.4 Interaction between perovskite microrods and upconversion nanomaterials

Figure 4.8. SEM images of the surface of perovskite microrods spin-coated by 1 wt% of UCNRs (a) and UCNPs (b). The inset in part (b) displays the magnified image of a single microrod covered by UCNPs. The scale bars are 1 μm for (a-b) and 100 nm for the inset in part (b).

In an attempt to investigate the interactions between upconversion nanoparticles and perovskite materials, 1wt% of upconversion nanomaterials in chlorobenzene are spin coated on the surface of the perovskite microrods. In order to find the proper concentration of UCNPs to completely cover PK microrods, SEM is used to check the surface. In Figure 4.8, UCNPs and UCNRs have completely covered the surface of PK microrods and no exposed surface of perovskite microrods is found, the coverage of the former is better than the latter due to the large specific surface area of nanoparticles. Additionally, the coverage is double checked by confocal microscope. The sample is excited by 808 nm laser and the emission of UCNPs is collected by using filter 720 nm

SP. As the emission of UCNPs is detected on the whole surface, the complete coverage of UCNPs on PK microrods is confirmed. The time-resolved PL intensity, PL enhancement factor (EF) and lifetime of 100 randomly chosen points from three samples: the bare perovskite microrods (PK), Er-UCNRs spin-coated perovskite microrods (Er-UCNR/PK) and NaYF₄ NRs (NaYF₄/PK), are investigated. Here the NaYF₄ NRs are used as control samples. In the investigation of their PL performances, the distributions of the initial and the final (600 s) PL intensities are shown in Figure 4.9a and 4.9b, respectively. The PL intensities increases in the order PK (17.1) < NaYF₄/PK (17.9) < Er-UCNR/PK (25.3) for both PL, but EF increases in the opposite order Er-UCNR/PK (5.1) < NaYF₄/PK (6.9) < PK (9.4) (Figure 4.9 c, d and e). The order of initial time-resolved lifetime for three samples is in same trend as that of PL intensities, however, for the lifetimes at 600 s, PK samples have the longest average lifetime (173.4 ns).

Similar trends were also observed when UCNPs were deposited on the perovskite microrods. In this case, the PL intensities increases in the order PK (4.2) = NaYF₄ UPs/PK (4.2) < Er-UCNPs/PK (12.4) for initial PL, and EF increases in the opposite order Er-UCNP/PK (13.1) < NaYF₄ UPs/PK (14.0) < PK (42.2) (Figure 4.10 c, d and e).

Figure 4.9. Histograms of the enhancement factor (EF), initial and final PL intensities and lifetime of perovskite microrods and perovskite microrods covered by UCNRs and NaYF₄ NRs. (a) Counts of initial intensity (b) Counts of final emission intensity (c) histograms of enhancement factor in 600s (d) initial lifetime (obtained from the monoexponential PL decays constructed from photons between 0 and 1.5s) (e) final lifetime (obtained from the monoexponential PL decays constructed from photons between 598.5s and 600s)

Figure 4.10. Histograms of the enhancement factor (EF), initial and final PL intensities and lifetime of perovskite microrods and perovskite microrods covered by UCNP and NaYF₄ NPs. (a) Counts of initial intensity (b) Counts of final emission intensity (c) histograms of enhancement factor in 10 min (d) initial lifetime (obtained from the monoexponential PL decays constructed from photons between 0 and 1.5s) (e) final lifetime (obtained from the monoexponential PL decays constructed from photons between 598.5s and 600s)

Similar as measurements on UCNRs and perovskite microrods, as shown in Figure Figure 4.10, the initial PL intensity of spin-coated perovskite microrods are obviously higher than those bare perovskite samples and the EF of PK is still the highest among the three samples. The trend of initial lifetimes are consistent with their initial PL intensity, while for the results of 600 s, in both UCNRs and UCNP there are no obvious difference on PL intensity and lifetimes between these three samples.

Here we propose three possible explanations to explain the results in Figure 4.9 and Figure 4.10.

1. Passivation effect on the perovskite microrods from oleic acid.

The synthesis methods include the used of oleic acid as stabilizer and ligands in both the completed thermal decomposition and hydrothermal synthesis methods. After the synthesis reaction is done, the particles are precipitated and washed with ethanol only once to prevent the loss of oleic acid from particle surface. In the spin coating step, as the perovskite materials are damaged in polar solvents, only nonpolar solvents like chlorobenzene are used to achieve a suspension of upconversion nanoparticles. It is reasonable to assume that some oleic acid is also dispersed in the UCNP or UCNRs chlorobenzene solution. Furthermore, the bonding of oleic acid to the UCNP surface is quite weak and several times of wash in ethanol can remove some of the oleic acid ligands. The oleic acid ligands is characterized in FTIR. In our

UCNRs sample, the IR characteristic peaks of alkene stretchings at 2926 cm^{-1} and 2851 cm^{-1} , asymmetric -COO- stretches at 1449 cm^{-1} are observed (Figure 4.11).

It is reported that oleic acid treatment can passivate the MAPbI_3 nanowires with reduction in trap density, extension of carrier lifetime and enhanced stability^{52c}. Hence in our study, the Er-UCNPs/PK samples and NaYF_4 /PK samples display stronger PL emission than PK samples.

Figure 4.11 FTIR spectra of oleate-capped UCNr (red line) and ligand-free UCNr.

2. Distance between perovskite microrods and upconversion nanomaterials.

Laura et al. have reported the cementing of MAPbBr_3 NPs to UCNPs by cucurbiturils¹²². There is no change in PL spectrum in free MAPbBr_3 NPs and free

UCNPs mixture solution even at high concentrations. By the cementing via cucurbituril, emission peaks of UCNPs were quenched by MAPbBr₃ NPs. In our case, the spin coated UCNPs on perovskite microrods may not be able to achieve the interaction distance.

3. Low PL efficiency of Nd³⁺-doped upconversion nanomaterials

As shown in Figure 4.9 and Figure 4.10, the performances of non-doped NaYF₄ NPs and Er³⁺-Nd³⁺-doped UCNPS on perovskite microrods are similar. Nd³⁺-doped upconversion nanomaterials have intrinsic low PL efficiency¹¹³. The 794 nm PL emission generated from FA_{0.24}MA_{0.76}PbI₃ perovskite microrods may be too weak to effectively excited enough UCNPs.

4.4 Conclusion

We have synthesized perovskite microrods in a two-step solution based method, in which the FA_{0.24}MA_{0.76}PbI₃ perovskite microrods are converted from pre-synthesized PbI₂ microrods by a fast in situ solid-liquid interfacial conversion reaction. To reach the maximum absorption wavelength of Nd³⁺-doped upconversion nanoparticles (795 nm), the emission of the perovskite microrods was precisely adjusted by controlling the FA/MA ratio. The cores of UCNRs were prepared by hydrothermal synthesis whereas the cores of UCNPs were synthesized in thermal decomposition method. The interactions between upconversion nanomaterials and perovskite microrods were investigated by spin coating UCNPs and UCNRs on top of the perovskite microrods.

The PK microrods covered by UCNPs do not show significant different optical behavior to those covered by NaYF₄, while the initial lifetime and PL intensity of the spin-coated microrods were enhanced compared to the bare perovskite microrods. The low PL efficiency of upconversion materials and passivation on perovskite microrods of oleic acid may give attribute to the result.

Chapter 5 Outlook And Future Work

5.1 Outlook

The fundamental study in Chapter 2 provides the detailed single colloidal particle motions in crystallization process. Apart from other studies that focus on the overall microgel crystallization process refer to different stimulations, the ratios of behavior types of single colloidal particles also indicate the different external environment. The study summarizes a conclusion that if the ratios between Brownian motion particles and directive motion particles are sample in two different colloidal systems (e.g. different microgel concentration and pH), then in macroscopic the crystallization speeds of these two colloidal systems will be the same. This may help to further study the microgel crystallization behavior and promote the synthesis of colloidal materials in manufacturing industry. Additionally, melting process is also very important in microgel system study, so we can use similar equipment set up to realize microgel melting study (the details of future work is in Section 5.2). As computer simulation can provide important insight into kinetics of nuclei formations and crystal growth, we should do a computer simulation based on data from chapter 2 to find more mechanism information in crystallization process (Section 5.3).

The facile synthesis method in Chapter 3 provides a new approach to realize PL tuning of QDs with high quantum yield. As the widely usage of perovskite material in optical and photovoltaic fields, we may try to use this product to make LED devices.

The intrinsic instability of organic component in PK QDs need to be improved. This

In Chapter 4, we are trying to realize excitation of UCNPs by the emission of perovskite materials, but this process has not been detected. This may due to the low quantum efficiency of UCNPs, so the emission of perovskite microrods is not strong enough to excite the upconversion process. This work provides some information to other researchers that it is quite hard to realize energy transfer from perovskite material to UCNPs. Nevertheless, the energy transfer from UCNPs to perovskite has been proved to work in other studies.

5.2 Visualizing melting behaviors in Three-dimensional soft colloidal crystal

Abstract: Time-lapse video microscopy is used to visualize the melting behaviors of colloidal system. Thermo-responsive p(NIPAm-co-AEMA) microgel is employed to study melting phase transition in three-dimensional crystal, both in the grain boundaries and in the bulky crystal region. The trajectories of individual particles undergoing crystal-to-fluid transitions can be extracted from real time videos captured via wide-field microscopy (WFM).

5.2.1. Introduction

On the basis that colloidal particles move in relative lower speed compared to atoms and have submicron sizes scale visible via optical microscope, therefore colloidal systems are widely used as experimental models to study phase behaviors

including transitions between fluid, crystal and glass states in molecular materials. Hard spheres like polymethylmethacrylate (PMMA) and PS¹²³ have been widely used in phase behavior study, however, multi-stimulative response soft spheres, like pNIPAm-based microgel, have attracted increasing attention due to their tunable interactions *in situ*. In the context of pNIPAm-based microgel containing ~90% of water, the similar refractive index to water makes it possibly to track melting phenomena at single-particle resolution. Furthermore, the intrinsic thermo-responsive property of pNIPAm-based microgel particles, i.e. reduction in particle size in response to increasing temperature^{15a}, enables thermal control of volume fraction *in situ*, thereby avoiding complicated data analysis, multi samples issue and introduction of ambiguities.

Crystal melting is an important phenomenon that has been studied for hundreds of years, however, there are still many unknown realms waiting for further explanations. Melting in three-dimension crystals and two-dimensional crystals undergo different routes. For 3D crystal, melting is a directive transition from solid state to fluid state, whereas for 2D crystal, melting has an extra mediate hexatic state between solid and fluid state, proposed by Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory¹²⁴. The KTHNY theory is evidently proven by a long-time behavior of 2D melting transition¹²⁵. Precise study of the role of dimensionality, or thickness in another word, in melting has been investigated¹²⁶. For monolayer crystals, melting is consistent with the KTHNY theory and experiences two steps^{126b}. In crystals containing two to

four layers, melting undergoes homogenous mechanism in one step. With increasing crystal layers, heterogeneous melting of the crystal under 12 layers exhibits coexistence of both grain-boundary melting and dislocation melting, while for thicker crystals, melting is mainly controlled by grain-boundary melting. In case of single crystals (more than 30 layers), melting only occurs on the film-wall interface. The reason that drives the difference between homogenous melting in thin film and heterogeneous melting in thick crystals is still unclear.

If a crystal is perfectly formed, which means there is hardly any defect in crystal regime, the crystal regime can keep long-range order at temperature even above the bulky melting point, known as superheating. By shearing pNIPAm-based microgel in a narrow channel, large domains of crystals are formed. According to recent study^{15b}, superheating is performed with a focused beam of light shining on a large domain of crystal at temperature above the melting point. When liquid nuclei induced by thermal fluctuation reach a critical size, bulky melting is initiated.

Figure 5.1. Bright-field images show that the premelting starts at a grain boundary of thermo-responsive pNIPAm-based crystal at temperatures (from 27.2°C to 28.2°C). Two crystallites are separated at an angle $\theta \sim 13^\circ$ by a grain boundary. (A) Sample at 27.2°C. The solid and dashed lines show the grain boundary and a partial dislocation, respectively. The grain boundary is composed of an array of dislocations. The inset indicates the two extra planes. (B) The grain boundary starts to premelt at 28.0°C. While nearby particles undergo liquid-like diffusion (inset), the partial dislocation, denoted by the dashed line, is not affected. (C) and (D) indicate the same sample at 28.1° and 28.2°C, respectively. The premelting region increases along the grain boundary. Scale bars=5 μm ¹²⁷.

Nevertheless, the effects arising from defects in crystal are significant in the phase behavior. Defects like grain boundaries and dislocations within the 3D bulky crystalline regime are thought to attribute to a reduced energy barrier for melting and induces the nucleation of liquid cluster for further melting of the bulky crystal. This

effect has been gradually proven both by recent experiments¹²⁸ and by simulations¹²⁹, and is called premelting. Premelting within the bulky crystal was first reported by Alsayed et al¹²⁷. With gradually elevated temperature, loss of crystalline order appears in adjacent regions to grain boundaries and dislocations, at temperature lower than the melting point of the bulky crystal. By measuring the 3D Lindemann parameter L , which measures the particle mean square fluctuation, at 28.1°C, the Lindemann parameters of particles in premelt boundary and partial dislocation are obviously larger than those in the bulky crystal, which confirms the premelting theory within the bulky crystal (Figure 5.1). The crucial mechanism that drives the premelting phenomenon is the interfacial free energy.

Figure 5.2. Two liquid regions gradually grow and merge into one. At (a) 0, (b) 80, (c) 230, and (d) 400 s. When the distance between two liquid regions is within about ten lattice constants, the crystalline region between them prefers to melt into a liquid tunnel,

as shown in (b). The dashed lines mark the liquid-crystal interfaces. These images show the bottom surface layer^{126a}.

Different types of defects generate different shapes of liquid clusters^{126a}. As shown in Figure 2, grain boundaries give rise to strips of fluid state along the grain while dislocations induce liquid lakes located randomly in the bulky crystal, then both of the liquid regions grow and finally merge into each other.

In addition to the melting effects derived from thermal responsive property of pNIPAm-based microgel, the softness distinguishes the microgel crystal from crystals composed of hard spheres. The ratio¹³⁰ of short-time diffusion coefficient to long-time diffusion coefficient D_L/D_S at melting point is evidently lower than the reported value for hard-sphere system¹³¹. This lower ratio arises due to the overlapping of dangling chains in the vicinity of the particle surface and the sub-diffusive behavior in concentrated suspension.

5.2.3. Conceptual Framework

Here we are concerned with the dynamic melting behaviors of single particles located both adjacent to grain boundaries and interior at the bulky crystal. Previous studies mainly focus on the thermal fluctuations of microgel particles undergoing crystal melting, wherein single-particle tracking is not available once particles merge

into fluid regime, and thus the particle dynamic motion in crystal-to-fluid transition is still unknown. By switching shutter from bright field to laser and back to bright field, the observation of crystal melting, equipped with ~2% fluorescently labeled particles, makes it possible to track the whole motions of individual particles during melting.

5.2.4 Instrumental Setup

Experiment performed on crystal melting is observed via wide-field microscopy (WFM) (Olympus IX71) equipped with a high-speed electron multiplying charge-coupled device (EMCCD) camera (Cascade II 512 Photometrics), oil immersion objective lens (magnification 100 $\times$, numerical aperture 1.3, Olympus) and 633 nm Laser (CUI Melles Griot HeNe Laser). The 2D video is captured in a 512 $\times$ 512 field window equal to 24.22 $\times$ 24.22 μm^2 in real scale.

The temperature of the sample is precisely controlled within 0.1 $^{\circ}\text{C}$ by FCS2 closed chamber system (Biotech). The chamber used to load the specimen is equipped with electrical enclosure (temperature sensor and heater electrode), glass slide coated with electrically conductive Indium-Tin Oxide (ITO), a glass coverslip (No. 1.5 thick with 40 mm Diameter), a gasket with an internal rectangular hole (0.25 mm thickness, 14 mm $\times$ 22 mm rectangular hole), another glass coverslip and a thermo-controlled metal base. With an exterior FCS2 Controller, the heating rate and the temperature of both the coated slide and the metal frame can be tuned manually, which effectively avoids peripheral thermal gradient. The sample is then loaded in the optical cavity,

constructed by the coverslips and gasket, and forms a quasi-cylindrical suspension column by capillary force.

5.2.5. Experimental challenges

a) Temperature gradient

As oil objective is used for observing the melting phenomenon, the contact between the oil and the coverslip is unavoidable. The temperature of the oil and the objective, which is always around 22~24°C, has a cooling effect on the specimen and evidently disturbs the controlled melting observation. A temperature controller for the objective is thus necessary to keep a constant temperature.

b) Other defects in crystal

Common homogenous crystallographic defects include point defects (vacancy defect), line defects (edge dislocation and screw dislocation), planar defects (grain boundary and stacking) and bulk defects (clusters of vacancies). The aim of this study focuses on the melting behaviors of microgel particles both adjacent to grain boundary and in bulky crystal area, therefore other defects like point, line and bulk defects need to be eliminated to the greatest extent. Furthermore, during the melting procedure, dislocations of crystal planes will drive vertical slippage in the bulky crystal regime, giving rise to the focused crystal plane running out of focus. Most of the unwanted defects can be removed effectively by annealing technique. After determination of the

appropriate concentration of microgel suspension, the specimen is perfused into the chamber, heated above the lower critical solution temperature (normally at $\sim 32^{\circ}\text{C}$) to achieve a fluid state in the entire area, then gradually decrease the temperature and keep the suspension at 25°C for hours resulting in crystal regime with a small number of defects. As the crystallization in this study occurs on the coverslip, the surface of the substrate initiates crystal nucleation by reducing the free energy barrier, in consequence, nucleation can arise in different regions simultaneously. Eventually, when crystallites formed from different nuclei grow and meet each other, due to various growing directions, grain boundaries begin to appear.

5.3 Computer simulation of crystallization in soft colloidal system

Computer simulation provides important insight into kinetics of nuclei formations and crystal growth. Both Monte Carlo (MC)¹³² simulations and molecular dynamic (MD)^{132b, 132c, 133} simulations are widely used. The first reported computer simulation of crystal growth was in 1972 by Gilmer and Bennema¹³⁴ based on MC method. Depending on the Boltzmann statistics, MC simulations focus on the possibility of the attachment of randomly virtual moving molecules on the edge of crystal and terminate the simulations when an equilibrium state is reached. In MC simulations, the configuration and the corresponding characteristic structures of crystal are well validated. However, as MC simulation is lack of the dynamical information during nucleation and crystallization, MD simulation is more comprehensive in explaining the kinetics containing molecular dynamical evolution. By combining the dynamic information within all the individual trajectories of the crystalized molecules, MD simulation has successfully revealed the shape and the size of crystal nuclei¹³⁵.

Homogeneous crystallization has been widely modeled both by experimental methods and computer simulation method, however, heterogeneous crystallization initiated by effects from impurities as well as side wall are inevitable in the real world crystallization.

The most basic and been well studied system is the hard sphere crystallization in the presence of a flat hard wall. In the presence of the wall, the nucleation barrier is hardly exists, therefore nucleation is formed in a very short time. As crystallization undergoes at an apparent slower speed than nucleation, the time scales of these two steps are separated. Crystallization occurs subsequently after the formation of nuclei and mainly forms the 111 planes of face-centered cubic (FCC) structure parallel to the flat wall, with rare random hexagonal close packing due to the crystal dislocations. A combination of experimental data and computer simulation (nonequilibrium Brownian dynamic simulation) is studied in fluorescent labeled polymethylmethacrylate (PMMA) crystallization (see Figure 4), which is a frequently studied model for hard sphere system¹³⁶. The entropy driven crystallization of hard spheres is only based on the volume fraction. A depletion zone is both theoretically and experimentally confirmed in front of the advancing crystal-fluid interface, with 5-particle-diameter extension at first and then gradually vanish due to stable interface is reached¹³⁶.

The depleted zone is not only observed in 3D crystallization but also in 2D crystal growth. 2D crystal form planar conformation on substrate surface. Crystal grows when the possibility for incoming molecules or particles detaching from the crystal is lower than the possibility for them to attaching to the crystal growing front. Atomic force microscope (AFM) has been used to further confirm the existence of a depletion zone, where the area occupied by adsorbed molecules is larger than that is needed by crystallized molecules^{132a}. In the context that the concentration in the depletion zone is

lower than that in the bulky concentration, it is reasonable to speculate different dynamic behaviors of molecules or particles when they diffuse from the bulky fluid regime towards the crystal growing front.

Figure 5.4 Snapshots of a sample (volume fraction $\Phi = 0.52$, time $t = 62\tau_B$) based on (A) Confocal microscopy and (B) simulations. In this reconstruction, only crystalline particles are shown and the simulation box is reduced in the z direction¹³⁶.

The computer simulation of soft colloidal system is still at its infant stage. For the flat hard wall induced crystallization, the behaviors of crystallization in soft colloids are analogous to that of hard sphere, while more grain boundaries and defects emerge due to softness¹⁴.

In fluid phase, the experimental radial distribution function is well reproduced by a Hertzian-type interaction potential with fixed repulsion strength and the properties of the monodisperse system are capable within the Rogers-Young closure relation^{133b}. The Hertz potential is commonly used to describe the repulsive interaction between weakly deformable spheres¹³⁷. The reliable physical system for Hertz potential is in which the particle-particle interaction is pure repulsive, elastic spheres and concentrations below overlapping. As the effective volume fraction is far below the freezing point, there is no obvious dependence of the particle-particle interaction and the diameter. Further computer simulations on condensed soft microgel particles and even overlapped conditions are still needed.

5.3.1. Conceptual Framework

The computer simulation of 3D crystallization is based on the experimental data achieved from the previous study on visualizing the growth of soft colloidal in real time. As the sample is loaded between two coverslips to form a quasi-cylinder shape, the hard flat wall plays an important role in reduce the free energy barrier and enhance crystallization, thus the fluid-to-crystal behavior is dominated by heterogeneous crystallization.

The depletion zone is predicted by previous hypothesis and experimental verified in hard sphere system. It's natural to speculate the presence of depletion zone in the crystallization of soft colloidal system, within which computer simulation is rarely

operated. Furthermore, in the visualizing crystallization of microgel particles study, two motions of individual particles undergoing fluid-to- crystal transition have been detected. Is there any relationship between the depletion zone and the motions of particles prior to the crystal-growing front? As the depletion zone locates in front of the advancing crystal-fluid interface and gradually disappear accompanying crystal growth, is the length of the depletion zone that distinguishes the two different motions? How is the intrinsic softness give rise to different crystallization comparing to that in hard sphere systems? Those questions are still unsolved mysteries and may be answered in molecular dynamic computer simulation.

According to Sandomirski et al¹³⁶, Brownian dynamic simulations neglect the hydrodynamic interactions. The Brownian time scale $\tau_B = \sigma^2/D_0$, where the short-time infinite-dilution diffusion coefficient D_0 is extracted from the DLS data. We can first set the dimensions $L_x \times L_y \times L_z$ of the simulation box containing $N=10000$ microgel particles and at the same effective volume fractions as the experimental data (for pH=3.5, $\Phi_{eff}=0.69$ and pH=11.0, $\Phi_{eff}=0.67$).

At pH=3.50, the p(NIPAm-co-AEMA) microgel particles possess purely repulsive particle-particle interaction due to the Coulombic repulsion derived from the protonated amine residues from AEMA. The effective volume fraction we used in visualizing real time crystallization is at 0.69, which is below the close-packed volume fraction 0.74 indicating the suspension isn't overlapped. In addition to the conditions above, pNIPAm-based particles have intrinsic softness. All of those conform to the

requirements of using Hertzian potential. For pH=11.02, the effective volume fraction and softness consist with the Hertzian model, while the particle-particle repulsion is much lower than interactions at low pH.

The Hertzian potential is described like this^{133b}:

$$U_{Hertz}(r) = \begin{cases} \epsilon_H(1 - r/\sigma)^{5/2}, & r \leq \sigma \\ 0, & r > \sigma \end{cases}$$

where σ is the diameter of the particles and ϵ_H is the repulsive strength of the potential. It is obvious that the repulsive strength of microgel suspension at pH=3.5 is stronger than that at pH=11.0. Rogers-Young (RY) closure approximation is known to guarantee thermodynamic consistency of the purely repulsive potential. The radial distribution function solved by Ornstein-Zernike equation with RY can be optimized compared to the experimental results¹³⁸. As the diameter and effective volume fraction can be extracted directly from experimental data, standard molecular dynamic simulation can be performed with adjusting the repulsive strength. Agreement between the experimental results and the computer simulation results can be improved by adding some noise and polydispersity effect.

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