DESIGN AND FABRICATION OF COLLOIDAL NANOCRYSTAL BASED 3D METAMATERIALS

FOR CHIROPTICAL APPLICATIONS

Jiacen Guo

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Supervisor of Dissertation

TACE

Cherie R. Kagan

Stephen J. Angello Professor, Electrical and Systems Engineering, Materials Science and Engineering, Department of Chemistry

Graduate Group Chairperson

Math

I-Wei Chen, Skirkanich Professor of Innovation, Materials Science and Engineering Dissertation Committee Christopher B. Murray, Richard Perry University Professor, Department of Chemistry, Materials Science and Engineering Nader Engheta, H. Nedwill Ramsey Professor, Department of Electrical and Systems Engineering

Mark G. Allen, Alfred Fitler Moore Professor, Department of Electrical and Systems Engineering

DESIGNING AND FABRICATION OF COLLOIDAL NANOCRYSTAL BASED 3D

METAMATERIALS FOR CHIROPTICAL APPLICATIONS

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For my family Without whom this path dims

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ABSTRACT

DESIGN AND FABRICATION OF COLLOIDAL NANOCRYSTAL BASED 3D METAMATERIALS FOR CHIROPTICAL APPLICATIONS

Jiacen Guo

Cherie R. Kagan

Electromagnetic metamaterials (EMs) are artificial materials constructed from subwavelength building blocks that are tailored in their size, shape, composition, and arrangement in order to control the amplitude, phase, polarization, and propagation of light. Although theoretical research has provided most of the design rules for EMs, fabrication of EMs is still quite challenging, especially as the necessity to be smaller than optical wavelengths requires nanoscale meta-atoms. Conventional nanofabrication methods have limited most optical metamaterials to 2D or, often with multiple patterning steps, simple 3D meta-atoms. These methods are also time-consuming processes and not compatible with high throughput, large-area fabrication. In this thesis, we create nanofabrication methods that overcome most of the challenges mentioned above by leveraging the unique properties of colloidal nanocrystals (NCs).

Colloidal NCs are hybrid materials composed of inorganic cores capped with organic ligands. Ligand exchange methods can replace as-synthesized long ligands with more compact ligands. Originally, these ligand exchange methods were developed to reduce interparticle distance and enhance electronic coupling in NC assemblies, which is desirable for NC-based electronic and optical devices. In addition to the electronic and optical properties, the ligand-exchange-induced reduction in interparticle distance can introduces a large misfit strain along the interface by constructing NC/bulk heterostructures, enabling

chemo-mechanical 2D to 3D shape transformation. We systematically studied the evolution of the mechanical properties of NC assemblies and put forward design rules for fabrication. We showed complex 3D meta-atoms through one-step patterning, either suspended in solution or anchored on rigid substrates. We also demonstrated the tunability in structure and function of these metamaterials by tailoring composition, incorporating metal or magnetic NCs, and size and shape through the 2D pattern design and their shape transformation via chemical and thermal treatments.

This fabrication methodology is exploited to create chiro-photonic devices. We demonstrated that metamaterials with 3D chiral meta-atoms can generate giant chiroptical responses that largely scatter right(left) hand circularly polarized light (RCP(LCP)) and transmit LCP(RCP). By designing the shape of the meta-atoms and the periodicity of the meta-atom arrays, we successfully showed ultra-thin photonic devices that are capable of switchable chirality and generating broadband circularly polarized light.

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CHAPTER 1 INTRODUCTION

1.1 From Natural Materials to Artificial Metamaterials

Materials are characterized by sets of constitutive parameters that describe its response to external stimuli. The values of the constitutive parameters of natural materials are bounded. As an example, permittivity (ϵ) and permeability (μ) are the two parameters characterizing the optical, electrical, and magnetic properties of materials. Natural materials can be classified into metals (- ϵ , + μ), dielectrics (+ ϵ , + μ) and diamagnetic materials (+ ϵ , - μ), however, there is no natural material with - ϵ and - μ (Figure 1.1). These limitations come from the fact that the size and shapes of atoms and the periodicities and structures of crystals are limited in natural materials. Metamaterials,¹⁻³ on the other hand, are artificially constructed from building blocks---meta-atoms,⁴ with carefully designed sizes,⁵ shapes,⁶ compositions,⁷ periodicities,⁸ and structures⁹, and therefore are able to realize extended ranges of constitutive parameters including regions that are inaccessible by natural materials.



Figure 1.1 Diagram showing the classification of materials based on the different combinations of ε and μ .

Materials that have constitutive parameters in these other regions open up the prospect of new properties. The double negative parameters, for example, the electromagnetic metamaterials with negative ε and μ as showing Figure 1.1, result in the negative refractive index. The earliest theoretic work dates back to Veselago¹⁰, who first considered the possibility of materials with - ε and - μ . The arguments come from the equation:

$$n^2 = \varepsilon \mu$$
 (1)

where n is the refractive index of materials. This relationship admits that either $+\epsilon$, $+\mu$ or $-\epsilon$, $-\mu$ is possible. However, the sign of n should be taken as negative when both ϵ and μ are negative, due to the dispersion relation of the materials. Mathematically speaking, Maxwell's equations relate the propagation of electromagnetic waves to materials properties ϵ , μ as follows:

$$\nabla \times E = -\frac{1}{c} \frac{\partial B}{\partial t}$$
$$\nabla \times H = \frac{1}{c} \frac{\partial D}{\partial t}$$
$$B = \mu H$$
$$D = \varepsilon E$$

which is equivalent to:

$$\nabla^{2}E - \varepsilon \mu \frac{\partial^{2}E}{\partial t^{2}} = 0$$
$$\nabla^{2}B - \varepsilon \mu \frac{\partial^{2}B}{\partial t^{2}} = 0$$

If a plane monochromatic wave is assumed as $e^{i(kZ-\omega t)}$, then the above two equations can be reduced to the following:

$$k \times E = \frac{\omega}{c} \mu H$$
 (2)
 $k \times H = -\frac{\omega}{c} \varepsilon E$ (3)

Equation (2) and (3) imply that if ε , μ are both positive, then E, H and k form a righthanded triplet of vectors, while if ε , μ are both negative, E, H and k form a left-handed triplet of vectors. The energy flow of electromagnetic waves is determined by the Poynting Vector S:

$$S = \frac{c}{4\pi}E \times H \quad (4)$$
3

Combining (2) to (4), we can see the direction of the energy flow forms a right-handed set with E and H. Therefore, if ε , μ are both negative, then the direction of S is opposite to the direction of k, which suggests the sign of n is negative.

Thirty-six years later, Pendry in his seminal paper¹¹ reconsidered the power of negative refractive index by proposing materials with negative refractive index can serve as perfect lenses, which can form images with resolution breaking the diffraction limit. A negative refractive index medium permits the focus of light even when the medium is in the form of a parallel-sided slab (Figure 1.2), as the refracted light and the incident light are on the same side of the normal direction of the interface. Also, a medium with a negative refractive index allows the amplification and collection of evanescent waves, which doesn't contribute to forming images in traditional optical components. Later on, these effects were experimentally verified.^{12,13}. As shown in Figure 1.3, a thin layer Ag, serving as perfect lens. Ag is deposited onto a structure containing nm-scale features. A beam of 365 nm light is illuminated through the pattern and the Ag thin layer and focused into the photoresist above the Ag. After developing the photoresist, 60 nm line features were resolved, demonstrating resolution breaking the diffraction limit.¹²



Figure 1.2 A thin, rectangular slab of metamaterials with negative refractive index shows the focus of light. The incident and refracted light are on the same side of the normal vector of the interface.¹¹



Figure 1.3 left: Optical superlensing experiment where the Ag serves as a metamaterial superlens. Right top: FIB image of the object. Right middle: AFM of the developed image with the Ag superlens. Right bottom: AFM of the developed image when the Ag is replaced by PMMA as a control experiment.¹²

1.1.1 Controlling the Light Path Through Artificially Tuning Refractive Index n of 2D Metamaterials

The spatial distribution of refractive index n determines the light path for transmission, reflection, and refraction, and therefore, provides a route to engineer the propagation of light. In the design of 2D metasurfaces, two strategies are mainly employed to engineer the effective refractive index of the medium.

As an example, the realization of the negative refractive index heavily relies on materials with a plasmonic resonance.^{14–20} When light drives the plasmonic resonance of materials, the values of their ε and μ can reverse their signs near the resonance, the Drude model can well describe the behavior of $\varepsilon^{21,22}$ for metals:

$$\varepsilon(\omega) = 1 - \frac{\omega_{pr}^2}{\omega^2} \quad (5)$$

where $\omega_{pr} = \sqrt{\frac{ne^2}{m\epsilon}}$, is the plasma frequency of the material, n is the electron density, e is the elemental charge, m is the effective mass of the electron and ω is the frequency of incident light. For typical metals, since the electron density n is large, ω_{pr} is very high, so they have negative permittivity even within the visible spectrum. Also, depending on the size, shape and compositions of meta-atoms, the electron density and the effective mass of the electron can be changed. For example, if heavily doped semiconductors are used to build the meta-atoms, the plasma frequency can be controlled and the window of the negative ε can also be tuned.

However, almost all of natural materials have positive μ spanning most of the electromagnetic spectrum. To overcome these limitations, coupled split-ring resonators (SRRs) are proposed to have the effective permeability μ_{eff} that can be expressed, near the resonance frequency, as^{23–25}:

$$\mu_{eff}(\omega) = 1 - \frac{\omega_{mpr}^2}{\omega^2} \quad (6)$$

where ω_{mpr} is termed as the "magnetic plasma frequency", determined by the geometric dimensions of the SRRs. SRRs typically contain loops of conducting wires. When SRRs are illuminated by light, the induced current circulates within the loops, generating a magnetic dipole. In particular, when the induced current is in phase with the incident light, a resonance happens, causing μ_{eff} to diverge, thus, admitting negative values around the resonance frequency. Similar to the tuning of ε , by designing the geometric dimensions of the SRRs, the magnetic plasma frequency is changed, so that the range of the negative μ_{eff} can be expanded or contracted. This idea is also verified experimentally by incorporating Cu wires and SRRs, in which Cu wires provide negative ε and SRRs provide negative μ^{26} (Figure 1.4). More powerfully, engineering combinations of meta-atoms with different values of ε and μ lead to metamaterials with effective ε and μ that have arbitrary spatial gradients, and it is therefore possible to control the path of the light, which is the topic of transformation optics.



Figure 1.4 Experimental verification of double negative indexes (ϵ and μ) by designing a metamaterial consisting of Cu split-ring resonators and Cu wires.¹³

The idea of negative constitutive parameters can be easily generalized to other domains involving waves, like acoustic^{27,28} and elastic^{29–31} waves. Take an acoustic wave as an example, the equation guiding its propagation is:

$$\nabla^2 P - \frac{\rho}{\kappa} \frac{\partial^2 P}{\partial t^2} = 0 \quad (7)$$

where P is pressure, ρ is the mass density, and κ is the bulk modulus. The speed of sound is given by $\sqrt{\frac{\kappa}{\rho}}$. Here, an analogy can be made such that $\rho \sim \epsilon$ and $\kappa \sim \mu^{-1}$. The underlying physics also relies on the resonance, where the dependence of effective mass density and effective bulk modulus on frequency can be acquired. A classical spring-mass model can easily explain how effective mass density become negative near the region of mechanical resonance (Figure 1.5)²⁷.



Figure 1.5 (A) A spring-coupled mass-in-mass oscillator. M₂ is assumed to slide without friction inside a cavity formed by M₁, and K is the spring constant. (B) The oscillator's apparent mass \overline{M} plotted as a function of angular frequency ω , where $\omega_0 = \sqrt{K/M_2}$ is the resonant frequency. \overline{M} is divergent at ω_0 and can take negative values in a narrow frequency region that is shaded gray. (C) If there are two resonances, the average displacement <x> can cross zero at an antiresonance frequency \widetilde{W} , at which the effective mass/mass density displays a frequency dispersion similar to that shown in (B). Here, the red and green dashed curves show the displacement associated with the first and second resonances, respectively. The black solid curve represents the sum of the two displacements, and it crosses zero at \widetilde{W} .²⁷

Similar to the combination of metal wires and SRRs in electromagnetic EM metamaterials, a combination of decorated membrane resonators (DMRs) and Helmholtz resonators in acoustic metamaterials can produce negative values of effective mass density and effective bulk modulus. Therefore, many exotic phenomena that exist in EM metamaterials, like superlensing, can also be achieved in acoustic metamaterials.
Another strategy is to focus on the engineering of the wavefront of scattered light in metamaterials. The distribution of the scattered light is not only determined by the constitutive parameters of each meta-atom, but also depends on how these meta-atoms are arranged spatially, as scattered light from the meta-atoms can interfere constructively or destructively. The final patterns of the scattered light can still be described by assigning effective n to the metamaterials.

As one example, the scattered light will have a leading or lagging phase with respect to the incident light, determined by the wavelength of the incident light and the size, shape and arrangements of the meta-atoms. ${}^{32-37}$ As the phase change happens as soon as the incident light is scattered, an ultra-thin, 2D metasurfaces is sufficient to complete the process. Imagine a metallic wire with the length $L=\frac{\lambda}{2}$, where λ is the wavelength of the incident wave. In this scenario, the induced current in the wire oscillates in phase with the driving wave, while a shorter or longer wire will generate oscillating current with leading or lagging phase. Therefore, by choosing different dimensions of metallic wires, one is able to control the phase of the oscillating current and thereby the phase of the scattered wave. By arranging the 2D meta-atoms properly, the constructive or destructive interference of scattered light can be controlled to alter the path of the scattered light.³⁸

The relationship between scattered and incident light is described by Fresnel's equations, which connect refraction and reflection to the n of the materials. The "phase jump" of the scattered light modifies Snell's law and also provides design rules for metasurfaces. An intuitive analogy comes from Lectures on Physics by Richard Feynman.³⁸ The refraction of light when it passes from one medium to another can be understood as what is the best

route for a lifeguard to reach a drowning man at sea (Figure 1.6)? The lifeguard runs faster than he swims, so there is an optimum path in which he can extend his running path in exchange for the swimming path, and this whole path is not a straight line. The conclusion is that the optimum path follows the equation: $\frac{Sin\theta_i}{v_{land}} = \frac{Sin\theta_t}{v_{sea}}$, which takes the same form as Snell's law (white dashed line, Figure 1,6). The existence of a metasurface can be modeled as a wall with certain height profile along the seashore, now the lifeguard should also take into account the time consumed in climbing the wall (yellow path, Figure 1.6).



Figure 1.6 Drowning man's dilemma. A wall with varying height along the seashore will change the optimal route for a lifeguard to reach a drowning man in the sea. Likewise, a gradient in phase at the interface between two optical media will change the path of stationary phase according to Fermat's principle, leading to a generalized Snell's law.³⁸

Now, Snell's law is modified to the following forms (Figure 1.7)³⁸:

$$n_{t}\sin\theta_{t} - n_{i}\sin\theta_{i} = \frac{1}{k_{0}}\frac{d\phi}{dx} \quad (8)$$

$$\cos\theta_{t}\sin\phi_{t} = \frac{1}{n_{t}k_{0}}\frac{d\phi}{dy} \quad (9)$$

$$\sin\theta_{r} - \sin\theta_{i} = \frac{1}{n_{t}k_{0}}\frac{d\phi}{dx} \quad (10)$$

$$\cos\theta_r \sin\varphi_r = \frac{1}{n_r k_0} \frac{d\phi}{dy} \qquad (11)$$

where the definition of angles is shown in Figure 1.7. $\frac{d\phi}{dx}$ and $\frac{d\phi}{dy}$ are the components of the phase gradient parallel and perpendicular to the plane of incidence, k_0 is the magnitude of free space wavevector. Equation (8) and (9) describe generalized refraction and (10), (11) describe generalized reflection when there exists a metasurface. Therefore, the control of light propagation is now transformed into designing the phase gradient induced by the metasurfaces. A classic example used a combination of V-antennas with different orientation (Figure 1.8).³⁹ In this layout, a negative phase gradient is achieved so that anomalous reflection and refraction can be measured.

By designing the proper phase gradients, equations (8) to (11) allow the control of θ_t , φ_t and θ_r , φ_r arbitrarily. Also, by combining these equations with the Fresnel equations, one can solve for the n_t of the metasurfaces.



Figure 1.7 A gradient of phase jump $d\Phi/dr$ provides an effective wavevector along the interface that can bend transmitted and reflected light in arbitrary directions. In particular, the component $d\Phi/dy$ normal to the plane of incidence leads to out-of-plane refraction and reflection.³⁸



Figure 1.8 (A) Scanning electron microscope (SEM) image of a representative antenna array fabricated on a Si wafer. The unit cell of the plasmonic interface (yellow) comprises eight gold V-antennas of width ~220 nm and thickness ~50 nm, and it repeats with a periodicity of 11 mm in the x direction and 1.5 mm in the y direction. (B) Schematic experimental setup for y-polarized excitation (electric field normal to the plane of incidence). (C and D) Measured far-field intensity profiles of the refracted beams for y- and x-polarized excitations, respectively. The refraction angle is counted from the normal to the surface. The red and black curves are measured with and without a polarizer, respectively. The polarizer is used to select the anomalously refracted beams that are cross-polarized with respect to the excitation. The amplitude of the red curves is magnified by a factor of two for clarity. The grey arrows indicate the calculated angles of anomalous refraction.³⁹

1.1.2 Artificially Tuning Effective Refractive Index n of 3D Metamaterials to Control Light Polarization

In the previous sections, we discussed how the tuning of n of 2D metasurfaces can be used to control the light path. As mentioned before, 2D metasurfaces include 2D meta-atoms, for which the thickness of the meta-atom is far less than the wavelength of the light. When the meta-atoms become $3D^{13,16,19,39,40}$, which means the thickness of the meta-atom is also comparable to the wavelength of the light, one more property, chirality, can be used to tune the effective n. Here, not only the light path can be controlled, but also the polarization of the light can also be controlled. Chirality refers to 3D systems that lack mirror symmetry and plays an important role in light-matter interactions. EM waves, in a sense, can also be regarded as chiral, as quantum mechanically, the photon has two distinct states, left-handed or right-handed spin, therefore, any light can be regarded as the superpositions of lefthanded or right-handed circularly polarized light (LCP/RCP). Chiral systems have different optical responses to LCP or RCP. They interact with circularly polarized light sharing the same handedness strongly, and weakly with light of the other handedness, leading to two sets of ε and μ , one characterizes the interaction with LCP and the other characterizes the interaction with RCP.

Two effects can occur when light interacts with chiral systems. Take a left-handed molecule as an example, when it interacts with linear polarized light, the direction of polarization will be rotated clockwise when the observer is facing the transmitted light, this effect is called optical activity (OA); when it interacts with LCP, the intensity of transmitted light will be smaller than that of transmitted light when it interacts with RCP,

the intensity difference between the two transmitted light is called circular dichroism $(CD)^{41}$.

The underlying physics of these two effects can be visualized as a two coupled spring system⁴² (Figure 1.10). There are two configurations for this system, which we can assign one as D-enantiomer (Figure 1.9 a) and the other as L-enantiomer (Figure 1.9 b). If we assume the incident light is circularly polarized, we can solve the coupled equations of motion:

$$\begin{aligned} x\ddot{(}t) + \gamma x\dot{(}t) + \omega_0 x(t) + \xi y &= -\frac{e}{m}E_x e^{-i\omega t + ik\left(z_0 + \frac{d}{2}\right)} + c.c. \\ y\ddot{(}t) + \gamma y\dot{(}t) + \omega_0 y(t) + \xi x &= -\frac{e}{m}E_y e^{-i\omega t + ik\left(z_0 - \frac{d}{2}\right)} + c.c. \end{aligned}$$

where γ denotes the loss in the oscillators, ω_0 is the frequency of the uncoupled oscillator, ξ is the coupling constant, e is elementary charge. and m is the mass of the ball. The incident light is assumed as a plane wave.



Figure 1.9 (a) Right (D)- and left (L)-handed classical coupled-oscillator models of optical activity. (b) Optical rotatory dispersion (ORD) and circular dichroism spectra (CD) calculated from the right-handed coupled-oscillator model.⁴⁶

By solving the above two equations, we can establish a relationship between the x(t) or y(t) and the external driving field. The displacement of the two balls oscillates with the external field. Also, as the two balls are assumed to carry charges, the oscillation of the coupled system generates oscillating electric dipoles, where the dipole density can be expressed as:

$$P(\omega, r) = N_0 ex(\omega, r) \quad (12)$$

where the ω is the frequency of the external light, r is the displacement, N_0 is the carrier density. Furthermore, for chiral systems, the dipole density, or the polarization density can be connected to the external field by:

$$P(\omega, r) = \varepsilon_0(\varepsilon - 1)E(\omega, r) + \Gamma \nabla \times E(\omega, r)$$
(13)

where ε is the permittivity of the chiral systems and Γ is the nonlocality parameter⁴⁶. The first term on the right hand side of the equation comes from the general contributions of electric dipoles induced by the electric field, for isotropic medium, only the electric field can induce the dipoles; the second term comes from the contributions of electric dipoles induced by the magnetic field. In a chiral system, the charge oscillation induced by the electric field can generate "magnetic dipoles" that can couple to the external magnetic field, therefore, magnetic field can also polarize the medium through this coupling effect.

 $x(\omega, r)$ $(y(\omega, r))$ can be obtained through solving the two coupled equations of motion. By plugging the solved $x(\omega, r)$ into equation (12) and comparing the two forms of equation (12) and (13), it can be concluded that:

$$\varepsilon = 1 + \frac{2N_0e^2}{3m} \frac{\omega_0^2 - i\gamma\omega - \omega^2}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 - \xi^2}$$

$$\Gamma = \frac{dN_0e^2}{3m} \frac{\xi}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 - \xi^2}$$

The ε captures feature of the general Lorentz resonance of the systems, regardless of the chiral or achiral system. While, the Γ captures the feature of the chiral resonance of the system. The real part of the Γ describes the phase change of the light when it interacts with chiral system, and the imaginary part of the Γ describe the extinction difference between the LCP and RCP when they interact with the chiral systems.

From these two equations, we can get the OA (per unit length):

$$\theta = \frac{\omega}{2c} Re(\Gamma)$$

and CD (per unit length):

$$A_L - A_R = \frac{\omega}{2c} Im(\Gamma)$$

Combining these two equations with respective Fresnel equations, it implies that the refractive index of a chiral system takes two different values for LCP and RCP:

$$n_{\pm} = \sqrt{\varepsilon\mu} \pm \chi,$$

where χ measures the chirality of the system. It is also straightforward that a negative refractive index can be possible without double negativity of ε and μ . In chiral systems, as long as χ is large enough, one can also get a negative refractive index, at least for one circular polarization. This effect is also experimentally verified.^{13,16,19}

From the Fresnel equations, for chiral systems, the reflectance can be expressed as:

$$\mathbf{R}_{\pm} = \left|\frac{n_1 - n_{\pm}}{n_1 + n_{\pm}}\right|^2$$

where n_1 is the refractive index of air. From this equation, it can be seen that the reflectance for LCP and RCP is different. Therefore, by engineering the chirality, theoretically, it is possible to make one reflectance very small while the other reflectance is very large, or similarly, one circularly polarized light can be transmitted while the other one is reflected.

It should be pointed out that in natural bio-molecules, the chiroptical response is extremely small, which is hard to detect.^{19,43,44} The emergence of chiral metamaterials resolves this issue, and the chiroptical response can be many orders of magnitude higher than that in natural bio-molecules, due to the strong interaction of plasmonic metals with light. This strong interaction has been taken advantage of to magnify the chiroptical response and detect chiral molecules.⁴³ Since the chiroptical response is very sensitive to the polarization of light, chiral metamaterials are powerful platforms to modulate the polarization of light,^{45–47} which is also a goal in this thesis.

1.2 Fabrication Methods of Metamaterials

Theoretical work has described a better world through the use of metamaterials, however, fabrication of metamaterials is quite challenging, especially for optical metamaterials. Typically, the building blocks or meta-atoms have sizes smaller than the wavelength, which means metamaterials targeting the optical spectrum should have sizes of meta-atoms on the nm scale. Also, to arbitrarily control the light-matter interaction, it requires that the shape of meta-atoms can be fabricated with complexity, not only in 1D and 2D, but also in 3D. Thirdly, metamaterials are typically made of arrays of meta-atoms, these arrays typically require 10^6 to 10^9 meta-atoms to be practically useful.

These features of metamaterials require 3D nanoscale fabrication with high throughput. In the following, an overview of current fabrication methods for metamaterials will be presented, and their pros and cons will be explained.

1.2.1 Electron Beam Lithography (EBL)

Electron beam lithography (EBL) is commonly used to pattern features at the nanoscale. A basic EBL process flow is (1) spin-coating an electron-sensitive resist onto a substrate, (2) exposure of the resist to the electron beam following a predesigned pattern, and (3) developing the resist to expose the patterned area. Material is then commonly deposited by (4) physical vapor deposition and the (5) resist is lifted-off (Figure 1.10). Instead of exposure of all patterns within seconds, as achieved in photolithography, the exposure in EBL is a serial process, creating patterns pixel-by-pixel. Therefore, this is a time-consuming process, in particular, to realize metamaterials consisting of high density, large area, complex meta-atoms. Also, EBL is intrinsically a 2D fabrication process.



Figure 1.10 Schematics for electron beam lithography (EBL). The substrate is first coated by spinning a resist and then transferred to EBL tool for exposure. The pattern is then developed, and the sample is then transferred to a tool for physical vapor deposition of material, and finally, after lift-off, the desired structures are fabricated.

It is possible to use EBL for 3D fabrication. This is achieved through the stacking of multilayers, and each layer is exposed by EBL. This strategy has been used extensively to fabricate 3D chiral structures.⁴⁶ However, this layer-by-layer fabrication can be very time-consuming. Also, alignment between neighboring layers is necessary to obtain the desired structures and therefore functions, increasing the challenges of the fabrication.

1.2.2 Nanoimprint Lithography (NIL)

Nanoimprint lithography (NIL) is a parallel fabrication method, similar to photolithography. Instead of using light, NIL uses pressure to transfer the patterns from a template to a resist. After pattern transfer, a descum process that is similar to the developing process in EBL fabrication will be used to remove the residual thermal resist to expose the substrate. The following fabrication process will be the same as (4) and (5) in EBL fabrication (Figure 1.11). Sub-10 nm features have been successfully fabricated by NIL. The templates are fabricated through EBL. The prominent advantage of NIL is high throughput. Due to the nature of parallel fabrication, the processing time is independent of the area or size of the template, and it takes less than 10 min for each run, which is compatible to industrial-scale fabrication. Also, the template can be reused. The template used a rigid substrate can be easily reused more than 100 times, while if a soft substrate is used, it can also support 60~80 times. However, the processing time for EBL is highly dependent on the size of the patterns.



Figure 1.11 The schematic showing the nanoimprint lithography with the pattern transferred from the template (top) to resist (bottom).

The key parameters in NIL are the thickness of the thermal resist, the processing temperature, and processing time. In general, the thickness of the thermal resist must match or be slightly higher than the relief height of the patterns on templates. If the thickness of the resist is too thin, then air bubbles can be formed during the imprinting process, ruining the fabrication. On the other hand, if the thickness of the resist is too thick, it will be hard to descum the residual resist. In addition, longer descum will deteriorate the predesigned feature size, as descum is isotropic etching, i.e., removal of resist in the vertical direction is accompanied by the removal of resist in the lateral direction. The processing temperature should be adjusted to the glass transition temperature of the resist. Lower or higher temperature will affect the viscosity of the resist and thereby affect the imprinting process. The processing time is dependent on the feature size. Smaller feature sizes require a shorter imprinting time, while if the feature size is μm scale, the imprinting time should be optimized to make sure the flow of the resist rearranges to accommodate the template.

NIL, although not limited by the pattern design, is also a 2D patterning method. In addition, unlike EBL which can do layer-by-layer exposure, the alignment resolution in NIL is poor.

1.2.3 Focused Ion Beam (FIB) lithography

The focused Ion Beam (FIB) technique, in general, uses gallium (Ga) ions to mill target materials. A beam of Ga ions is accelerated by a gun and focused onto the surface of target materials. The high kinetic energy of Ga sputters atoms from the surface. Therefore, this technique allows the direct etching of patterns in the target materials. The resolution of the etching is determined by the beam size and also the interaction volume, which depends on the acceleration voltage. A typical feature size of 50 nm is possible. Most FIBs are integrated with a scanning electron microscope (SEM) system, so one can monitor in-situ the milling/etching process.

Another advantage of FIB is that this technique allows the deposition of various materials as well. By scanning the area of interest, a precursor gas can be injected through a separate nozzle and will be decomposed into volatile and non-volatile components after being impinged by the ions, and the non-volatile components, like tungsten or platinum, will remain on the surface. The combination of FIB-etching and deposition allows fabrication of structures with various shapes and compositions.

As FIB-etching can easily reach several μ m, it is a suitable 3D fabrication method. With the assistance of FIB-deposition, various 3D structures can be obtained, like helices.^{48,49} In addition, one effect of Ga ion etching is that it amorphizes surface material, due to energy transfer during the etching. Unavoidably, they also introduce strain/stress between the amorphous and crystalline phases. The creation of strain/stress has been taken advantage of to fabricate more complicated 3D structures⁵⁰ (Figure 1.12).



Figure 1.12 FIB induced 2D to 3D transformation. Left: SEM image of 2D structures array etched by FIB. Right: SEM image of transformed 3D structures after the ion irradiation.⁵⁴

However, FIB is also a serial fabrication process, which is time-consuming. Limited by the chamber size, it is not possible to fabricate large-area patterns by FIB. In addition, during the etching process, Ga ions can also be injected into the materials altering some optical properties.

1.2.4 Two-Photon Direct Laser Writing

Two-Photon direct laser writing, also called multiphoton lithography, is a patterning method that can directly manufacture 3D structures with µm scale or even smaller features. It is a serial process involving pixel-by-pixel exposure. Unlike EBL, this technique adopts a focused laser to expose the resist, and the exposure process is at least a second-order or even third-order optical processes.

In general, the resist is transparent to the wavelength of the laser. However, the focus of the laser greatly increases the local electric field intensity, therefore, higher-order optical processes are possible so that the energy of multiple photons can be transferred simultaneously to cross-link the resist. During the process, the focus point can be controlled to move within the resist in all three dimensions, so that 3D structures can be fabricated.

The development of this technique overcomes the challenge of direct 3D fabrication limited by EBL and NIL, at the same time, it doesn't cause damage to the target materials like that in FIB. Direct laser writing has successfully been used to fabricate Au helical structures that serve as broadband circular polarizers⁴⁵ (Figure 1.13).



Figure 1.13 Au helical structures fabricated by two-photon direct laser writing⁴⁹

However, there are still several limitations. Exposure by the laser is a diffraction-limited process, therefore, the resolution of this technique is less than that possible in EBL, NIL and FIB. Second, after exposure, the 3D structures have to be infilled, for example using electroplating of metal, which is difficult for 3D structures with complicated networks.

This limits the choice of composition. Third, as a serial process, it is still time-consuming and not compatible with large-scale fabrication.

1.2.5 Glancing Angle Deposition (GLAD)

Glancing angle deposition (GLAD) is an extension of physical vapor deposition (PVD), and can produce more complicated structures than that by a conventional PVD system.^{51– ⁵³ GLAD is based on deposition at oblique angles, where the flux of evaporated materials is at a glancing angle to the substrate (Figure 1.14), during the deposition, the substrate can also rotate.}



Figure 1.14 (a) Definition of the deposition angle α and the substrate rotation angle φ . The deposition plane is defined by a plane containing the incident flux direction and the substrate normal. (b) The GLAD apparatus as it is typically implemented in a standard PVD system. Substrate movement is accomplished by two independent motors. The motors are computer-controlled, receiving feedback from thickness monitors.⁵⁵

This method only modifies the deposition step. Therefore, the fundamental patterning is still performed by EBL or NIL. However, unlike those two processes, where the final structures are completely determined by the predesigned patterns, GLAD greatly modifies the morphology of final structures by setting various deposition angles α and rotating speeds. One example is shown in Figure. Here, NIL is used to pattern an array of holes, then, GLAD is used to fabricate homo- or hetero- plasmonic dimers with sub-10 nm gaps (Figure 1.15).



Figure 1.15 Schematic of dimer array fabrication. Step 1: resist spin-coating. Step 2: nanoimprinting with a pillar-patterned template. Step 3: dry-etching and wet-etching to form undercut structures. Step 4: first-run angular e-beam evaporation of metal with an angle α with respect to the wafer normal. Step 5: second-run angular deposition of metal with an angle β with respect to the wafer normal, having a 180 azimuthal angle with respect to the first-run deposition. Step 6: lift-off to expose the dimer array on the substrate. Left shows the SEM images of fabricated structures.⁵⁷

However, there are several limitations. First, the shape of the final structures cannot be arbitrarily designed. Second, materials deposited in GLAD have intrinsic anisotropic properties, which can affect the optical properties.

1.2.6 Other Fabrication Methods

There are still many other fabrication methods, including colloidal nanohole lithography,⁵⁴ which is an extension of GLAD; on-edge lithography³⁹; hydrogel networks, which takes advantages of the property that hydrogel can expand by absorbing water and shrink by losing water to fabricate programmable 3D structures⁵⁵. However, all these methods can only be applied to some very specific shapes and materials, which limit their applications.

In this thesis, we developed a fabrication process that overcomes many of the existing challenges in the fabrication of metamaterials. This fabrication process is based on NIL, therefore, it is a high resolution and high throughput process. In addition, we take advantage of unique properties of colloidal nanocrystals (NCs), so that 3D nanofabrication can be achieved by using NIL.

1.3 Colloidal Nanocrystals (NCs) and Their Optical Properties

Colloidal nanocrystals (NCs) are a class of materials with at least one dimension smaller than 100 nm. More specifically, spherical colloidal NCs have all three dimensions smaller than 100 nm. Up to now, most of the bulk materials can find their counterparts in NCs, of which semiconductor NCs are also referred to as quantum dots (QDs)⁵⁶.

1.3.1 Structure of Colloidal NCs

Colloidal NCs are most commonly synthesized using wet chemical methods and are typically composed of inorganic cores and organic ligands. The organic ligands cap the surface of the inorganic cores, forming a shell structure that provides stability of the NCs as dispersions in sovlents.

With the dimensions reduced to the nm scale, many unique properties that are absent from the bulk materials begin to occur in NC systems.⁵⁷ For metal NCs, localized surface plasmon resonances provide opportunities for electric field enhancement and sensing⁵⁸; for QDs, size-dependent bandgap modulation offers the opportunities for new optoelectronic devices.^{59,60}

1.3.2 Plasmonic Resonances of Single Metal NCs

Mie theory is a suitable model to describe the light-NC interaction, as the main assumption of Mie theory is that the size of the particle is much smaller than the wavelength of the light. Qualitatively speaking, when a small metallic particle is irradiated by light with a wavelength much larger than the size of the particle, the electrons within the particles can oscillate with the external electric field in phase⁶¹ (Figure 1.16). The restoring force comes from the Coulomb attraction between the electrons and the positive ion cores. The oscillation frequency depends on the density of the electrons, the effective mass of the electrons, and the size and shape of the particle. The collective electron oscillation is called dipole plasmon resonance.



Figure 1.16 Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.⁶⁵

Quantitatively, we can treat the optical properties of NCs as follows⁶² (Figure 1.17). Assume an isotropic sphere of radius **a** irradiated by an light electric field E_0 . The surrounding medium is isotropic and non-absorbing with dielectric constant ε_m . The dielectric response of the sphere is described by a dielectric function $\varepsilon(\omega)$. The equation used to describe the interaction is Laplace's equation: $\nabla^2 \psi = 0$, from which we can calculate the electric field: $E = -\nabla \psi$, where ψ is the electrical potential The boundary condition for this problem is that the electric potential is continuous at the surface of the sphere and the displacement field is also continuous at the surface.



Figure 1.17 Schematic of a homogeneous sphere placed into an electrostatic field⁶⁶

Therefore, we can get the following relationships:

$$\psi_{in} = -\frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 r \cos\theta$$
$$\psi_{out} = -E_0 r \cos\theta + \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 a^3 \frac{\cos\theta}{r^2}$$

We further assume the electric field induces a dipole moment P, which can be related to the electric field E_0 and polarizability α as $P = \varepsilon_0 \varepsilon_m \alpha E_0$:

$$P = 4\pi\varepsilon_0\varepsilon_m a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0$$

Therefore, we can conclude:

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

The corresponding cross sections for scattering (σ_{sca}) and absorption (σ_{abs}) can be calculated:

$$\sigma_{sca} \sim |\alpha|^2$$

 $\sigma_{abs} \sim Im(\alpha)$

From the above equations, we can conclude the resonance happens when $\varepsilon(\omega) = -2\varepsilon_m$. ε_m is the dielectric constant of the environment, from this condition, it is possible to theoretically predict the resonance frequency if $\varepsilon(\omega)$ is assumed to be described by

Drude model: $\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\frac{Ne^2}{m\varepsilon_0}}{\omega^2 + i\omega\gamma}$. Here N is the electron density, e is the elementary charge, m is the mass of the electron, γ is the damping coefficient, ε_{∞} is the residual term when the driving frequency goes to infinity.

1.3.3 Plasmonic Resonances of Metal NCs Assembly

From the above discussion, it can be seen that the plasmonic resonance frequency of a single NC is independent of the particle size and shape. This is the consequence of the quasi-static approximation used in Mie theory, as we assumed the size of the particle is negligible compared to the wavelength of the light.

However, when NCs assemble into solids with the overall size comparable to the wavelength of the light, the assumption used above fails. To theoretically describe the plasmonic resonance of the NCs assembly, it is necessary to take into account the size and shape of the NCs assembly. From example, if NCs assemble into a wire with the length comparable to the wavelength of the light and width far less than the wavelength, then the plasmonic resonance is different when the light is polarized in the direction of the width or polarized in the direction of the length. Furthermore, there can be multiple

oscillation modes of electrons along the direction of length, like a dipole mode, a quadrupole mode or even higher modes.

For simplicity, take a sphere of volume V with radius a comparable to the wavelength of the light, from the exact Mir theory, the dominant mode yields for the polarizability:

$$\alpha = \frac{1 - \frac{1}{10}(\varepsilon + \varepsilon_m)x^2 + O(x^4)}{\left(\frac{1}{3} + \frac{\varepsilon_m}{\varepsilon - \varepsilon_m}\right) - \frac{1}{30}(\varepsilon + 10\varepsilon_m)x^2 - i\frac{4\pi^2\varepsilon_m^3}{3}\frac{V}{\lambda_0^3} + O(x^4)}V$$

where $x = \frac{\pi a}{\lambda_0}$, is the normalized size parameter. Unlike the plasmonic resonance condition for a single NC, in this equation, the size parameter greatly affects the resonance condition.

1.3.4 Ligand Exchange of Colloidal NCs Assembled Solids

As-synthesized NCs are typically capped with bulky ligands, such as trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), oleylamine (OLAM), and oleic acid (OA)⁶³. These ligands are very useful for sterically stabilizing the colloidal NCs system. However, applications of NCs in generally require the NCs to be assembled into a solid. The bulky ligands, which set the interparticle distance in solid-state thin films, reduce the electronic coupling between neighboring NCs, resulting in highly insulating NCs solids. Therefore, a process called ligand exchange is used to replace the original bulky ligands with more compact ligands to improve the electronic coupling. Two ligand exchange methods are available, namely solution ligand exchange and solid-state ligand exchange. Many compact ligands have been discovered showing enhanced coupling between neighboring NCs. They range from smaller organic molecules to inorganic molecules and atomic ions. The ligand exchange process is driven by the different affinities between ligands and NCs, and the concentration of the ligands. Larger binding energy and higher concentration make the ligand exchange process easily happen.⁶³ Depending on specific ligands and applications, the time taken to finish the ligand exchange varies from seconds to hours. For this thesis, we only choose ammonium thiocyanate (NH₄SCN) as the compact ligands, and the time for ligand exchange only takes seconds to no more than 2 min.

Ligand exchange can also greatly alter the optical properties of metal NC assemblies. Our group previously has been shown by using ligands with different length, it is possible to tune the dielectric functions of NC solids continuously from positive values to negative values across the optical spectrum,²² in other words, ligand exchange can be applied to trigger a metal-to-insulator (MIT) transition in NC assembled solids (Figure 1.18). We also showed by tuning the kinetics of ligand exchange through the ligand exchange time and concentration, we can control the amounts of ligands being replaced.⁶⁴ In this way, interparticle distance can be controlled in a continuous way such that not only the real part of the dielectric function can be tuned, but also the imaginary part of the dielectric function can be tuned. We, therefore, demonstrate a strong optical absorber made of Au NCs assembled solid (Figure 1.19)⁶⁴.



Figure 1.18 Optical properties of spincast and thermally evaporated Au films. Top: transmittance spectra at normal incidence (black) and reflectance spectra at 45° (red). Bottom: real (black) and imaginary (red) parts of the dielectric functions versus wavelength. (a–b) Oleylamine (OLA)-capped, (c–d) ethanedithiol (EDT)-capped, and (e–f) thiocyanate (SCN)-capped Au NC solids. (g–h) Thermally evaporated Au thin film.²²



Figure 1.19 (a) Transmittance spectra of the assemblies with different reaction times, a complete SCN-exchanged (CSE) assembly, and a bulk Au thin film (90 nm thickness, dashed curve). (b) Wavelength of the

localized surface plasmon resonance (LSPR) of OAm-capped Au NCs in hexane ("Sol") and of the assemblies with different reaction times. (Inset) Transmittance spectra in the LSPR region for the assemblies and for OAm-capped Au NCs in hexane (blue dashed curve). (c) Reflectance spectra of the assemblies with different reaction times, a CSE assembly, and a bulk Au thin film.⁶⁴

In addition to altering the optical and electronic properties of NC assemblies, ligand exchange can alter the mechanical properties of NC solids as well⁶⁵. When bulky ligands are replaced by compact ligands, the interparticle distance is reduced, inducing volume shrinkage in NC solids. As an example, NCs capped with OA ligands have an interparticle distance of ~2 nm when they are assembled into solid.⁶⁶ After ligand exchange with SCN, the interparticle distance is reduced to ~ 0.5 nm to even touching or fusion (degrees which depend on the composition of the NCs), causing a 56% volume reduction in NCs solid.⁶⁵ Accompanying enhanced electronic coupling after ligand exchange, NC solids form partially fused networks with ultimate tensile strengths of about ~700 MPa.⁶⁷ while NC solids before ligand exchange only have ultimate tensile strengths of less than 10 MPa.⁶⁸ The volume reduction by ligand exchange also introduces strain/stress profile into the NCs solid. NCs near to a substrate don't experience free shrinkage as the rest of NCs when their bulky ligands are replaced by shorter ones, therefore, the volume reduction is nonuniform through the vertical direction of NC solids, which leads to strain/stress profiles. In the next section, we will show how the strain/stress profile can be engineered to produce various 3D structures.

1.4 Bilayer Mechanical Model

Timoshenko⁶⁹ first proposed this model to explain the bending of a bi-metallic layer under heating. As two metals have different thermal expansion coefficients α , the one with larger α expands more than the one with small α under heating. An intuitive picture tells that the bending is always toward the layer with small α . Similar to this case, heterostructures between NC solids and substrates can also be regarded as bi-layer structures. The ligand exchange process can be analogous to the heating in bi-metallic case, causing the shrinkage of NC solids, but having no effect on the substrate. Incidentally, the bending of NC/substrate heterostructures is always toward to the NCs solid side, while it is also possible to use a longer ligand for the exchange process, so instead of shrinkage, expansion of the NC solids is possible to drive the bending toward to the substrate side.

The model develops the relationship between the radius of curvature of the bilayer structure after bending and the mechanical parameters of materials. In Figure 1.20, it is shown the definitions of the total thickness (h), layer thickness (a), Young's modulus (E), stress (P) and bending moment (M). After bending, the bilayer structure shows a radius of curvature p.



Figure 1.20 Schematics of the bilayer mechanical model. (a) front view of the bilayer structure. (b) cross section view. (c) bilayer structure after bending.⁷³

Here, we follow the original Timoshenko' path, while instead of considering the bilayer bending caused by the heating, we treat the bilayer bending caused by the ligand exchange. Both cases involve the build-up of misfit strain along with the interface between two different materials. In Timoshenko's case, the heating causes expansion strain $\alpha_1(T - T_0)$ $(\alpha_2(T - T_0))$ of layer 1 (layer 2). The difference between these two expansion strains is defined as the misfit strain. Similarly, in the NC/substrate case, we simply define a misfit strain quantity as ε .

Forces and moments equilibrium require that:

$$P_1 = P_2 = P$$
 (1)
 $\frac{Ph}{2} = M_1 + M_2$ (2)

Where P is the tensile/compressive stress induced by the ligand exchange. h is the total thickness of the bilayer structure, and M is the bending moment generated by the two layers to balance the bending moment generated by P. The bending moment is related to the radius of curvature and mechanical parameters of materials by:

$$M_{1} = \frac{E_{1}I_{1}}{\rho} \quad (3)$$
$$M_{2} = \frac{E_{2}I_{2}}{\rho} \quad (4)$$

where *I* is the moment of inertia of the material. For a rectangular shape with the thickness of d and width b, $I = \frac{db^3}{12}$. E is Young's modulus, and ρ is the curvature after bending. On the interface, the two materials should have the same total strain, modulated by the misfit strain, therefore:

$$\varepsilon + \frac{P_1}{E_1 a_1} + \frac{a_1}{2\rho} = -(\frac{P_2}{E_2 a_2} + \frac{a_2}{2\rho})$$
 (5)

Where a is the thickness of each layer. We assume the width as a unit, therefore, by combining equation (1) to (5), we get:

$$\rho = \frac{h(3(1+m)^2 + (1+mn)(m^2 + \frac{1}{mn}))}{6\varepsilon(1+m)^2}$$
(6)

where $m = \frac{a_1}{a_2}, n = \frac{E_1}{E_2}$.

The width has a negligible effect on the final radius of curvature. If we assume the width is increased from unity to $1 + \delta$, the equation (6) will be modified as:

$$\rho = \frac{h(3(1+m)^2(1+\delta) + (1+mn)(m^2(1+\delta) + \frac{1}{mn}))}{6\varepsilon(1+m)^2(1+\delta)}$$
(7)

By plotting the $\frac{h}{\rho}$ vs $\frac{a_2}{h}$ and assuming the δ changes from 0 to 0.5, there are on significant change (Figure 1.21).



Figure 1.21 Plots showing the effect of width on the final radius of curvature in bilayer structures.

However, the ratio between the width and length affects how the bilayer structure bends. If the length is much longer than the width, which is the case we described above, the bending is parallel to the direction of width; if the length is similar to the width, the bending is no longer happening in one direction, but in two dimensions. Figure 1.22 shows a qualitative picture that possible bending morphologies when the ratio is 5 (in comparison, cases in our structures have the ratio of ~30)⁷⁰.



Figure 1.22 (A) Some of the possible shapes that a thin bending plate can take, illustrate for a length to width ratio of 5, upon contraction of the upper face (blue). (B) Bilayer geometry.⁷⁴

1.5 Thesis overview

In this thesis, we developed a 3D nanofabrication method by taking advantage of the chemical addressability of the NC surface. This method uses NIL as the fundamental patterning tool to define 2D layouts of the final 3D structures. The 2D to 3D transformation is made possible by the ligand exchange process in NC/metal heterostructures, in which a misfit strain is built-up along the interface and guides the bending of the original 2D structures. We also introduce a post-fabrication treatment step by using thermal annealing to densify the NC solids to further drive the bending in a tunable fashion. We systematically studied the effects of various processing parameters, like the concentration of NCs, the

thickness of the NCs and metals, the dimension of the 2D structures, and the annealing temperature, on the morphology of final structures; we used the bilayer mechanical model to extract the mechanical properties of the NCs solids, which otherwise are hard to directly measure; we further propose sets of design rules that help us design various complex 3D structures and 3D chiral metamaterials, finally, we showed how we apply this fabrication method to fabricate large scale chiroptical devices.

Chapter 2 focuses on the development of 3D nanofabrication methods, especially for freestanding 3D structures. We show the process flow that combines the NIL and the ligand exchange process to induce bending of the bilayer straight structures. Then the bilayer mechanical model is used to explain and fit the experimental data, through which the mechanical properties of NCs solids can be obtained. Based on the understandings of processes and the mechanical properties, we designed various 2D layouts to achieve complex 3D structures, and finally, we show that potentially the whole NCs library can be used in this fabrication method to diversify the functionalities of the 3D structures.

Chapter 3 focuses on the fabrication of 3D chiral metamaterials, which uses the same process idea but is modified so that all the 3D structures can be anchored on a rigid substrate. In this chapter, we proposed thermal annealing as a post-fabrication treatment and systematically studied the evolution of the morphology and optical properties under the annealing. We then design and fabricate the 3D chiral metamaterials showing giant chiroptical responses. At last, we demonstrate two preliminary chiroptical devices showing switchable chirality and broadband chiroptical response.

Chapter 4 focuses on the development of a broadband circular polarizer based on the broadband chiroptical responses and fabrication process mentioned in Chapter 3. We further study the effect of annealing temperature, annealing time and concentration of NCs on the spectra of the metamaterials. The bilayer mechanical model is also applied to extract the mechanical properties of the metamaterials from before and after annealing, which leads to a "phase diagram" we can use to guide the design of the metamaterials. By varying the periodicity of the chiral metamaterials, we see electromagnetic coupling emerges among the meta-atoms array. We study the coupling effect and take advantage of it to fabricate broadband circular polarizer.

Chapter 5 proposes some future directions about how we can apply this fabrication method. With some preliminary results, we also show the integration of the 3D structures and 3D metamaterials with an external field like an acoustic wave or magnetic field can generate many active metamaterials.

1.6 References

- Soukoulis, C. M.; Wegener, M. Past Achievements and Future Challenges in the Development of Three-Dimensional Photonic Metamaterials. *Nat. Photonics* 2011, 5 (9), 523–530. https://doi.org/10.1038/nphoton.2011.154.
- (2) Zheludev, N. I.; Kivshar, Y. S. From Metamaterials to Metadevices. *Nat. Mater.* **2012**, *11* (11), 917–924. https://doi.org/10.1038/nmat3431.

- (3) Smith, D. R.; Smith, D. R.; Pendry, J. B.; Wiltshire, M. C. K. Metamaterials and Negative Refractive Index. *Science (80-.).* 2012, *305* (2004), 788–792. https://doi.org/10.1126/science.1096796.
- (4) Zheludev, N. I.; Plum, E. Reconfigurable Nanomechanical Photonic Metamaterials. *Nat. Nanotechnol.* 2016, *11* (1), 16–22. https://doi.org/10.1038/nnano.2015.302.
- Poddubny, A.; Iorsh, I.; Belov, P.; Kivshar, Y. Hyperbolic Metamaterials. *Nat. Photonics* 2013, 7 (12), 958–967. https://doi.org/10.1038/nphoton.2013.243.
- West, P. R.; Ishii, S.; Naik, G. V.; Emani, N. K.; Shalaev, V. M.; Boltasseva, A.
 Searching for Better Plasmonic Materials. *Laser Photonics Rev.* 2010, *4* (6), 795–808. https://doi.org/10.1002/lpor.200900055.
- (7) Caglayan, H.; Hong, S. H.; Edwards, B.; Kagan, C. R.; Engheta, N. Near-Infrared Metatronic Nanocircuits by Design. *Phys. Rev. Lett.* 2013, *111* (7), 1–5. https://doi.org/10.1103/PhysRevLett.111.073904.
- (8) Gansel, J. K.; Wegener, M.; Burger, S.; Linden, S. Gold Helix Photonic
 Metamaterials : A Numerical Parameter Study. 2010, *18* (2), 11822–11829.
- Ni, X.; Ishii, S.; Kildishev, A. V.; Shalaev, V. M. Ultra-Thin, Planar, Babinet-Inverted Plasmonic Metalenses. *Light Sci. Appl.* 2013, 2 (APRIL). https://doi.org/10.1038/lsa.2013.28.
- (10) Veselago, V. G. The Electrodynamics of Substances with Simultaneously Negative
Values of ε and M. Sov. Phys. uspekhi 1968, 10 (4), 509–514.

- (11) Pendry, J. B. Negative Refraction Makes a Perfect Lens. *Phys. Rev. Lett.* 2000, 66 (18), 0–3.
- (12) Fang, N.; Lee, H.; Sun, C.; Zhang, X. Sub-Diffraction-Limited Optical Imaging with a Silver Superlens. *Science* (80-.). 2005, 308 (5721), 534–537. https://doi.org/10.1126/science.1108759.
- (13) Panpradit, W.; Sonsilphong, A.; Soemphol, C.; Wongkasem, N. Negative Refractive Index in Chiral Metamaterials. J. Opt. (United Kingdom) 2012, 14 (7), 1–4. https://doi.org/10.1088/2040-8978/14/7/075101.
- (14) Chen, Y.; Gao, J.; Yang, X. Chiral Metamaterials of Plasmonic Slanted Nanoapertures with Symmetry Breaking. *Nano Lett.* 2018, *18* (1), 520–527. https://doi.org/10.1021/acs.nanolett.7b04515.
- Ma, W.; Xu, L.; De Moura, A. F.; Wu, X.; Kuang, H.; Xu, C.; Kotov, N. A. Chiral Inorganic Nanostructures. *Chem. Rev.* 2017, *117* (12), 8041–8093. https://doi.org/10.1021/acs.chemrev.6b00755.
- Wang, Z.; Cheng, F.; Winsor, T.; Liu, Y. Optical Chiral Metamaterials: A Review of the Fundamentals, Fabrication Methods and Applications. *Nanotechnology* 2016, 27 (41). https://doi.org/10.1088/0957-4484/27/41/412001.
- (17) Alù, A.; Engheta, N. Achieving Transparency with Plasmonic and Metamaterial Coatings. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* 2005, 72 (1), 1–9.

https://doi.org/10.1103/PhysRevE.72.016623.

- Jain, P. K.; Xiao, Y.; Walsworth, R.; Cohen, A. E. Surface Plasmon Resonance Enhanced Rotation Enhancement in Gold-Coated Iron Oxide Nanocrystals. *Nano Lett.* 2009, 9 (4), 1644. https://doi.org/10.1021/nl900007k.
- (19) Valev, V. K.; Baumberg, J. J.; Sibilia, C.; Verbiest, T. Chirality and Chiroptical Effects in Plasmonic Nanostructures: Fundamentals, Recent Progress, and Outlook. *Adv. Mater.* 2013, *25* (18), 2517–2534. https://doi.org/10.1002/adma.201205178.
- (20) Ozbam, E. Plasmonics : Merging Photonics And. *Science* (80-.). 2006, 311
 (2006), 189–194. https://doi.org/10.1126/science.1114849.
- (21) Zhao, Q.; Zhou, J.; Zhang, F.; Lippens, D. Mie Resonance-Based Dielectric
 Metamaterials. *Mater. Today* 2009, *12* (12), 60–69. https://doi.org/10.1016/S1369-7021(09)70318-9.
- (22) Fafarman, A. T.; Hong, S. H.; Caglayan, H.; Ye, X.; Diroll, B. T.; Paik, T.;
 Engheta, N.; Murray, C. B.; Kagan, C. R. Chemically Tailored Dielectric-to-Metal Transition for the Design of Metamaterials from Nanoimprinted Colloidal Nanocrystals. *Nano Lett.* 2013, *13* (2), 350–357. https://doi.org/10.1021/nl303161d.
- (23) Armelles, G.; Cebollada, A.; García-Martín, A.; González, M. U.Magnetoplasmonics: Combining Magnetic and Plasmonic Functionalities. *Adv.*

Opt. Mater. **2013**, *1* (1), 10–35. https://doi.org/10.1002/adom.201200011.

- (24) Bonanni, V.; Bonetti, S.; Pakizeh, T.; Pirzadeh, Z.; Chen, J.; Nogués, J.;
 Vavassori, P.; Hillenbrand, R.; Åkerman, J.; Dmitriev, A. Designer
 Magnetoplasmonics with Nickel Nanoferromagnets. *Nano Lett.* 2011, *11* (12),
 5333–5338. https://doi.org/10.1021/nl2028443.
- (25) Pendry, J. B.; Holden, A. J.; Robbins, D. J.; Stewart, W. J. Magnetism from Conductors and Enhanced Nonlinear Phenomena. *IEEE Trans. Microw. Theory Tech.* 1999, 47 (11), 2075–2084. https://doi.org/10.1109/22.798002.
- Shelby, R. A. Experimental Verification of a Negative Index of Refraction.
 Science (80-.). 2001, 292 (5514), 77–79. https://doi.org/10.1126/science.1058847.
- (27) Cummer, S. A.; Christensen, J.; Alù, A. Controlling Sound with Acoustic Metamaterials. *Nat. Rev. Mater.* 2016, *1* (16001).
 https://doi.org/10.1038/natrevmats.2016.1.
- Ma, G.; Sheng, P. Acoustic Metamaterials: From Local Resonances to Broad Horizons. *Sci. Adv.* 2016, 2 (2). https://doi.org/10.1126/sciadv.1501595.
- (29) Zheng, X.; Lee, H.; Weisgraber, T. H.; Shusteff, M.; DeOtte, J.; Duoss, E. B.;
 Kuntz, J. D.; Biener, M. M.; Ge, Q.; Jackson, J. A.; et al. Ultralight, Ultrastiff
 Mechanical Metamaterials. *Science (80-.).* 2014, *344* (6190), 1373–1377.
 https://doi.org/10.1126/science.1252291.
- (30) Nicolaou, Z. G.; Motter, A. E. Mechanical Metamaterials with Negative

Compressibility Transitions. *Nat. Mater.* **2012**, *11* (7), 608–613. https://doi.org/10.1038/nmat3331.

- (31) Frenzel, T.; Kadic, M.; Wegener, M. Three-Dimensional Mechanical Metamaterials with a Twist. *Science (80-.).* 2017, *358* (6366), 1072–1074. https://doi.org/10.1126/science.aao4640.
- (32) Segal, N.; Keren-Zur, S.; Hendler, N.; Ellenbogen, T. Controlling Light with Metamaterial-Based Nonlinear Photonic Crystals. *Nat. Photonics* 2015, *9* (3), 180– 184. https://doi.org/10.1038/nphoton.2015.17.
- Ni, X.; Kildishev, A. V.; Shalaev, V. M. Metasurface Holograms for Visible Light.
 Nat. Commun. 2013, 4 (1), 1–6. https://doi.org/10.1038/ncomms3807.
- (34) Metalenses at Visible Wavelengths: Diffraction-Limited Focusing and Subwavelength Resolution Imaging. 2016, *352* (6290).
- (35) Kildishev, A. V; Boltasseva, A.; Shalaev, V. M. Planar Photonics with Metasurfaces Planar Photonics with Metasurfaces. *Science (80-.).* 2013, *339* (March). https://doi.org/10.1038/nmat3431.
- (36) Jacob, Z.; Alekseyev, L. V; Narimanov, E. Optical Hyperlens : Far-Field Imaging beyond the Diffraction Limit. 2006, 14 (18), 8247–8256.
- (37) Aieta, F.; Genevet, P.; Yu, N.; Kats, M. A.; Gaburro, Z.; Capasso, F. Out-of-Plane Reflection and Refraction of Light by Anisotropic Optical Antenna Metasurfaces with Phase Discontinuities. **2012**. https://doi.org/10.1021/nl300204s.

- (38) Yu, N.; Capasso, F. Flat Optics with Designer Metasurfaces. *Nat. Mater.* 2014, *13*(2), 139–150. https://doi.org/10.1038/nmat3839.
- (39) Capasso, F.; Gaburro, Z. Light Propagation with Phase Reflection and Refraction.
 Science (80-.). 2011, No. October, 333–338.
- (40) Sun, F.; Zheng, B.; Chen, H.; Jiang, W.; Guo, S.; Liu, Y.; Ma, Y.; He, S. Transformation Optics: From Classic Theory and Applications to Its New Branches. *Laser Photonics Rev.* 2017, *11* (6), 1–27. https://doi.org/10.1002/lpor.201700034.
- (41) Pendry, J. B.; Schuring, D.; Smith, D. R. Controlling Electromagnetic Fields. Science (80-.). 2011, 1780 (2006), 1780–1782. https://doi.org/10.1126/science.1125907.
- (42) Milton, G. W.; Nicorovici, N. A. P. On the Cloaking Effects Associated with Anomalous Localized Resonance. *Proc. R. Soc. A Math. Phys. Eng. Sci.* 2006, 462 (2074), 3027–3059. https://doi.org/10.1098/rspa.2006.1715.
- (43) He, Y.; Larsen, G. K.; Ingram, W.; Zhao, Y.; Esposito, M.; Tasco, V.; Todisco, F.; Cuscunà, M.; Benedetti, A.; Sanvitto, D.; et al. Circular Dichroism from Chiral Nanomaterial Fabricated by On-Edge Lithography. *ACS Nano* 2012, *24* (9), 321– 325. https://doi.org/10.1002/adma.201203424.
- (44) Guo, J.; Kim, J. Y.; Zhang, M.; Wang, H.; Stein, A.; Murray, C. B.; Kotov, N. A.;Kagan, C. R. Chemo- A Nd Thermomechanically Configurable 3D Optical

Metamaterials Constructed from Colloidal Nanocrystal Assemblies. *ACS Nano* **2020**, *14*, 1427–1435. https://doi.org/10.1021/acsnano.9b08452.

- (45) Hentschel, M.; Schäferling, M.; Duan, X.; Giessen, H.; Liu, N. Chiral Plasmonics.
 Sci. Adv. 2017, *3* (5), 1–13. https://doi.org/10.1126/sciadv.1602735.
- (46) Yin, X.; Schäferling, M.; Metzger, B.; Giessen, H. Interpreting Chiral Nanophotonic Spectra: The Plasmonic Born-Kuhn Model. *Nano Lett.* 2013, *13*(12), 6238–6243. https://doi.org/10.1021/nl403705k.
- (47) Hendry, E.; Carpy, T.; Johnston, J.; Popland, M.; Mikhaylovskiy, R. V.; Lapthorn, A. J.; Kelly, S. M.; Barron, L. D.; Gadegaard, N.; Kadodwala, M. Ultrasensitive Detection and Characterization of Biomolecules Using Superchiral Fields. *Nat. Nanotechnol.* 2010, *5* (11), 783–787. https://doi.org/10.1038/nnano.2010.209.
- (48) Zhao, Y.; Askarpour, A. N.; Sun, L.; Shi, J.; Li, X.; Alù, A. Chirality Detection of Enantiomers Using Twisted Optical Metamaterials. *Nat. Commun.* 2017, *8*, 6–13. https://doi.org/10.1038/ncomms14180.
- (49) Rill, M. S.; Linden, S.; Gansel, J. K.; Thiel, M.; Decker, M.; Bade, K.; von Freymann, G.; Saile, V.; Wegener, M. Gold Helix Photonic Metamaterial as Broadband Circular Polarizer. *Science (80-.).* 2009, *325* (5947), 1513–1515. https://doi.org/10.1126/science.1177031.
- (50) Zhao, Y.; Belkin, M. A.; Alù, A. Twisted Optical Metamaterials for Planarized Ultrathin Broadband Circular Polarizers. *Nat. Commun.* 2012, *3* (May).

https://doi.org/10.1038/ncomms1877.

- (51) Kaschke, J.; Blume, L.; Wu, L.; Thiel, M.; Bade, K.; Yang, Z.; Wegener, M. A Helical Metamaterial for Broadband Circular Polarization Conversion. 2015, 1411–1417. https://doi.org/10.1002/adom.201500194.
- (52) Esposito, M.; Tasco, V.; Todisco, F.; Cuscunà, M.; Benedetti, A.; Sanvitto, D.;
 Passaseo, A. Triple-Helical Nanowires by Tomographic Rotatory Growth for Chiral Photonics. *Nat. Commun.* 2015, *6*, 1–7. https://doi.org/10.1038/ncomms7484.
- (53) Fazio, R. H.; Zanna, M. P.; Cooper, J. Three Dimensional Chiral Metamaterial Nanospirals in the Visible Range by Vertically Compensated Focused Ion Beam Induced-Deposition. *J. Exp. Soc. Psychol.* **1977**, *13* (5), 464–479. https://doi.org/10.1080/01425690701737481.
- Liu, Z.; Du, H.; Li, J.; Lu, L.; Li, Z. Y.; Fang, N. X. Nano-Kirigami with Giant Optical Chirality: Supplementary Material. *Sci. Adv.* 2018, *4* (July), 1–9. https://doi.org/10.1126/sciadv.aat4436.
- (55) Hawkeye, M. M.; Brett, M. J. Glancing Angle Deposition: Fabrication, Properties, and Applications of Micro- and Nanostructured Thin Films. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **2007**, *25* (5), 1317. https://doi.org/10.1116/1.2764082.
- (56) He, Y.; Larsen, G. K.; Ingram, W.; Zhao, Y. Tunable 3D Helically Stacked
 Plasmonic Layers on Nanosphere Monolayers. *Nano Lett.* 2014, *14* (706), 1976–

1981.

- (57) Zhang, M.; Large, N.; Koh, A. L.; Cao, Y.; Manjavacas, A.; Sinclair, R.;
 Nordlander, P.; Wang, S. X. Hetero- Plasmonic Dimers with Universal Sub-10-Nm Gaps. ACS Nano 2015, 9 (9), 9331–9339.
- (58) Frank, B.; Yin, X.; Schäferling, M.; Zhao, J.; Hein, S. M.; Braun, P. V.; Giessen,
 H. Large-Area 3D Chiral Plasmonic Structures. *ACS Nano* 2013, 7 (7), 6321–
 6329. https://doi.org/10.1021/nn402370x.
- (59) Gladman, A. S.; Matsumoto, E. A.; Nuzzo, R. G.; Mahadevan, L.; Lewis, J. A.
 Biomimetic 4D Printing. *Nat. Mater.* 2016, *15* (January).
 https://doi.org/10.1038/NMAT4544.
- (60) Bawendi, M.G., Murray, C.B., Kagan, C. R. SYNTHESIS AND
 CHARACTERIZATION OF MONODISPERSE NANOCRYSTALS AND
 CLOSE-PACKED NANOCRYSTAL ASSEMBLIES. *Annu. Rev. Mater. Sci.*2000, No. 30, 545–610.
- (61) Bawendi, M. G.; Steigerwald, L. THE QUANTUM MECHANICS OF LARGER SEMICONDUCTOR CLUSTERS (" QUANTUM DOTS "). Annu. Rev. Phys. Chem 1990, No. 4, 477–496.
- (62) Saboktakin, M.; Ye, X.; Chettiar, U. K.; Engheta, N.; Murray, C. B.; Kagan, C. R.
 Plasmonic Enhancement of Nanophosphor Upconversion Luminescence in Au
 Nanohole Arrays. ACS Nano 2013, 7 (8), 7186–7192.

https://doi.org/10.1021/nn402598e.

- (63) Zhao, T.; Goodwin, E. D.; Guo, J.; Wang, H.; Diroll, B. T.; Murray, C. B.; Kagan,
 C. R. Advanced Architecture for Colloidal PbS Quantum Dot Solar Cells
 Exploiting a CdSe Quantum Dot Buffer Layer. ACS Nano 2016, 10 (10), 9267–
 9273. https://doi.org/10.1021/acsnano.6b03175.
- (64) Choi, J. H.; Fafarman, A. T.; Oh, S. J.; Ko, D. K.; Kim, D. K.; Diroll, B. T.;
 Muramoto, S.; Gillen, J. G.; Murray, C. B.; Kagan, C. R. Bandlike Transport in
 Strongly Coupled and Doped Quantum Dot Solids: A Route to High-Performance
 Thin-Film Electronics. *Nano Lett.* 2012, *12* (5), 2631–2638.
 https://doi.org/10.1021/nl301104z.
- (65) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. J. *Phys. Chem. B* 2003, *107* (3), 668–677. https://doi.org/10.1021/jp026731y.
- (66) Maier, S. A. FUNDAMENTALS AND APPLICATIONS PLASMONICS : FUNDAMENTALS AND APPLICATIONS.
- (67) Boles, M. A.; Ling, D.; Hyeon, T.; Talapin, D. V. The Surface Science of Nanocrystals. *Nat. Mater.* 2016, *15* (3), 364. https://doi.org/10.1038/nmat4578.
- (68) Chen, W.; Guo, J.; Zhao, Q.; Gopalan, P.; Fafarman, A. T.; Keller, A.; Zhang, M.;
 Wu, Y.; Murray, C. B.; Kagan, C. R. Designing Strong Optical Absorbers via Continuous Tuning of Interparticle Interaction in Colloidal Gold Nanocrystal

Assemblies . *ACS Nano* **2019**, *13* (7), 7493–7501. https://doi.org/10.1021/acsnano.9b02818.

- (69) Zhang, M.; Guo, J.; Yu, Y.; Wu, Y.; Yun, H.; Jishkariani, D.; Chen, W.; Greybush, N. J.; Kübel, C.; Stein, A.; et al. 3D Nanofabrication via Chemo-Mechanical Transformation of Nanocrystal/Bulk Heterostructures. *Adv. Mater.* 2018, *30* (22), 1–6. https://doi.org/10.1002/adma.201800233.
- (70) Fafarman, A. T.; Koh, W. K.; Diroll, B. T.; Kim, D. K.; Ko, D. K.; Oh, S. J.; Ye, X.; Doan-Nguyen, V.; Crump, M. R.; Reifsnyder, D. C.; et al. Thiocyanate-Capped Nanocrystal Colloids: Vibrational Reporter of Surface Chemistry and Solution-Based Route to Enhanced Coupling in Nanocrystal Solids. *J. Am. Chem. Soc.* 2011, *133* (39), 15753–15761. https://doi.org/10.1021/ja206303g.
- (71) Zhang, M.; Magagnosc, D. J.; Liberal, I.; Yu, Y.; Yun, H.; Yang, H.; Wu, Y.; Guo, J.; Chen, W.; Shin, Y. J.; et al. High-Strength Magnetically Switchable Plasmonic Nanorods Assembled from a Binary Nanocrystal Mixture. *Nat. Nanotechnol.* 2017, *12* (3), 228–232. https://doi.org/10.1038/nnano.2016.235.
- (72) Gauvin, M.; Wan, Y.; Arfaoui, I.; Pileni, M. P. Mechanical Properties of Au Supracrystals Tuned by Flexible Ligand Interactions. *J. Phys. Chem. C* 2014, *118*(9), 5005–5012. https://doi.org/10.1021/jp411896c.
- (73) Timoshenko, B. Y. S. ANALYSIS OF BI-METAL THERMOSTATS. *JOSA* 1925, No. 1, 233–255.

(74) Alben, S.; Balakrisnan, B.; Smela, E. Edge Effects Determine the Direction of Bilayer Bending. *Nano Lett.* 2011, *11* (6), 2280–2285.
https://doi.org/10.1021/nl200473p.

CHAPTER 2 3D NANOFABRICATION VIA CHEMO-MECHANICAL TRANSFORMATION OF NANOCRYSTAL/BULK HETEROSTRUCTURES

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3D patterning on the micro- or nano-scale can realize unique device functionalities not achievable by conventional 2D lithographic methods, such as creating nanorobots that capture and deliver cargo for therapeutics and impurity scavenging and chiral metasurfaces for enantiomer-selective catalysis and sensing.¹⁻⁴ An important strategy is to realize shape transformations by folding 2D lithographically defined structures into 3D configurations.⁵ Most reports use mechanically 'soft' organic materials.⁶⁻⁹ Although structurally successful, they generally lack electronic, optical, and magnetic functionalities, and are typically larger than 100 microns in size. In contrast, inorganic materials have desired functionalities,¹⁰⁻¹² yet they are mechanically 'hard' and their deformations require either processing at an elevated temperature¹³ or via high-energy ion-beam bombardment.^{14,15}

Solution-processable colloidal nanocrystals (NCs) are hybrid systems composed of inorganic cores and organic/inorganic ligand shells.¹⁶ The combination of their size-dependent physical properties and low-cost processability is driving exploration of NC-based electronic, optical, and magnetic devices.¹⁷⁻²¹ To achieve targeted device performances, NC films are often assembled "bottom-up," to define their nano- to meso-scale structure, and patterned "top-down," to control their micro- to macro-scale structure.²²⁻²⁴ Here, we exploit the chemical addressability of the NC ligand shell, 'soft' mechanical properties of NC assemblies, and unique physical properties of the NC cores

to create large-scale, 3D, functional NC/bulk bilayer hetero-structures suitable for cellsized machines/devices. Chemical modification of the NC surface, exchanging long ligands for more compact chemistries, decreases the interparticle distance, triggers a large volume shrinkage of the NC layer, and drives bending of the heterostructures. We construct design rules to demonstrate the versatility of this fabrication approach and to create multiple 3D superstructures. By selecting superparamagnetic NC building blocks, we realize 3D 'claws' that are actuated by an external magnetic field.

2.1 Generic Methodology of 3D Nanofabrication via Colloidal Nanocrystal Based Heterostructures

2.1.1 Fabrication Process Flow

As a basic element, NC/bulk bilayer nanowires are fabricated (**Figure 2.1**a), by sequentially evaporating Ti and spin-coating Au NCs in a tri-layer resist template patterned via scalable nanoimprint lithography (NIL) with 3-µm-long nanowire trenches.²⁵ Each nanowire trench is 60-nm wide in the top thermal resist layer (unless otherwise specified, noted as w), and has an undercut structure in the middle poly (methyl glutarimide) (PMGI) layer. Due to the different deposition characteristics, the evaporated Ti has a width defined by w, while the spin-coated Au NCs occupy the entire PMGI undercut area, typically with a width 50-nm larger than w. A bottom resist layer of Durimide allows us to ultimately harvest the nanowires from the substrate surface by dissolving the resist layer.



Figure 2.1 Fabrication of Au NC/Ti hetero-structure nanowires and their bending. a) Schematic of the bilayer nanowire fabrication through sequential Ti evaporation and Au NC spin-coating onto a tri-layer resist film patterned by NIL. b) Schematic of an initially OLA-capped Au NC/Ti bilayer nanowire bending upon LE with NH₄SCN. The LE process replaces the long organic chains separating neighboring NCs, causing neighboring NCs to touch, and the bilayer nanowire to bend. c,d) TEM images of the bilayer nanowire c) with LE and d) without LE (scale bar: 500 nm). In both images, the nanowires lie on substrates on their sides.

2.1.2 Morphology Characterization of Structures

The Au NCs have an average core diameter of 4.9 ± 0.3 nm and an oleylamine (OLA) shell thickness of 0.8 ± 0.2 nm, leading to an OLA ligand/Au volume ratio of 1.3. After lift-off of the thermal resist, the long OLA ligands are replaced with compact SCN⁻ ligands via a ligand exchange (LE) process in which the samples are immersed in a solution of the new ligand. Previous work has shown that LE of similar-size, OLA-capped Au NCs with SCN⁻ ligands creates a 56% volume reduction in Au NC films²⁶ and nanowires.¹⁷ This volume change is significantly larger than the 10% volume change of a NC assembly using LE with DNA chemistry²⁷ and thus drives a large bending effect in the NC/bulk bilayer nanowires (Figure 2.1b), as seen in transmission electron microscopy (TEM) images (Figure 2.1c). While LE of NC/bulk nanowires shows a large bending effect, without LE nanowires only have a slight curvature (Figure 2.1d), possibly due to the residual stress introduced by the deposition processes. Cross-sectional images and 3D renderings constructed by electron tomography confirm the NC/bulk morphology and bending and the large volume reduction in the NC layer upon LE (Figure 2.2).



Figure 2.2 Electron tomography results on the cross section of a NC/bulk bilayer nanowire a) without LE and b) with LE. Scale bar: 50 nm. c) HAADF-STEM image of the bilayer nanowire in b) with the Au layer appearing bright and the Ti layer appearing grey due to the atomic number difference. Scale bar: 200 nm.

Combined volume and surface renderings of electron tomographic reconstructions of the 3D structure of nanowires d) without LE, that form mostly straight nanowires, and e) with LE, clearly showing bending with the Ti layer on the outside (orange: Ti and yellow: Au). In addition, the internal porosity in the Au NC part of the nanowire is visible. These results also show that there is no relative sliding between the Au NC and Ti layers.

2.1.3 Analysis of Mechanical properties

The bending of the nanowires can be described using a well-established bilayer model.²⁸ Here, we assume that LE has introduced an initial compressive strain of ε_0 in the length direction of the Au NC layer, also known as the misfit strain between the Au NC/Ti layers, causing the nanowire to bend with a curvature $1/\rho$ (**Figure 2.3**a). The ratio between the nanowire thickness h and ρ can be expressed as:

$$\frac{h}{\rho} = \frac{\varepsilon_0}{f(k,t)} \tag{1}$$

where,

$$f(k,t) = \frac{1}{2} + \frac{1}{6} \left[k(1-t)^3 + t^3 \right] \left[\frac{1}{k(1-t)} + \frac{1}{t} \right]$$
(2)

Here, k is the Young's modulus ratio between the Au NC and the Ti bulk layers, and t is the ratio of the Ti layer thickness a_{Ti} to the total bilayer thickness h. While it is difficult to control the thickness of the Au NC layer deposited in the templates, a_{Ti} can be tuned to modulate t and study the thickness dependence of the bending effect (Figure 2.4). At least five nanowires are measured for each t point, and their h/ ρ values are plotted in Figure 2.3b. We fit the average h/ ρ values at different t points found experimentally to the classic bilayer model. More careful treatment can be conducted by taking into account the variation of measured h/ ρ , revealing a distribution of ε_0 and k values as shown in Figure 2.3c. Consequently, ε_0 takes the value of 0.064±0.018, consistent with the earlier reported length reduction of 0.09 upon LE for single Au NC nanowires.¹⁷ For comparison, bending created by the differential thermal expansion of an inorganic copper/steel bi-metallic strip only has a misfit strain of 0.005 with a 1000 K temperature change.²⁹ The large misfit strain is consistent with the large Au NC volume reduction, providing a large driving force to bend the bilayer nanowire.

The fitting process further yields k between 0.0019 and 0.0079 with 1σ significance, corresponding to a Au NC layer elastic modulus between 210 MPa and 870 MPa (the elastic modulus of bulk crystalline Ti is 110.3 GPa²⁹), orders of magnitude lower than the bulk Au modulus (79 GPa²⁹). The decrease in modulus for NC layers is consistent with nanoporous Au systems formed by selective etching of Ag in a Au-Ag alloy.³⁰ However, in those systems, a larger modulus of 2.7-3.2 GPa is reported. The discrepancy cannot be explained by the different relative Au density, as our Au NC layers have an even higher Au density.¹⁷ However, unlike systems built from tens-of-micron-sized grains, our Au NC layer has a coherence length of only 15.8 nm, suggesting limited grain growth during LE from the original 4.9-nm NCs. Due to atomic disorder, grain boundaries typically have a reduced elastic modulus, and this is especially the case for the current Au NC system considering that it is constructed initially from randomly oriented NCs. Therefore, it suggests that the grain boundaries in our nanometer grain size Au NC systems play an essential role in determining the ensemble elastic modulus, and therefore contribute to its

smaller value. Importantly, the orders-of-magnitude smaller Young's modulus in the 'soft' Au NC layer facilitates the shape deformation of the bilayer.



Figure 2.3 Dependence of the bending effect on the nanowire's geometrical parameters. a) Illustration of misfit strain ε_0 and of nanowires with thickness *h* bending upon LE, creating curvature $1/\rho$. b) Experimental (black dots) dependence of the bending effect, characterized by the normalized curvature h/ρ , on the relative Ti layer thickness normalized by the overall nanowire thickness *h*. Fitting (red curve) of the average experimental value of h/ρ to a stressed bilayer model. c) Distribution of the fitted misfit strain ε_0 (red) and the Young's modulus ratio between the Au NC layer and Ti layer (blue) by assigning a normal distribution to the measured h/ρ data in b). d-g) SEM images of bilayer nanowires fabricated from d,e) w=100 nm and f,g) w=200 nm templates. Nanowires d,f) as fabricated on a Durimide layer and e,g) upon release and deposition on a lacey carbon grid (scale bar: 500 nm).



Figure 2.4 Typical morphology of bilayer nanowires with different Ti thickness: a) 10 nm; b) 15 nm; c) 20 nm; d) 30 nm. Scale bar: 1 μm

In the following discussion, the Ti layer thicknesses are maintained at 20 nm, and unless otherwise noted, the same fabrication procedure is used. The nanowire trench width w is modulated to also control the bending effect. For example, scanning electron microscopy (SEM) images show that the 100-nm template yields nanowires with a similar bending curvature as does the 60-nm template (Figure 2.3d-e). However, as w increases to 200 nm, the nanowires appear almost straight (Figure 2.3f-g). Careful inspection reveals different cross-sectional profiles for these two samples that arise from interfacial, energetic differences in lift-off (Figure 2.5). The large-w nanowires are found to have a NC layer 2.5 times as thick as the small-w counterparts (100-nm thick), leading to their smaller curvature.



Figure 2.5 a,b) 52° tilted cross-sectional view of the bilayer nanowire right after Au NC deposition and before lift-off for a) w=100 nm and b) w=200 nm samples, respectively, showing Au NCs extending into the thermal resist layer. During lift-off, the Au NCs will break at the interface between the thermal resist and PMGI layer in a) and at the two side edges in b) as indicated by the red lines, causing a different nanowire thickness between the two cases. Scale bars: 200 nm. Samples are prepared by focused ion-beam cutting.

2.2 Fabrication and Characterization of Complex 3D Nanostructures

Taking advantage of the 'rules' to create bending upon LE of NC/bulk bilayer heterostructures, 3D cell-sized structures are designed with different curvatures at different locations by changing the NC layer thickness through the modulation of w. As an example, we fabricated curled-L structures with two orthogonally patterned nanowire segments L_w (w=150 nm, 4-µm long) and L_t (w=60 nm, 19-µm long) over large areas (**Figure 2.6**a). There is a 500-nm wide, smoothly curved transition region at the junction point to prevent stress at the corner. Consistently, the wider segment L_w appears to have a larger thickness than L_t, in turn leading to different bending behavior once released. We suspend the curled-L structures upon release in N-methyl pyrrolidone (NMP) and study their 3D structures by bright-field optical microscopy. At an elevated temperature (90 °C), Brownian motion exceeds gravitational forces, and the structures tumble frequently, revealing an unambiguous 3D morphology (Figure 2.6b-d). As expected, the smaller-w L_t region curves and forms a loop whereas the larger-w L_w region remains a straight short tip. The loop has a radius of 2.6 μ m, slightly larger than the average radius of curvature for nanowires with a 20-nm Ti layer (ρ =2.2 μ m, Figure 2.3b, and 2.4c), due to the flat transition region on the junction side of L_t.

Increasing in design complexity, Figure 3e shows an example of a claw structure. Macrosized claws/grippers have already been reported to capture large objects,³¹ while cell-sized claws could be useful in trapping micro-organisms. A '+' sign-shaped 2D pattern with four 5-µm-long arms is designed and fabricated over large area, with a similar smoothly curved transition region in the center (Figure 2.7). Once released, the four arms curl up toward the NC side, forming a claw structure (Figure 2.6f-h and 2.7b). Owing to the large bending curvature, these claws are less than 10 μ m in size, making them suitable to interact with similarly-sized tumor cells and bacteria. As a demonstration, these claws can wrap around $2.5-\mu$ m silica beads, with their arms following the curved bead surface (Figure 2.7c-d). In the future, the surface chemistry of these claws could be modified to allow their transfer to physiologically benign media, to increase their binding affinity with cells, and to create a triggering process to realize a capturing motion. Another example is a helical structure, which is actively explored in realizing artificial motors² and chiral optical metamaterials.^{1,3} Here, five 60-nm-wide 4-µm-long nanowires are aligned in the same direction, connected head-to-tail sequentially through junction rectangles (300-nm wide, 1-µm long) and each shifted by 240 nm from its predecessor in the transverse direction (Figure 2.6i). Consequently, all five nanowires bend and form arcs, which are arranged helically (Figure 2.6j-l). Among different 3D structure designs, more than 90% yields are achieved for both

the curled-L and claw structures, and 40% yield for the more complicated helical structure. Each of the curled-L, claw, and helical patterns are fabricated using 2-cm-by-2-cm NIL stamps to yield approximately 10⁷ 3D structures. Further scaling-up can be achieved using even larger stamps.^{17,32} The 3D structures are stable and no structural degradation is observed during a 5-month storage period.



Figure 2.6 Various 3D NC/bulk bilayer structures created by bending. a,e,i) Schematics of transformations from planar to 3D structures with the yellow color representing the Au NC/bulk hetero-structure and b-d,f-h,j-l) optical microscope images of 3D structures suspended in solution captured at different times for a-d) curled-L structures, e-h) claw structures and i-l) helical structures. Scale bar: 10 µm.



Figure 2.7 a) Large-area view of the '+' sign 2D pattern before release to form the claw structures; inset shows magnified view of one '+' 2D pattern. b) Multiple claw structures after release and drying on a lacey carbon grid. The arms are slightly distorted due to the influence of the underlying grid. c,d) SEM images of a claw structure demonstrating its favorable morphology in 'capturing' micron-sized silica beads. These silica beads have a diameter of 2.5 μ m, and are deposited and stacked on top of the '+' sign 2D pattern (the precursor for the claw structure). After release, sample suspensions are deposited and dried on a lacey carbon TEM grid for SEM characterization. Scale bar: 50 μ m in a), 5 μ m in b), 2 μ m in inset of a), c) and d).

2.3 Magnetic Nanocrystals Based 3D Nanostructures

The versatility of this technique also lies in the choice of different functional NC building blocks to create 3D structures with unique physical properties. For example,

superparamagnetic NCs are widely used in biomedical research, and their zero-remanence properties are crucial to prevent spontaneous magnetic-dipole-induced aggregation in solution.¹⁰ Here, a superparamagnetic claw is fabricated from 12.6±0.5 nm diameter $Zn_{0.2}Fe_{2.8}O_4$ NCs (**Figure 2.8**a), whose rotation can be magnetically actuated. The radius of curvature of the claw arms is 4.2 µm, larger than the Au-NC case, as the larger size of the Zn_{0.2}Fe_{2.8}O₄ NCs leads to a smaller ligand/NC core volume ratio and therefore a reduced initial compressive strain ε_0 upon LE. To demonstrate magnetic actuation, a permanent magnet is used to approach the claw suspension (starting at 0 s), generating a magnetic field of 150 Oe. In response, the magnetic claw stabilizes with their arms facing down on the substrate, and one of the angular bisectors aligned with the external field. From 10 s to 30 s, the magnetic field is rotated clockwise and counter-clockwise alternately, and the claw motion follows synchronously. The experiment indicates the dominant role of the magnetic interaction in the process. Further evidence lies in magnetic simulations, where the total magnetic energy is calculated for different external field orientations (Figure 2.8b-c) with respect to the claw structure. The highest energy occurs when the field is along two of the arms horizontally (Config. III), as here the field is transverse to the other two arms, forcing their magnetizations to align unfavorably (Figure 2.9). Local energy minima occur at Config. I (field along the central axis) and Config. II (field aligned horizontally and at 45° to all the arms). Config. I has an energy 58.4 eV higher than Config. II, which can again be understood by the energy penalty of the transverse magnetization at the junction point (Figure 2.9). The transformation between these two configurations requires overcoming an energy barrier of 103 eV at the midpoint $(\theta=45^\circ, \varphi=45^\circ)$. Consistent with the experimental results, the simulation predicts that the

claw will take Config. II to minimize the system energy, and that the energy barrier, which is much higher than the thermal fluctuation energy at room temperature, locks the claw in the stable state and forces it to move synchronously with the rotating magnetic field. The successful magnetic manipulation of the magnetic claw provides a route for cell manipulation/sorting, once these claws are attached to the cell surface.



Figure 2.8 Magnetic claw in response to an external magnetic field. a) Optical microscope images capturing the evolution of a magnetic claw with a permanent magnet approaching and aligned in the horizontal direction (0-10 s), rotating clockwise (10-15 s), counter-clockwise (15-25 s) and clockwise again (25-30 s). Red arrows represent the magnetic field orientations. b) Schematic of a magnetic claw with central axis oriented in the

z-direction, and the xy-projection of the arms in x- and y-directions. The direction of the external field H_{ex} is defined by the angle θ with respect to the z-axis and the azimuthal angle φ . Here, the yellow color represents the magnetic NC/bulk hetero-structure. c) The total magnetic system energy of the claw with different H_{ex} orientations. From left to right, the plots show the energy in situations of different θ at $\varphi=45^{\circ}$; different φ at $\theta=90^{\circ}$; and different θ at $\varphi=0^{\circ}$. The numbers in the plots label Config. I (field aligned with the central axis), Config. II (horizontal field aligned 45° with respect to the arms) and Config. III (horizontal field aligned with one pair of the arms), respectively.



Config. II



Figure 2.9 a) Schematic of a claw in the magnetic field H_{ex} used for magnetic simulations. b-d), the 3D vector plot reflecting the direction and relative magnitude of the magnetization distribution of the magnetic claw in b) Config. I; c) Config. II and d) Config. III, respectively. The red arrows indicate the external field direction.

2.4 Conclusions

In summary, we report a room-temperature, solution-based LE process that can chemomechanically transform planar NC/bulk hetero-structures into 3D configurations. This 3D nanofabrication method features large structural transformation, mechanically soft structures, and flexibility in both structural design and NC selection, providing access to the unique physical properties of inorganic NCs and expanding the functionalities of existing organic natural/artificial 3D counterparts. Combined with NIL, the process is costeffective and readily scalable.

Looking forward, due to the 'hybrid' nature of the colloidal NCs, this technique creates cell-sized 3D structures, that can be designed to also possess optical, magnetic, chemical, and mechanical functionalities, not readily accessible in existing folded structures of similar dimension.^{13,33} The NC cores can be made of quantum dots,¹⁶ superparamagnetic,¹⁷ or catalytic³⁴ NCs, facilitating optical tracking, magnetic manipulation, or propulsion of the 3D structures, respectively. Their ligand chemistry can also be tailored, to exchange the OLA with bulkier groups³⁵ causing the NC layer to expand for reverse bending, or with photo-³⁶ or thermally³⁷ switchable compounds for reconfigurable, in-situ modulation of the 3D structures. The bulk metal layer can also be replaced with other inorganic or organic materials, allowing further tuning of the mechanical properties of the heterostructures. This technique promises to enable the design of functional, 3D structures, which have already

shown their leading roles in a variety of fields including artificial motors, nano-robots, and chiral optical metasurfaces.

2.5 References

[1] H. H. Jeong, A. G. Mark, T. C. Lee, M. Alarcón-Correa, S. Eslami, T. Qiu, J. G. Gibbs,P. Fisher, *Nano Lett.* 2016, *16*, 4887.

[2] S. Tottori, L. Zhang, F. Qiu, K. K. Krawczyk, A. Franco-Obregón, B. J. Nelson, Adv. Mater. 2012, 24, 811.

[3] J. K. Gansel, M. Thiel, M. S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden, M. Wegener, *Science* 2009, *325*, 1513.

[4] Y. Kim, B. Yeom, O. Arteaga, S. J. Yoo, S. G. Lee, J. G. Kim, N. A. Kotov, *Nat. Mater*.2016, *15*, 461.

[5] Y. Zhang, F. Zhang, Z. Yan, Q. Ma, X. Li, Y. Huang, J. A. Rogers, *Nat. Rev. Mater*. 2017, 2, 17019.

[6] J. Kim, J. A. Hanna, M. Byun, C. D. Santangelo, R. C. Hayward, *Science* 2012, *335*, 1201.

[7] S. J. Jeon, R. C. Hayward, Adv. Mater. 2017, 29, 1606111.

[8] A. S. Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan, J. A. Lewis, *Nat. Mater*.2016, *15*, 413.

[9] A. Cangialosi, C. Yoon, J. Liu, Q. Huang, J. Guo, T. D. Nguyen, D. H. Gracias, R. Schulman, *Science* 2017, 357, 1126.

[10] M. Zhang, C. M. Earhart, C. Ooi, R. J. Wilson, M. Tang, S. X. Wang, *Nano Res.* 2013, 6, 745.

[11] M. Zhang, X. Xie, M. Tang, C. S. Criddle, Y. Cui, S. X. Wang, *Nat. Commun.* 2013, 4, 1866.

[12] M. Zhang, N. Large, A. L. Koh, Y. Cao, A. Manjavacas, R. Sinclair, P. Nordlander,S. X. Wang, *ACS Nano* 2015, *9*, 9331.

[13] T. G. Leong, P. A. Lester, T. L. Koh, E. K. Call, D. H. Gracias, *Langmuir* 2007, 23, 8747.

[14] Y. Mao, Y. Zheng, C. Li, L. Guo, Y. Pan, R. Zhu, J. Xu, W. Zhang, W. Wu, Adv. Mater. 2017, 29, 1606482.

[15] K. Chalapat, N. Chekurov, H. Jiang, J. Li, B. Parviz, G. S. Paraoanu, Adv. Mater.2013, 25, 91.

[16] C. B. Murray, C. R. Kagan, M. G. Bawendi, Annu. Rev. Mater. Sci. 2000, 30, 545.

[17] M. Zhang, D. J. Magagnosc, I. Liberal, Y. Yu, H. Yun, H. Yang, Y. Wu, J. Guo, W. Chen, Y. J. Shin, A. Stein, J. M. Kikkawa, N. Engheta, D. S. Gianola, C. B. Murray, C. R. Kagan, *Nat. Nanotechnol.* 2017, *12*, 228.

[18] F. Prins, D. K. Kim, J. Cui, E. D. Leo, L. L. Spiegel, K. M. McPeak, D. J. Norris, *Nano Lett.* 2017, *17*, 1319.

[19] W. Chen, M. Tymchenko, P. Gopalan, X. Ye, Y. Wu, M. Zhang, C. B. Murray, A. Alu, C. R. Kagan, *Nano Lett.* 2015, 15, 5254.

- [20] J. H. Choi, H. Wang, S.J. Oh, T. Paik, P. S. Jo, J. Sung, X. Ye, T. Zhao, B. T. Diroll,C. B. Murray, C. R. Kagan, *Science* 2016, *352*, 205.
- [21] C. R. Kagan, E. Lifshitz, E. H. Sargent, D. V. Talapin, Science 2016, 353, 885.
- [22] Y. Wang, I. Fedin, H. Zhang, D. V. Talapin, Science 2017, 357, 385.
- [23] T. Paik, H. Yun, B. Fleury, S. H. Hong, P. S. Jo, Y. Wu, S. J. Oh, M. Cargnello, H.Yang, C. B. Murray, C. R. Kagan, *Nano Lett.* 2017, *17*, 1387.
- [24] J. Yang, M. K. Choi, D. H. Kim, T. Hyeon, Adv. Mater. 2016, 28, 1176.
- [25] W. Hu, M. Zhang, R. J. Wilson, A. L. Koh, J. S. Wi, M. Tang, R. Sinclair, S. X. Wang, *Nanotechnology* 2011, 22, 185302.
- [26] A. T. Fafarman, S. H. Hong, H. Caglayan, X. Ye, B. T. Diroll, T. Paik, N. Engheta,C. B. Murray, C. R. Kagan, *Nano Lett.* 2013, *13*, 350.
- [27] T. S. Shim, Z. G. Estephan, Z. Qian, J. H. Prosser, S. Y. Lee, D. M. Chenoweth, D.Lee, S. J. Park, J. C. Crocker, *Nat. Nanotechnol.* 2017, *12*, 41.
- [28] S. Timoshenko, J. Opt. Soc. Am. 1925, 11, 233.
- [29] R. E. Bolz, G. L. Tuve, *CRC Handbook of Tables for Applied Engineering Science*, CRC Press, Boca Raton, Ed. 2 1973.
- [30] T. J. Balk, C. Eberl, Y. Sun, K. J. Hemker, D. S. Gianola, J. Microsc. 2009, 61, 26.
- [31] F. Ilievski, A. D. Mazzeo, R. F. Shepherd, X. Chen, G. M. Whitesides, *Angew. Chem. Int. Ed.* 2011, *50*, 1890.

[32] M. Zhang, D. J. B. Bechstein, R. J. Wilson, S. X. Wang, Nano Lett. 2014, 14, 333.

[33] M. Z. Miskin, K. J. Dorsey, B. Bircan, Y. Han, D. A. Muller, P. L. McEuen, I. Cohen, Proc. Nat. Acad. Sci. 2018, 115, 466.

[34] S. Sundararajan, P. E. Lammert, A. W. Zudans, V. H. Crespi, A. Sen, Nano Lett. 2008, 8, 1271.

[35] D. Jishkariani, B. T. Diroll, M. Cargnello, D. R. Klein, L. A. Hough, C. B. Murray, B. Donnio, J. Am. Chem. Soc. 2015, 137, 10728.

[36] L. D. Zarzar, V. Sresht, E. M. Sletten, J. A. Kalow, D. Blankschtein, T. M. Swager, Nature. 2015, 518, 520.

[37] X. He, M. Aizenberg, O. Kuksenok, L. D. Zarzar, A. Shastri, A. C. Balazs, J. Aizenberg, Nature. 2012, 487, 214.

CHAPTER 3 CHEMO- AND THERMOMECHANICALLY CONFIGURE 3D OPTICAL METAMATERIALS CONSTRUCTED FROM COLLOIDAL NANOCRYSTAL ASSEMBLIES

This work has been published as Guo, J., Kim, J., Zhang, M., Wang, H., Stein, A., Murray, C. B., Kotov, N. A., Kagan, C. R. Chemo- and Thermomechanically Configurable 3D Optical Metamaterials Constructed from Colloidal Nanocrystal Assemblies ACS Nano 2020, 14, 1427-1435

Semiconductor manufacturing processes of lithography, deposition, and etch allow exquisite nanoscale patterning of layers of materials on the surface of substrates. This technology has enabled the fabrication of highly-scaled, high-performance electronic, microelectromechanical (MEMS), and microfluidic devices. More recently, the scientific community has exploited these processes to fabricate structures with sizes smaller than the wavelength of light and tailored in size,⁵ shape,⁶ composition,⁷ and arrangement⁷¹ to create metamaterials with exotic optical properties^{11,13,72} that increase the freedom by which matter can control the amplitude, phase, and polarization of light.^{2,73} Single-layer, twodimensional (2D) metamaterials (i.e., metasurfaces) have been fabricated to realize ultrathin, flat optics, such as metalenses,⁹ holograms,³³ polarizers,⁴⁶ and waveplates.³⁸ However, 2D metasurfaces have intrinsic limitations. Their short optical path lengths constrain the strength of light-matter interactions and, as 2D layers, functionalities like intrinsic chirality that are properties of three-dimensional (3D) objects are inaccessible. Up to now, it has been challenging to fabricate large cm²-area 3D optical metamaterials with high throughput. The most common route to achieve 3D metamaterials is the layer-uponlayer stacking of 2D metasurfaces,^{19,41,46,74,75} which is time consuming and restricts device design complexity and large-area scalability. Yet, optical metamaterials composed of 3D meta-atoms,¹ which are building blocks of 3D metamaterials, can possess significantly

more complicated structures, like triple-helical spirals,⁴⁸ and properties, like second harmonic generation¹⁶ and polarization rotation,⁷⁶ can be greatly enhanced.

Here, we report large cm²-area, optical metamaterials composed of complex, 3D, surfacebound, meta-atoms achieved by exploiting the distinct chemical addressability, thermal configurability, and mechanical softness of colloidal nanocrystal (NC) assemblies in NC/metal bilayer structures. NCs are high surface-to-volume materials composed of inorganic cores capped with ligands shells.^{59,77} We exchange longer for shorter ligands to drive a large change in NC assembly volume and pre-strain 2D NC/metal bilayer structures. Upon selective release from the substrate surface, regions of the bilayer structures fold to form 3D, surface-bound meta-atoms. Subsequent mild thermal annealing is used to drive NC fusion, creating additional strain to morph the meta-atom shape. The chemically- and thermally-controlled change in NC assembly structure and meta-atom shape is used to tune the optical properties of 3D metamaterials. We exemplify the utility of this 3D fabrication process to demonstrate 3D, helical metamaterials with giant chiroptical responses of as high as ~40% transmission difference between left-hand (LCP) and right-hand (RCP) circularly polarized light ($\Delta T = T_{RCP} - T_{LCP}$). By tailoring the length, number, and curvature of distinct, 3D-folded, helical structures in each meta-atom, we create single-layer metamaterials that show broadband chiroptical responses and that switch the polarity of optical chirality upon thermally configuring their shape. The measured ΔT exceeds many multi-layer metamaterials operating in a similar spectral range.^{14,46,52,54,74,78,79}

3.1 Fabrication of Metamaterials With 3D Meta-atoms Arrays

3D meta-atom arrays are realized through the transformation of pre-patterned 2D planar structures (Fig. 3.1a-d). Atop Cr-coated, Si wafers, e-beam or nanoimprint lithography is used to define 2D planar structures in bilayer resists (Fig. 3.2) designed to have square pads, with areas of 2.25 to 4 μ m², connected to narrow, 0.06 to 0.12 μ m wide rod-shaped "arms", tailored in their length (from 1 to 2.5 µm), number (4, 8, or 12), and curvature (from radii of curvature of 0 to 2.3 µm). Then, Ti and colloidal Au NC dispersions are deposited by evaporation and spin-coating, respectively (Fig. 3.1a). The NCs are composed of Au cores capped by oleylamine (OLA) ligand shells and form assemblies with ~2 nm interparticle spacing(Fig. 3.1b).²² The bilayer resist is removed to leave patterned heterostructures composed of ~15 nm Ti and ~200 nm thick, OLA-capped Au NC films. To achieve the 2D to 3D transformation, the 2D planar structures are pre-strained by exchanging longer OLA ligands with more compact thiocyanate (SCN⁻) ligands (Fig. 3.1c). Away from the Ti/Au NC interface, the NC assemblies undergo shrinkage, reducing the film thickness to ~120 nm (Fig. 3.3b) and the interparticle distance to where the NCs touch and begin to fuse. NCs near the interface are constrained by the Ti layer, introducing misfit strain along the interface. We have previously shown unlike bulk Au, the SCN-exchanged Au NC assemblies are mechanically soft with a Young's modulus <1 GPa, and for the Ti and SCN-exchanged, Au NC thinkness employed, a large mistfit strain of ε ~0.06 is created.⁶⁵ The arms are selectively released by etching the underlying Cr layer to give a radius of curvature of ~1.80 µm out-of-the-plane, while residual Cr beneath the square pads anchors the meta-atoms to the substrates (Fig. 3.1d).



Fig 3.1 Fabrication and shape morphing of 3D optical metamaterials. (**a**) Schematic of the fabrication of nanocrystal (NC)/metal bilayer heterostructures on top of Cr-coated Si wafers. Electron-beam (nanoimprint) lithography is used to pattern a bilayer resist of ZEP-520A (Nanonex thermal imprint resist) and polymethylglutarimide (PMGI). Ti is deposited by electron-beam evaporation and colloidal Au NCs are deposited by spin-coating. Schematics of the fabrication of 3D meta-atoms as (**b**) samples are immersed in NH₄SCN solutions to (**c**) exchange longer oleylamine for shorter SCN⁻ ligands, decreasing the interparticle distance in the NC layer and creating a compressive strain in the Ti layer. (**d**) Samples are transferred to a Cr etchant to partially remove the Cr layer, releasing and allowing selective folding of the NC/Ti bilayer where Cr is removed and anchoring the meta-atoms to the substrate where residual Cr remains. (**e-g**) Representative SEM images of 3D meta-atom arrays and example 3D meta-atom designs. (**h**) Overlaid SEM images of meta-atoms (black) as their shapes morph upon annealing at 160 °C for 5 min (blue) and 60 min (red).



Fig 3.2 SEM cross-sectional view of the lithographically-patterned and developed bilayer resist of ZEP-520A (ZEP) and polymethylglutarimide (PMGI) on top of the sacrificial Cr layer and Si substrate.



Fig 3.3 Cross-sectional views of 2D, Au NC/Ti bilayer structures before (a) and after (b) ligand exchange.
Using this method, we fabricate large-area arrays (Fig. 3.1e) of meta-atoms (Fig. 3.1f,g). We show the generality of this method to exploit the arbitrary patterning of 2D lithography and create more complicated 3D meta-atoms. In addition to fabricating meta-atoms with one arm on each side (Fig. 3.1f), we also demonstrate meta-atoms with two (Fig. 3.1g and Fig. 3.4) or three (Fig. 3.5) arms on each side. Below, we tailor the length and curvature of the arms to realize 3D metamaterials with optical properties that are difficult to achieve by conventional semiconductor manufacturing processes.



Fig 3.4 Pattern design for (**a**) generating 3D meta-atoms with two arms on each side, eight arms in total. (**b**) SEM image of a large-area array and inset, a higher-resolution image of an example single, two-arm-perside, meta-atom.



Fig 3.5 Pattern design for (a) generating 3D meta-atoms with three arms on each side, twelve arms in total.(b) SEM image of patterned structures in resist. (c) SEM image of a large-area array, and inset, a higher-resolution image of an example single, three-arm-per-side, meta-atom.

The adaptability of the Au NC assembly^{64,67,80} layer provides a route for post-fabrication manipulation of the structure and therefore the optical response of the meta-atoms. SEM images show the shape evolution of the meta-atoms (Fig. 3.1h) when they are annealed at 160 °C for times of 5 min and 60 min. For 2D planar structures (Fig. 3.4a) designed to have a 2.25 μ m²-area, square pad and 2.5 μ m × 0.06 μ m arms, upon SCN-exchange and after Cr etching, the arms fold up with their tips at a height of 1.20 ± 0.10 μ m above the substrate surface (Fig. 3.4b inset). The shape transformation depends on the moment of inertia and therefore on the geometric dimensions of the arms. For rectangular beams, the deflection *y* scales with L^3/I , where *L* is the length and *I* is the moment of inertia of the beams. To characterize the shape transformation, we normalize geometrical effects and use the figure of merit (*FOM*):

$$FOM = \frac{y * I}{L^3}$$

In our structures, the *FOM* upon ligand exchange is $1.33 \times 10^{-5} \,\mu\text{m}^2$. After annealing at 160 °C for 5 min (and 60 min) (Fig. 3.1h), the tips lift to a height of $1.40 \pm 0.15 \,\mu\text{m}$ (and 1.70 $\pm 0.11 \,\mu\text{m}$) and the *FOM* increases by 17% to $1.55 \times 10^{-5} \,\mu\text{m}^2$ (and 25.8% to $1.98 \times 10^{-5} \,\mu\text{m}^2$). In contrast, active 2D metasurfaces integrated into MEMS devices and controlled by an electrical signal, report a *FOM* of only $9.11 \times 10^{-11} \,\mu\text{m}^2$ as the large device size yields small shape displacements.⁸¹

3.2 Characterizations of Metamaterials with 3D Meta-atoms Arrays

To better understand the meta-atoms' conformational progression upon ligand exchange and annealing, we combine transmission electron microscopy (TEM, Fig. 3.6a-c), X-ray diffraction (XRD, Fig. 3.6d), Fourier transform infrared spectroscopy (FTIR, Fig. 3.6e), and spectroscopic ellipsometry (Fig. 3.6f) to investigate the evolution of the structure, composition, and optical properties of the NC assembly layer. As previously reported, TEM images of OLA-capped Au NCs form assemblies with ~2 nm interparticle spacing (Fig. 3.6a). Optical spectra show a localized surface plasmon resonance (LSPR) at ~558 nm, characteristic of the constituent NCs in the dielectric environment of the assembly in comparison to the well-known ~520 nm LSPR of dispersed Au NCs(Fig. 3.7).⁸² Thiocyanate-exchange is seen by the loss of the C-H stretch of OLA and the introduction of the C-N stretch of SCN⁻ ligands in FTIR measurements (Fig. 3.6e), and by a reduction in the interparticle spacing in assemblies to where the Au NCs touch and begin to fuse (Fig. 3.6b). At this stage, the individual character of the NCs can still be identified, consistent with XRD measurements and a Scherrer grain size of 7.8 ± 0.6 nm, slightly larger than the 5.1 ± 0.4 nm size found for OLA-capped NCs (Fig. 3.6d). The complex dielectric constant of the Au NC assemblies changes substantially upon ligand exchange (Fig. 3.6f and Fig. 3.8). We previously reported a dielectric-to-metal phase transition upon exchange of OLAcapped to SCN-capped Au NC assemblies,²² consistent with the lost ligand volume and densification of the Au NC assemblies to form metals "diluted" by remaining ligand and free volume. As the NC assemblies are annealed at 160 °C for 5 min, the C-N stretch in FTIR spectra is lost (Fig. 3.6e), consistent with ligand decomposition;⁶⁰ TEM images show greater NC fusion and grain growth (Fig. 3.6c); and XRD reflections narrow, yielding an increase in Scherrer grain size to 18.2 ± 1.4 nm (Fig. 3.6d). Ligand decomposition exposes the Au NC surface and drives mass exchange between neighboring NCs at elevated temperature. As the Au NC network further densifies, the dielectric function approaches that of bulk Au, as the real part (ε_1) becomes more negative and the imaginary part (ε_2) become smaller (Fig. 3.6f). For annealing times exceeding 5 min, the Au grains cease to grow, but the films continue to densify, and the dielectric function becomes slightly more metallic in character.



Fig 3.6 Characterization of the chemically- and thermally-driven shape morphing. TEM images of Au NC assemblies capped with oleylamine (**a**), after SCN-ligand exchange (**b**) and after 5 min annealing at 160°C (**c**). (**d**) X-ray diffraction (XRD) patterns of Au NC assemblies upon ligand exchange and annealing. The inset shows the Scherrer grain sizes extracted from XRD measurements. (**e**) FTIR measurements and (**f**) ellipsometry measurements of the real (ε_1) and imaginary (ε_2) parts of the dielectric functions of Au NC assemblies. (**g**) Transmission spectra and (inset) resonance peak position of the metamaterials in Fig. 1e,f upon annealing. In all figures, grey represents as-synthesized Au NC assemblies, black represents Au NC assemblies after ligand exchange, and blue (5 min), green (15 min), orange (30 min) and red (60 min) represent different times of annealing at 160 °C of SCN-exchanged Au NC assemblies.



Fig 3.7 UV-vis spectra for OLA-capped Au NCs dispersed in hexane (black) and assembled to form a film on a glass substrate (red). Spectra are normalized to the LSPR peak intensities.



Fig 3.8 Real (black) and imaginary (red) permittivity of OLA-capped Au NC assemblies prepared by spincoating.

Concomitant with the chemically- and thermally-driven change in structure, the optical properties of the patterned 3D metamaterials change significantly and depend on the dielectric constant of the NC layer and the meta-atom geometry. For the 3D metamaterials in Fig. 1g, the LSPR (Fig. 3.6g) of SCN-exchanged structures is broad (FWHM of 828 cm⁻¹) and centered at 2122 cm⁻¹. Upon annealing, the LSPR progressively narrows and blue-shifts (Fig. 3.9a). After annealing at 160 °C for 60 min, the LSPR narrows to 404 cm⁻¹ and shifts to 2728 cm⁻¹, corresponding to a 26.3% modulation in wavenumber (Fig. 3.6g). The blue shift of the LSPR upon annealing is consistent with the more negative ε_1 , as the electron density increases, and the increase in arm curvature, as densification of the assembly creates additional misfit strain in the NC/Ti bilayer structures (Fig. 3.1h, Fig. 3.10). The narrowing of the LSPR is consistent with the smaller ε_2 upon annealing, as the surface area for scattering decreases with the densification of the NC assembly and the increase in grain size. It should be emphasized here that the structures are stable at room temperature, as the shape and LSPR is unchanged after two months (Fig. 3.9b).



Fig. 3.9 Evolution of the transmission spectra for the 3D, two-arm-per-side, meta-atoms (**a**) upon annealing at 80 °C, the decomposition temperature of thiocyanate, and (**b**) stored at room temperature in the laboratory for different time periods (spectra are vertically offset for clarity).



Fig 3.10 Electromagnetic simulations of a one-arm-per-side meta-atom (with dimensions the same as Supplementary Fig. 9). To demonstrate the effect of curvature on the spectral evolution of chiral meta-atoms, the dielectric function of the meta-atoms is fixed to that of SCN-exchanged Au NC films (before annealing). The curvature is quantified by the height from the tip of the arm to the surface of the substrate where the height is $1.05 \,\mu$ m (black), $1.27 \,\mu$ m (blue), and $1.47 \,\mu$ m (red).

3.3 Chiroptical Responses From Chiral Meta-materials

We exploit this fabrication methodology to create metamaterials composed of chiral metaatoms. Instead of lithographically patterning straight 2D arms (Fig. 3.1), here we pattern arms that are curved left ("enantiomer A") or right ("enantiomer B") like a "pinwheel" (Fig. 3.11a,b top left). Upon ligand exchange and release, 3D meta-atoms are produced with arms that maintain the direction of twist defined lithographically and break mirror symmetry (Fig. 3.11a,b bottom left). Using nanoimprint lithography, we fabricated large, ~9 mm², highly-uniform 3D meta-atoms arrays (Fig. 3.11a,b). A mechanical model is constructed to simulate the 2D to 3D transformation of these structures (Fig. 3.12). The 2D twisted arm can be regarded as the connection of many small 2D straight segments, each 1/100th the size of the whole arm and pointing at a slightly different direction along the curve. Upon folding the 2D straight segments will bend out-of-plane along the direction of curvature with an additive height from the surface of the Si substrate to the tip of the 3D arm. For the 2D pinwheel designs, simulation results predict the arms will bend to a height of 1.18 µm upon ligand exchange and release, in agreement with an experimentally measured height of $1.20 \pm 0.11 \,\mu m$ (Fig. 3.12a,b). After annealing, the height increases to $1.40 \pm 0.06 \,\mu m$ (Fig. 3.12c).



Fig 3.11 3D chiral metamaterials. SEM images of the 3D chiral metamaterials with enantiomer A (**a**) and enantiomer B (**b**). The left upper panel shows the top view of the planar meta-atoms before release; lower panel shows 52° tilt views after release to form the 3D meta-atoms. (**c**) Schematic of the metamaterials illuminated by circularly polarized light. (**d**) Experimental spectra of the transmission difference between right circularly polarized (RCP) and left circularly polarized (LCP) light. The black (red) represents enantiomer A (enantiomer B). Dashed (solid) curves represent the spectra before (after) annealing. (**e**) Electromagnetic simulations of the spectra for the same structures shown in (**a**) and (**b**). The different curves represent the sample before annealing (dashed), with experimental dielectric functions after annealing (dotted), with experimental dielectric functions after annealing averaged with 20% (dash-dot) and 40% (solid) reported dielectric functions of bulk Au. (**f**) Calculations of the evolution of absorption and scattering to the incident light for enantiomer B before (upper panel) and after (lower panel) annealing. Left (right) color bar represents energy dissipation density (relative electric field) with unit W/m³ (V/m).



Fig 3.12 (a) Mechanical simulations for the chiral structures. The black curve represents the starting 2D structures. The blue curve represents the transformed 3D meta-atoms, which reach a height of 1.18 μ m from the tip to the substrate surface after ligand exchange. (b) SEM image of single chiral 3D meta-atom before annealing, showing a height of 1.21 μ m from the tip to the substrate surface. (c) SEM image collected at a tilt angle of 90° showing a column of chiral 3D meta-atoms after annealing. The average height of the tip of the arms from the substrate is 1.42 μ m. Note the sample is tilted with respect to the holder, so the heights of the four arms appear to be slightly different.

We measure the transmission spectra of 3D chiral enantiomeric metamaterials in response to unpolarized light (Fig. 3.13) and to LCP and RCP light (Fig. 3.11c, Fig. 3.14). Before annealing, the transmission spectra of enantiomer A (enantiomer B) under unpolarized illumination show resonances at 2513 cm⁻¹ (2553 cm⁻¹), with extinction of 41.2% (43.9%) and a FWHM of 689 cm⁻¹ (648 cm⁻¹) (Fig. 3.13). For illumination by circularly polarized light, enantiomer A (enantiomer B) show resonances with positions matched to those for unpolarized light, but with extinction of 50.4% (55.4%) to RCP (LCP) light with weak extinction of 36.4% (36.2%) to LCP (RCP) (Fig. 3.14). The difference in transmission for RCP and LCP illumination is a signature of chiroptical materials properties. The chiroptical response ΔT is 23.9% (29.5%) for enantiomer A (enantiomer B) at 2275 cm⁻¹ (2276 cm⁻¹) (Fig. 3d, dashed lines). After annealing, the resonances in transmission spectra blue-shift to 2725 cm⁻¹ (2733 cm⁻¹), and become sharper with FWHM of 496 cm⁻¹ (455 cm⁻¹) (Fig. 3.13, 3.14), consistent with an increase in the metallicity of the Au NC layer and an increase in the curvature of the meta-atoms. The chiroptical response is enhanced to 37.6% (38.3%) at 2706 cm⁻¹ (2718 cm⁻¹) (Fig. 3.11d, solid lines).



Fig 3.13 Transmission spectra of enantiomer A (red) and enantiomer B (black) for illumination with unpolarized light before annealing (dashed lines) and after annealing (solid lines).



Fig 3.14 Transmission spectra of enantiomer A (**a**) and enantiomer B (**b**) for illumination with LCP (dashed lines) and RCP (solid lines) before annealing (blue) and after annealing (red).

We simulate the chiroptical responses of enantiomers A and B before and after annealing, employing the experimental dielectric functions for SCN-exchanged and annealed Au NC thin films and the dimensions used in the 2D design and found from mechanical simulations for 3D-folded structures (Fig. 3.11e). Before annealing, ΔT spectra show broad, 1781 cm⁻¹ FWHM resonances centered at 2084 cm⁻¹ with a difference in ΔT of 18.4%. After annealing, the resonances narrow to 680 cm⁻¹ FWHM and blue-shift to 2304 cm⁻¹ with an enhanced ΔT of 40.6% (Fig. 3.11e dotted lines). The simulated spectral characteristics are similar to those found experimentally, with two exceptions. First, the experimental spectra show a small blue-shift and a narrower FWHM compared to simulated spectra. We hypothesize that this disparity originates from experimental nonuniformities in NC film thickness (Fig. 3.3), and differences in the dielectric functions of the Au NC assemblies in thin films, and used in the simulation, from those in patterned structures. In Au NC thin films, cracks or voids are seen to form on a 500 nm-lengthscale after ligand exchange due to shrinkage. However, patterned arm structures with feature size ~100 nm do not show cracks or voids, as confinement effects may exclude their formation. Therefore, the Au NC films in the patterned arms are likely more metallic in character and responsible for the slightly blue-shifted and narrower experimental spectra. Second, the experimental spectra blue-shift more substantially upon annealing than do simulated spectra. Again, we hypothesize that the dielectric function in the arms is more metallic in character than in films upon annealing, as cracks and voids do not form in the arms and as compressive strain may densify the Au NC layer in the twisted arms. To capture the increased metallicity in the meta-atom arms, we generate a series of metallic

dielectric functions for simulated Au NC assemblies by averaging the experimental dielectric functions of the SCN-exchanged and annealed Au NC thin films with increasing weights of 20% and 40% of the reported dielectric function of bulk Au.²² Simulations show the increased metallicity in the arms blue-shifts and narrows the resonances of the structures after annealing. The simulated spectra for meta-atoms with arms that have more metallic dielectric functions, created by averaging in 20% bulk Au, match the experimental data. Simulations also reveal the evolution in contributions from absorption and scattering of the incident light by the structures before and after annealing. At the resonant frequency, before annealing enantiomer A (enantiomer B) more greatly absorbs and scatters LCP (RCP). After annealing, the scattering of LCP (RCP) is greatly enhanced and the absorption process is suppressed with a larger absorption difference between LCP(RCP) and RCP(LCP), consistent with the increased metallicity and amplified chiroptical response of the 3D chiral metamaterials (Figure 3.11f, Fig. 3.15).



Fig 3.15 Simulation results for absorption (**a**) and scattering (**b**) of LCP (dashed lines) and RCP (solid lines) from enantiomer A before (blue lines) and after (red lines) annealing.

3.4 Chiro-Photonic Devices Based On Chiro-Plasmonic Resonances

We further design a metamaterial with more complex 3D meta-atom building blocks to demonstrate switchable chirality. Since the resonance position and sign of chiral metamaterials depends on the dimensions and direction of curvature of the meta-atom arms, we design and fabricate metamaterials from meta-atoms each with two sets of arms having different dimensions and directions of curvature (Fig. 3.16a). In the fabricated structures, the long (short) arms have a radius of curvature of $1.7 \,\mu m (1.3 \,\mu m)$, contributing to resonances at 2209 cm⁻¹ (2883 cm⁻¹) with a negative (positive) optical polarity (Fig. 3.17, blue curves), creating a ΔT that reverses its sign at 2551 cm⁻¹ (Fig. 3.16b). Upon annealing, the spectral contributions from both sets of arms blue shift, shifting the crossover point where ΔT reverses sign, and thus switching the polarity of the ΔT signal over an interval of the spectral range. Experimentally the resonances shift to 2654 cm⁻¹ (3246 cm⁻¹) for the long (short) arms (Fig. 3.17, red curves) and the crossover point shifts to 3073 cm⁻¹, yielding a switch in optical polarity from before to after annealing between 2549 cm⁻¹ and 3073 cm⁻¹ (Fig. 3.16b). Switchable chirality has only been reported once previously by thermally driving a phase change in the dielectric environment of a multilayer stacked, 2D metasurfaces.⁸³ Here, we show switchable chirality can be achieved by altering the structure and properties of the constituent meta-atoms through a simple fabrication process that leaves the surroundings accessible for strong interactions with chiral molecules.



Fig 3.16 Complex and large-area fabrication of 3D metamaterials. (**a**) (inset) High and low-resolution SEM images of 3D metamaterials with meta-atoms having two-sets of arms of different length and curvature. (upper inset) Mechanism of thermally-driven, switchable chirality. (**b**) Transmission difference for RCP and LCP light for the metamaterial in (**a**). The yellow shaded area highlights the spectral range of chirality reversal. (**c**) High and low-resolution SEM images of large-area chiral meta-atoms fabricated by nanoimprint lithography, with five sets of arms of different length to form a broadband circular polarizer. (inset) Photograph of the 1 cm²-area 3D metamaterials in comparison to a US quarter. (**d**) Transmission difference for RCP and LCP light for the metamaterial in (**c**). In the spectra, the black (violet) curves represent samples before (after) annealing.

In addition, by creating meta-atoms with five sets of arms of different length, we further demonstrate $\sim 1 \text{ cm}^2$ area, broadband chiral metamaterials (Fig. 3.16c, upper inset) with a giant chiroptical response ΔT of bigger than 15% (peak value of 31%) over a spectral range of 2170 to 3570 cm⁻¹ (Fig. 3.16d). As demonstrated above, the meta-atom resonances depend on the length of the arms, by designing meta-atoms to have arms with different lengths, their additive response creates a broadband response. We believe further optimization of the density of arms, the arrangement of meta-atoms and the dimensions of the arms could yield much better broadband chiral responses.



Fig 3.17 Transmission spectra of 3D meta-atoms with different length and curvature arms (design in Fig. S11) in response to RCP (solid lines) and LCP (dashed lines) for metamaterials before annealing (blue) and

after annealing (red). The blue (red) solid (dotted) arrows indicate the resonance from the long (short) arms before (after) annealing.

3.5 CONCLUSIONS

In summary, we report a one-step patterning method to design and fabricate complex, 3D optical metamaterials through the chemically-driven transformation of lithographically-defined 2D Au NC/bulk bilayers to form surface-bound, 3D meta-atoms, and their subsequent thermally-driven shape morphing to tune meta-atom structure and function. This process can be scaled to allow larger area fabrication using nanoimprint lithography. We scale the one-arm-per-side 3D meta-atoms to create ~1 cm² area chiral metamaterials (Fig. 3.18). These chiral metamaterials are suitable for ultra-thin lenses, polarizers, and waveplates that can be fabricated with high throughput over large areas.



Fig 3.18 (a) SEM image of large-scale chiral metamaterials fabricated by nanoimprint lithography. Inset shows a photograph of the 1 cm \times 1 cm patterned area. (b) ΔT spectrum for sample in (a).

3.6 References

- Caglayan, H.; Hong, S. H.; Edwards, B.; Kagan, C. R.; Engheta, N. Near-Infrared Metatronic Nanocircuits by Design. *Phys. Rev. Lett.* 2013, *111*, 1–5.
- Poddubny, A.; Iorsh, I.; Belov, P.; Kivshar, Y. Hyperbolic Metamaterials. *Nat. Photonics* 2013, *7*, 958–967.
- West, P. R.; Ishii, S.; Naik, G. V.; Emani, N. K.; Shalaev, V. M.; Boltasseva, A.
 Searching for Better Plasmonic Materials. *Laser Photonics Rev.* 2010, *4*, 795–808.
- Pendry, J. B.; Schuring, D.; Smith, D. R. Controlling Electromagnetic Fields.
 Science. 2011, *1780* (2006), 1780–1782.
- (5) Pendry, J. B. Negative Refraction Makes a Perfect Lens. *Phys. Rev. Lett.* 2000, 66, 0–3.
- Tsakmakidis, K. L.; Boardman, A. D.; Hess, O. "Trapped Rainbow" Storage of Light in Metamaterials. *Nature* 2007, 450, 397–401.
- Panpradit, W.; Sonsilphong, A.; Soemphol, C.; Wongkasem, N. Negative
 Refractive Index in Chiral Metamaterials. *J. Opt. (United Kingdom)* 2012, *14*, 1–4.
- (8) Zheludev, N. I.; Kivshar, Y. S. From Metamaterials to Metadevices. *Nat. Mater.*2012, *11*, 917–924.
- Ou, J. Y.; Plum, E.; Jiang, L.; Zheludev, N. I. Reconfigurable Photonic Metamaterials. *Nano Lett.* 2011, *11*, 2142–2144.
- (10) Ni, X.; Ishii, S.; Kildishev, A. V.; Shalaev, V. M. Ultra-Thin, Planar, Babinet-Inverted Plasmonic Metalenses. *Light Sci. Appl.* **2013**, *2-6* (APRIL).
- Ni, X.; Kildishev, A. V.; Shalaev, V. M. Metasurface Holograms for Visible Light.
 Nat. Commun. 2013, 4, 1–6.

- (12) Zhao, Y.; Belkin, M. A.; Alù, A. Twisted Optical Metamaterials for Planarized Ultrathin Broadband Circular Polarizers. *Nat. Commun.* 2012, *3-8* (May).
- (13) Yu, N.; Capasso, F. Flat Optics with Designer Metasurfaces. *Nat. Mater.* 2014, *13*, 139-149
- (14) Hentschel, M.; Schäferling, M.; Duan, X.; Giessen, H.; Liu, N. Chiral Plasmonics.
 Sci. Adv. 2017, *3*, 1–13.
- (15) Valev, V. K.; Baumberg, J. J.; Sibilia, C.; Verbiest, T. Chirality and Chiroptical Effects in Plasmonic Nanostructures: Fundamentals, Recent Progress, and Outlook. *Adv. Mater.* 2013, *25*, 2517–2534.
- (16) Decker, M.; Ruther, M.; Kriegler, C. E.; Zhou, J.; Soukoulis, C. M.; Linden, S.;
 Wegener, M. Strong Optical Activity from Twisted-Cross Photonic Metamaterials.
 Opt. Lett. 2009, *34*, 2501-2503.
- (17) Cui, Y.; Kang, L.; Lan, S.; Rodrigues, S.; Cai, W. Giant Chiral Optical Response from a Twisted-Arc Metamaterial. *Nano Lett.* **2014**, *14*, 1021–1025.
- (18) Soukoulis, C. M.; Wegener, M. Past Achievements and Future Challenges in the Development of Three-Dimensional Photonic Metamaterials. *Nat. Photonics* 2011, 5, 523–530.
- (19) Esposito, M.; Tasco, V.; Todisco, F.; Cuscunà, M.; Benedetti, A.; Sanvitto, D.;
 Passaseo, A. Triple-Helical Nanowires by Tomographic Rotatory Growth for Chiral Photonics. *Nat. Commun.* 2015, *6*, 1–7.
- Wang, Z.; Cheng, F.; Winsor, T.; Liu, Y. Optical Chiral Metamaterials: A Review of the Fundamentals, Fabrication Methods and Applications. *Nanotechnology* 2016, *27*. *1-20*

- (21) Yeom, B.; Zhang, H.; Zhang, H.; Park, J. II; Kim, K.; Govorov, A. O.; Kotov, N. A. Chiral Plasmonic Nanostructures on Achiral Nanopillars. *Nano Lett.* 2013, *13*, 5277–5283.
- (22) Zhao, T.; Goodwin, E. D.; Guo, J.; Wang, H.; Diroll, B. T.; Murray, C. B.; Kagan,
 C. R. Advanced Architecture for Colloidal PbS Quantum Dot Solar Cells
 Exploiting a CdSe Quantum Dot Buffer Layer. ACS Nano 2016, 10, 9267–9273.
- (23) Zhao, Q.; Zhao, T.; Guo, J.; Chen, W.; Zhang, M.; Kagan, C. R. The Effect of Dielectric Environment on Doping Efficiency in Colloidal PbSe Nanostructures. *ACS Nano* 2018, *12*, 1313–1320.
- (24) Hentschel, M.; Schäferling, M.; Metzger, B.; Giessen, H. PlasmonicDiastereomers: Adding up Chiral Centers. *Nano Lett.* 2013, *13*, 600–606.
- (25) Frank, B.; Yin, X.; Schäferling, M.; Zhao, J.; Hein, S. M.; Braun, P. V.; Giessen,
 H. Large-Area 3D Chiral Plasmonic Structures. *ACS Nano* 2013, *7*, 6321–6329.
- (26) He, Y.; Larsen, G. K.; Ingram, W.; Zhao, Y. Tunable 3D Helically Stacked
 Plasmonic Layers on Nanosphere Monolayers. *Nano Lett.* 2014, *14*, 1976–1981.
- (27) Chen, Y.; Gao, J.; Yang, X. Chiral Metamaterials of Plasmonic Slanted Nanoapertures with Symmetry Breaking. *Nano Lett.* 2018, *18*, 520–527.
- (28) Chen, Y.; Yang, X.; Gao, J. 3D Janus Plasmonic Helical Nanoapertures for Polarization-Encrypted Data Storage. *Light Sci. Appl.* **2019**, *8*. 1-9
- (29) Fafarman, A. T.; Hong, S. H.; Caglayan, H.; Ye, X.; Diroll, B. T.; Paik, T.; Engheta, N.; Murray, C. B.; Kagan, C. R. Chemically Tailored Dielectric-to-Metal Transition for the Design of Metamaterials from Nanoimprinted Colloidal Nanocrystals. *Nano Lett.* **2013**, *13*, 350–357.

- (30) Zhang, M.; Guo, J.; Yu, Y.; Wu, Y.; Yun, H.; Jishkariani, D.; Chen, W.; Greybush, N. J.; Kübel, C.; Stein, A.; Murray, C.B.; Kagan, C.R. 3D Nanofabrication via Chemo-Mechanical Transformation of Nanocrystal/Bulk Heterostructures. *Adv. Mater.* 2018, *30*, 1–6.
- (31) Chen, W.; Guo, J.; Zhao, Q.; Gopalan, P.; Fafarman, A. T.; Keller, A.; Zhang, M.;
 Wu, Y.; Murray, C. B.; Kagan, C. R. Designing Strong Optical Absorbers via Continuous Tuning of Interparticle Interaction in Colloidal Gold Nanocrystal Assemblies . *ACS Nano* 2019, *13*, 7493–7501.
- (32) Zhang, M.; Magagnosc, D. J.; Liberal, I.; Yu, Y.; Yun, H.; Yang, H.; Wu, Y.; Guo, J.; Chen, W.; Shin, Y. J.; Stein, A.; Kikkawa, J. M.; Engheta, N.; Gianola, D. S.; Murray, C. B.; Kagan, C. R. High-Strength Magnetically Switchable Plasmonic Nanorods Assembled from a Binary Nanocrystal Mixture. *Nat. Nanotechnol.* 2017, *12*, 228–232.
- (33) Chen, W.; Liu, W.; Jiang, Y.; Zhang, M.; Song, N.; Greybush, N. J.; Guo, J.;
 Estep, A. K.; Turner, K. T.; Agarwal, R.; Kagan, C. R. Ultrasensitive,
 Mechanically Responsive Optical Metasurfaces via Strain Amplification. ACS
 Nano 2018, 12, 10683–10692.
- (34) Ou, J. Y.; Plum, E.; Zhang, J.; Zheludev, N. I. An Electromechanically Reconfigurable Plasmonic Metamaterial Operating in the Near-Infrared. *Nat. Nanotechnol.* 2013, *8*, 252–255.
- (35) Diroll, B. T.; Gaulding, E. A.; Kagan, C. R.; Murray, C. B. Spectrally-Resolved Dielectric Functions of Solution-Cast Quantum Dot Thin Films. *Chem. Mater.*2015, 27, 6463–6469.

- (36) Choi, J. H.; Fafarman, A. T.; Oh, S. J.; Ko, D. K.; Kim, D. K.; Diroll, B. T.;
 Muramoto, S.; Gillen, J. G.; Murray, C. B.; Kagan, C. R. Bandlike Transport in Strongly Coupled and Doped Quantum Dot Solids: A Route to High-Performance Thin-Film Electronics. *Nano Lett.* 2012, *12*, 2631–2638.
- (37) Yin, X.; Schäferling, M.; Michel, A. K. U.; Tittl, A.; Wuttig, M.; Taubner, T.;Giessen, H. Active Chiral Plasmonics. *Nano Lett.* 2015, *15*, 4255–4260.
- (38) Fafarman, A. T.; Koh, W. K.; Diroll, B. T.; Kim, D. K.; Ko, D. K.; Oh, S. J.; Ye, X.; Doan-Nguyen, V.; Crump, M. R.; Reifsnyder, D. C.; Murray, C. B.; Kagan, C. R. Thiocyanate-Capped Nanocrystal Colloids: Vibrational Reporter of Surface Chemistry and Solution-Based Route to Enhanced Coupling in Nanocrystal Solids. *J. Am. Chem. Soc.* 2011, *133*, 15753–15761.
- (39) Timoshenko, B. Y. S. ANALYSIS OF BI-METAL THERMOSTATS. JOSA 1925, No. 1, 233–255.
- (40) Mash, D.; Motulevich, G. P. Optical Constants and Electronic Characteristics of Titanium. Sov. Phys. JETP 1973, 36. 516-519

CHAPTER 4 BROADBAND CIRCULAR POLARIZER VIA OPTICAL COUPLING OF 3D META-ATOMS

4.1 Introduction

Light can be described by its decomposition into a linear combination of the basis set of right- and left-hand circular polarizations (RCP and LCP). Since the electric and magnetic fields of RCP and LCP light rotate clockwise and counter-clockwise, respectively, around the direction of propagation, they manifest as two fundamental spin angular momentum states of photons and find potential applications in quantum optics.⁸⁴ The interaction of RCP and LCP light with matter is also different for materials that are chiral, in particular for many biomolecules, and therefore circularly-polarized light is widely used in medical applications, like cancer diagnostics.⁸⁵

RCP and LCP light is conventionally generated upon the transmission of unpolarized light through a combination of linear polarizers and quarter-waveplates, or stacks of cholesteric liquid crystals.⁸⁶ However, typically these optical elements are physically bulky and only operate in a narrow spectral band.⁸ Optical metamaterials promise to overcome these issues by exploiting the strong interaction of plasmonic metals with light to create ultra-thin optical polarizers.^{1–3} By engineering the size, shape, and arrangement of plasmonic metal structures, also known as "meta-atoms", the oscillation modes of electrons induced by the incident light can be tuned to generate broadband chiroptical responses.

One example is utilizing Au helical structures that vary in pitch along their lengths, and therefore electromagnetically couple to a broad spectral range of RCP and LCP light.⁴⁵ While these helical structures are beautiful, they are complex and their fabrication by direct laser writing is diffraction-limited and serial, making it hard to scale down the size of the helices and incompatible with large-area production. Another strategy relies on the twisted layer-by-layer stacking of achiral Au nanorods, which mimic the continuous structure of helices.⁴⁶ The electromagnetic coupling between neighboring twisted layers also produces

a broadband response. Although the nanorod structure is much simpler than the helix and the size of building blocks can be easily reduced to nanometer scales, the fabrication involves the notoriously time-consuming process of electron beam lithography to expose and align each layer as the stacked structure requires.

4.2 Plasmonic Resonance Dependence on The Size of The Meta-atoms

Previously we reported a one-step patterning process that enables the fabrication of largearea, single-layer, 3D meta-atoms by triggering the folding of NC/bulk bilayers to form helical structures. The folding process takes advantage of the different chemical, mechanical, and thermal properties of colloidal Au NC assemblies and bulk materials.⁴⁰ By engineering the length, curvature, and number of helical structures in constituent 3D meta-atoms, large circular dichroism (CD) can be achieved and tailored at different wavelengths. By integrating different length helical structures, a broadened chiroptical response is achieved. In this report, we show that by optimizing the lengths, number of the helical arms within each meta-atom, and the annealing process and by reducing the periodicity between meta-atoms, a phase diagram of the structures of the 3D meta-atoms is developed and 3D meta-atom arrays can yield even larger extinction ratios between RCP and LCP light and a wider operating band. The broad response originates from the synergistic chiroptical responses from arms with different length and near-field, electromagnetic coupling from the meta-atoms array, which is different from previous reports.

Chiroptically-active meta-atoms (Figure 4.1, Figure. 4.2a) are fabricated by modifying a process we previously reported.^{40,65} The meta-atoms are designed from planar structures

(Figure 4.2a, left inset) to have a middle, square pad with a side (s, ranging from 1.5 µm to 2 µm) and curved "arms" tailored in their number (from 4 to 12) and design radius of curvature (R, from 1.4 µm to 2 µm). Three different resists layers (Durimide, PMGI, and Nanonex) are sequentially spin-coated onto a 550 µm thick, double-polished Si wafer. Nanoimprint lithography is used to transfer the design from a fabricated template into the PMGI and Nanonex resist layers (Figure 4.3a). A 20 nm thick Au layer is thermally deposited and colloidal, oleylamine-capped Au nanocrystals (NCs) ~5 nm in diameter (Figure 4.3b) are deposited by spin-coating. Immersion of the samples in a solution of ammonium thiocyanate (NH4SCN) exchanges the oleylamine ligands at the surface of the NCs with more compact SCN⁻ ligands, triggering volume shrinkage in the Au NC layer and thus building up misfit strain ε at the interface of the Au NC/Au bilayer. Durimide serves as a sacrificial layer (Figure 4.2a, right inset). It is selectively dry-etched so that the layer under the middle pads remains and anchors the meta-atoms to the substrate, while the rest is removed releasing the arms from the substrate, allowing their free bending, and the 2D to 3D transformation of the arms forming the meta-atoms (Figure 4.3c, Figure 4.2a). Previously, we used Cr as the sacrificial layer. Compared to the wet etching of Cr, which requires critical point drying to minimize the surface tension of the 3D structures when the sample is transferred from the etching solution to air, dry etching of Durimide provides better control of the uniformity and much higher yield of the meta-atoms.



Figure 4.1 The 2D design of the meta-atom, the radius of curvature of the arms R is 2 μ m, the width of the arm W is 60 nm and the length of the side s is 2.5 μ m.



Figure 4.2. (a) Schematics of a 3D chiral meta-atom composed of a Au NC/evaporated Au bilayer anchored to a Si substrate. (left inset) The parent planar design of the structure consists of a middle square pad with side s and arms with radius of curvature R defined. (right inset) The design is imprinted into a trilayer of imprint resist, PMGI, and Durimide. Au is thermally evaporated and colloidal Au NCs are deposited by spin-coating. Upon ligand exchange and selective removal of the Durimide, the arms are released and bend up from the surface, leaving the middle pad anchored to the substrate. (b) SEM images of meta-atoms with R of 2 μ m (black), 1.8 μ m (red), 1.6 μ m (orange) and 1.4 μ m (blue) before annealing (upper row) and after annealing at 150 °C for 24 h (lower row). (c) Extinction cross-sections for meta-atoms of varying R, corresponding to those shown in (b). (d) The meta-atom resonance peaks blue-shift from before to after annealing at 150 °C (red), 120 °C (orange) and 90°C (blue) for 24 h. The inset shows the resonance peak shift. Each data point contains at measurements of at least 3 samples. The black data points represent samples before annealing and red data points represent samples after annealing.



Figure 4.3 (a) Schematic of a sample after nanoimprint lithography, the pattern has been transferred into the thermal resist (green). (b) Schematic of a sample after deposition of NC/metal bilayer. The thermal resist has been lifted-off, and PMGI (purple) and Durimide (brown) are still on the surface. (c) Schematic of a sample after dry etching, showing a 3D, surface-bound meta-atom.

Representative images of meta-atoms designed with various R are shown in Figure 4.2b. The bending of the meta-atom arms is driven by the induced misfit strain ε and can be well described by the bilayer mechanical model.⁶⁹ The high surface-to-volume ratio of the Au NCs provides a knob for post-fabrication, shape morphing of the meta-atoms through thermal annealing. At elevated temperatures, diffusion of Au and therefore fusion of the

Au NCs densifies the NC layer, forming a porous Au network and increasing ε at the interface of the Au NC/Au bilayer. Figure 4.2b, bottom row shows representative images of the meta-atoms and the increase in the bending of the arms after annealing.

4.3 Effects of Annealing Temperature and Time on Spectral Evolution

FT-IR spectroscopy is used to systematically study the chemically and thermally induced bending of the meta-atoms with various pre-designed R on the plasmonic resonances of their arrays. The resonance wavelength is proportional to the pre-defined R (Figure 4.2c), as larger R offers a longer oscillation path for electrons when they resonantly interact with incident light. Transmission measurements (Figure 4.4) are used to quantify their extinction cross-sections (Figure 4.2c). Meta-atoms arrays upon ligand exchange and release have resonances with an extinction cross-section that increases from 15.1 μ m² to 18.3 μ m² and a FWHM that decreases from 1284.3 cm⁻¹ to 703.0 cm⁻¹ as R increases from 1.4 μ m to 2 μ m. Thermal annealing of these arrays at 150 °C for 24 h, drives a blue-shift in their resonance peaks with similar extinction cross-sections of 14.7 μ m² to 18.9 μ m² and narrower FWHM of 800.7 cm⁻¹ to 459.9 cm⁻¹ (Figure 4.2c).



Figure 4.4 Transmission spectra of metamaterials with R=2 μ m (black), 1.8 μ m (red), 1.6 μ m (orange), 1.4 μ m (blue) from before (solid) and after (dashed) annealing.

The shift in the resonance peak of the arrays of $361\pm60 \text{ cm}^{-1}$ (0.047±0.007 eV) is independent of R and is dominated by the more metallic dielectric function caused by annealing (Figure 4.5). Figure 4.2d follows the resonance peak position for various metaatom R as a function of the annealing temperature at 90 °C, 120 °C, and 150 °C. The evolution in the resonance peak depends on temperature, as does Au diffusion, but at long annealing times, the structures evolve toward steady states that are independent of the chosen annealing temperature (Figure 4.6). No obvious changes are seen spectrally by changing the Au NC concentration used in spin-coating the NC layer (Figure 4.7).



Figure 4.5 The evolution of dielectric functions of NCs from before (dashed) to after (solid) annealing.



Figure 4.6 Transmission spectra for the samples annealing at 90°C (a), 120°C and 150°C(c) for 5 min (red), 2 h (orange) and 24 h (blue). The black spectra represent the transmission of the samples before annealing.



Figure 4.7 FT-IR spectra showing the transmission of metamaterials constructed from NCs with different concentrations. (a) Metamaterials before annealing. (b) Metamaterials after annealing. (c) Dependent of resonance peak on the NC concentrations for samples before and after annealing.

4.4 Phase Diagram for The Structures of Meta-atoms From Before and After Annealing

We combine AFM and SEM to monitor the structural evolution of the meta-atoms before and after annealing and build a model to map the change in their mechanical properties. The mechanical theory relates the radius of curvature ρ of a bent bilayer structure to misfit strain ε and to n, the ratio of the Young's moduli for the Au NC and evaporated Au layers defined as $\frac{E_{Au NC}}{E_{Au}}$. As the arms are patterned with a pre-designed R, after the 2D to 3D transformation, the height H from the tip of the arms to the substrate (Figure 4.8a, inset) follows the formula:

$$H = 2\rho(\varepsilon, n) \sin^2\left(\frac{\pi R}{4\rho(\varepsilon, n)}\right)$$
(1)

AFM is used to measure the height profiles along the arms (Figure 4.2a and Figure 4.9). It is worth pointing out that H is not always the highest value, H^{max} , along the arms as ρ

decreases. This can be seen in the meta-atoms after annealing in Figure 1b and can be confirmed by equation 1 (Figure 4.8b, blue curves), as ρ becomes smaller. For example, for R= 2 μ m, H gradually increases and then undergoes a rapid decrease when ρ hits a critical value (ρ ~1.35 μ m).



Figure 4.8 (a) Tapping-mode AFM image of a single meta-atom with R of 1.6 μ m used to measure the arm height (H), as defined in the inset. (b) H(ρ ,R) and n(ρ , ε) are plotted to show the "phase diagram" of the metaatom structural evolution from before annealing to after annealing. (c) H-R relation from equation (1) is used to fit the experimental data of H measured by AFM. The fitting processes generate the distribution of ε (upper inset) and n (lower inset).



Figure 4.9 (a) Tip path for measuring the height profile of a single meta-atom in AFM. (b) AFM measurement result from (a).

Samples before annealing have relatively large ρ , and therefore, H can be assigned to H^{max} values measured from AFM. For each R, at least 10 meta-atoms are measured and their

average values with 3σ variations are plotted in Figure 4.8c. Assuming Gaussian distributions of the measured height variations (Figure 4.10), we fit the experimental data acquired from AFM to equation 1 and extract the distribution of ε and n (Figure 4.8c, insets). ε takes a value of 0.067±0.003, and n takes a value of 0.0048±0.0002. Therefore, the meta-atom structures fall into the region sandwiched by the orange solid (ε =0.065) and dashed (ε =0.07) curves (Figure 4.8b). Given a Young's modulus for bulk Au of 79 GPa,⁸⁷ the Young's modulus of the Au NC network before annealing is 380±16 MPa. These values for ε and $E_{Au NC}$ are consistent with our previous report⁶⁵ and yield similar 3D structures from mechanical simulations (Figure 4.11), while having much narrower distributions for the samples before annealing.



Figure 4.10 (a) Random generations of 1000 points of height values according to the Gaussian distribution from the experimental data in Figure 4.8c. (b) The fitting results for extracting the distribution of ε and n.



Figure 4.11 Mechanical simulations showing the simulated 3D structures with the R of 1.4 μ m (a), 1.6 μ m (b), 1.8 μ m (c) and 2 μ m (d)

Since ρ becomes small after annealing, the point of H^{max} is no longer at the end of the arms (Figure 4.12). This brings difficulties in accurately measuring H by either AFM or SEM measurements. However, we can estimate ε and n by comparing the model (Figure 4.8b) with our observations that H is less than H^{max} for R>1.4 µm, but H is close to H^{max} for R=1.4 µm (Figure 4.2b). This limits the ε to between 0.1 to 0.15. The densification of the Au NC network upon annealing increases its Young's modulus with the distribution of n taking the range of 0.032 to 0.045 to match the ε required by the bilayer model (Figure 4.8b, ε of 0.1 and 0.15), corresponding to a Young's modulus between 2.5 GPa to 3.5 GPa, in good agreement with the Young's modulus of reported for porous gold⁶⁸. The blue shaded area in Figure 4.8b, bounded by the orange curve ε =0.1 and ε =0.15, for which H^{max}(ρ , R=1.4 µm) and H^{max}(ρ , R=2 µm) first intersect with $\rho(\varepsilon, n)$, set the accessible region by meta-atoms after annealing.



Figure 4.12 SEM image showing the helical arms with small ρ after annealing. H^{max} is no longer at the end of the arms.

4.5 Near Field Electromagnetic Coupling Among Meta-atoms in Array

We fabricate samples of R=1.6 μ m with varying periodicities ranging from 3.5 μ m to 7.5 μ m (Figure 4.13a, b, Figure 4.14). FT-IR spectroscopy is used to study the effects of periodicity on the spectra of unpolarized and RCP and LCP light. The transmission of unpolarized light decreases as the periodicity is reduced and the extinction cross-sections in denser arrays increases (Figure 4.13c, d). For samples before annealing with periodicity larger than 3.5 μ m, only one primary plasmonic resonance can be identified at ~2550 cm⁻¹ with a FWHM of 1120 cm⁻¹±300 cm⁻¹, which is consistent with Figure 4.2c. For the sample with a periodicity of 3.5 μ m (Figure 4.13c), the primary resonance is slightly red-shifted to ~2490 cm⁻¹ with a FWHM of 518 cm⁻¹ and a small secondary resonance is resolved at
\sim 3800 cm⁻¹ with a FWHM of 460 cm⁻¹. The two peaks are shifted to the red and blue of the peak observed for arrays with larger periodicity, similar to the orbital splitting seen in hybridization when two molecules are brought together. After annealing, all the spectra blue-shift with the primary peak for array periodicities larger than 3.5 μ m at ~2970 cm⁻¹ with a FWHM of 750 cm⁻¹ \pm 80 cm⁻¹. The sample with the periodicity of 3.5 µm further shows a relatively broad resonance with unresolved shoulders at ~ 2740 cm⁻¹ and ~ 3150 cm^{-1} , separated by ~410 cm^{-1} in the transmission spectrum (Figure 4.13d).



Figure 4.13 SEM images of meta-atom arrays with periodicities of 6.5 μ m (a) and 3.5 μ m (b). FT-IR transmission spectra of meta-atom arrays with the periodicity of 7.5 μ m (green), 6.5 μ m (blue), 5.5 μ m (orange), 4.5 µm (red), 3.5 µm (black) before (c) and after (d) thermal annealing at 150 °C for 24 h. (e) FT-IR transmission spectra under RCP (black) and LCP (red) for the samples from (a) and (b). scale bar: 10 μm

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Figure 4.14 Metamaterials with periodicity of 6.5 μ m (a), 5.5 μ m (b) and 4.5 μ m (c)

Transmission spectra for RCP and LCP illumination can help resolve the broad resonance seen for unpolarized illumination of arrays with a 3.5 µm periodicity, as strong light-matter interactions occur selectively when the curvature of the arms matches the helicity of the circular polarization. For the sample in Figure 4.13b, the spectrum for RCP illumination shares a similar shape with the spectrum from unpolarized light, while the spectrum for LCP illumination resolves two strong chiroplasmonic peaks at ~2670 cm⁻¹ and ~3130 cm⁻¹, corresponding to a gap of ~460 cm⁻¹, consistent with the separation in the transmission spectrum for unpolarized light, while for the sample with large periodicity in Figure 4.13a, only one chiroplasmonic peak can be resolved at ~2910 cm⁻¹ under either LCP or RCP illumination (Figure 4.13e).

4.6 3D Metamaterials Based Broadband Circular Polarizer

To construct broadband chiroptical responses, we fabricate metamaterials consisting of meta-atoms integrating four sets of arms with R=1.4, 1.6, 1.8 and 2 μ m. They are arranged to have three arms with different R per side (Figure 4.15a, Figure 4.16). RCP and LCP spectroscopy is used to characterize the chiroptical responses of these metamaterials (Figure 4.15b). After annealing, the metamaterial with the periodicity of 10 μ m shows a broad chiroplasmonic resonance originating from the overlap of spectra coming from arms with different R. Comparing to the spectra in Figure 4.2c, the spectra in Figure 4.15b cannot be decomposed into the additive sum of the spectra from the constituent four individual R

spectra. This may be due to the mutual interactions between different arms within the metaatoms when they are under illumination. The region where the $\Delta T (T_{RCP}-T_{LCP}) <0$ is from 2.5 µm to ~4.0 µm with a maximum ΔT of -11.3%. To further broaden the chiroptical responses, a metamaterial with a periodicity of 6.3 µm is fabricated and shows a much broader resonance peak with a chiroptical response ranging from 2.5 µm to 5 µm (Figure 4.15b) and with a maximum ΔT of -43% (Figure 4.17). We attribute this broadening effect to the near field electromagnetic coupling among the meta-atoms array, similar to the mechanism discussed above.



Figure 4.15 (a) SEM images of broadband metamaterials with the periodicity of 10 μ m (top) and 6.3 μ m (bottom). The inset of the top image shows a single meta-atom, which has three arms per side with a different combination of arms with R=1.4, 1.6, 1.8 and 2 μ m. (b) FT-IR transmission spectra under RCP (black) and LCP (red) illumination for the samples with the periodicity of 10 μ m (top) and 6.3 μ m (bottom). scale bar: 20 μ m



Figure 4.16 2D structure design of the meta-atom for broadband circular polarizer. The meta-atom integrates 12 arms with the radius of curvature of 2 μ m (black), 1.8 μ m (red), 1.6 μ m (orange) and 1.4 μ m (blue).



Figure 4.17 Transmission difference between RCP and LCP for the sample with periodicity of 10 μ m (black) and 6.3 μ m (red).

In summary, we reported a one-step patterning method that can fabricate large-scale, ultrathin, broadband circular polarizers with high throughput by engineering the integration of various length helical structures and near field electromagnetic coupling in meta-atoms array. We systematically studied the structural and mechanical properties of the metamaterials and proposed a "phase diagram" for the design of metamaterials. We believe with further optimization of the design of the meta-atom and the periodicity of the array, larger ΔT of the circular polarizer can be achieved.

4.7 Reference

- Togan, E.; Chu, Y.; Trifonov, A. S.; Jiang, L.; Maze, J.; Childress, L.; Dutt, M. V. G.; Sørensen, A. S.; Hemmer, P. R.; Zibrov, A. S.; et al. Quantum Entanglement between an Optical Photon and a Solid-State Spin Qubit. *Nature* 2010, *466* (7307), 730–734. https://doi.org/10.1038/nature09256.
- Kunnen, B.; Macdonald, C.; Doronin, A.; Jacques, S.; Eccles, M.; Meglinski, I.
 Application of Circularly Polarized Light for Non-Invasive Diagnosis of
 Cancerous Tissues and Turbid Tissue-like Scattering Media. *J. Biophotonics* 2015, 8 (4), 317–323. https://doi.org/10.1002/jbio.201400104.
- Yang, Z. Y.; Zhao, M.; Lu, P. X.; Lu, Y. F. Ultrabroadband Optical Circular Polarizers Consisting of Double-Helical Nanowire Structures. *Opt. Lett.* 2010, *35* (15), 2588–2590.
- (4) Gansel, J. K.; Wegener, M.; Burger, S.; Linden, S. Gold Helix Photonic

Metamaterials : A Numerical Parameter Study. 2010, 18 (2), 11822–11829.

- (5) Soukoulis, C. M.; Wegener, M. Past Achievements and Future Challenges in the Development of Three-Dimensional Photonic Metamaterials. *Nat. Photonics* 2011, 5 (9), 523–530. https://doi.org/10.1038/nphoton.2011.154.
- (6) Smith, D. R.; Smith, D. R.; Pendry, J. B.; Wiltshire, M. C. K. Metamaterials and Negative Refractive Index. *Science (80-.).* 2012, *305* (2004), 788–792. https://doi.org/10.1126/science.1096796.
- (7) Zheludev, N. I.; Kivshar, Y. S. From Metamaterials to Metadevices. *Nat. Mater.* **2012**, *11* (11), 917–924. https://doi.org/10.1038/nmat3431.
- Rill, M. S.; Linden, S.; Gansel, J. K.; Thiel, M.; Decker, M.; Bade, K.; von Freymann, G.; Saile, V.; Wegener, M. Gold Helix Photonic Metamaterial as Broadband Circular Polarizer. *Science (80-.).* 2009, *325* (5947), 1513–1515. https://doi.org/10.1126/science.1177031.
- (9) Zhao, Y.; Belkin, M. A.; Alù, A. Twisted Optical Metamaterials for Planarized Ultrathin Broadband Circular Polarizers. *Nat. Commun.* 2012, *3* (May). https://doi.org/10.1038/ncomms1877.
- (10) Guo, J.; Kim, J. Y.; Zhang, M.; Wang, H.; Stein, A.; Murray, C. B.; Kotov, N. A.; Kagan, C. R. Chemo- And Thermomechanically Configurable 3D Optical Metamaterials Constructed from Colloidal Nanocrystal Assemblies. *ACS Nano* 2020, *14*, 1427–1435. https://doi.org/10.1021/acsnano.9b08452.
- (11) Zhang, M.; Guo, J.; Yu, Y.; Wu, Y.; Yun, H.; Jishkariani, D.; Chen, W.; Greybush,

N. J.; Kübel, C.; Stein, A.; et al. 3D Nanofabrication via Chemo-Mechanical
Transformation of Nanocrystal/Bulk Heterostructures. *Adv. Mater.* 2018, *30* (22),
1–6. https://doi.org/10.1002/adma.201800233.

- (12) Timoshenko, B. Y. S. ANALYSIS OF BI-METAL THERMOSTATS. JOSA 1925, No. 1, 233–255.
- Wu, B.; Heidelberg, A.; Boland, J. J. Mechanical Properties of Ultrahigh-Strength Gold Nanowires. *Nat. Mater.* 2005, *4* (7), 525–529.
 https://doi.org/10.1038/nmat1403.
- (14) Gauvin, M.; Wan, Y.; Arfaoui, I.; Pileni, M. P. Mechanical Properties of Au Supracrystals Tuned by Flexible Ligand Interactions. *J. Phys. Chem. C* 2014, *118*(9), 5005–5012. https://doi.org/10.1021/jp411896c.

CHAPTER 5 FUTURE WORKS AND CONCLUSION

5.1 Active (Reconfigurable) Metamaterials

Metamaterials can be regarded as the components that transform the input signals to output signals. Early research on metamaterials focused on exploring the various transformations possible by designing the layouts of plasmonic and non-plasmonic building blocks. For a specifically designed metamaterial, its transformation of input signals is static, in a sense that given the fixed inputs, the outputs are also fixed. More recently, the community has begun to explore the possibility of adding more "coupling knobs" into the metamaterials. besides the input signals, these knobs can couple to other signals so as to modulate the transformations of input signals. These metamaterials show dynamic tuning of their behavior and are called active metamaterials or reconfigurable metamaterials.

Electrostatic coupling is one way to build the control knob. A DC voltage is applied to different parts of the metamaterials, creating an attractive electrostatic force. An increase of the voltage leads to an increase of the attractive force, so the morphology of the metamaterials can be changed. The structural change of metamaterials further changes the transformation processes of input signals. As an example, 5.1.1 shows an active metamaterial.⁸¹ The applied voltage changes the gap between two segments through the electrostatic force, and thus, the transmission can be reversibly modulated (Figure 5.1.2). In another example, the structural change of tmetamaterials⁸⁸ can also change the reflection of the light through the applied voltage (Figure 5.1.3).



Figure 5.1.1 Electrically reconfigurable photonic metamaterial. a, Scanning electron microscope (SEM) image of the device. b, Schematic of the driving circuit (black) and a section of the metamaterial pattern consisting of a gold nanostructure (yellow) supported by silicon nitride strings (brown). The driving voltage U causes positive (red) and negative (blue) charging and thus electrostatic forces acting in opposite directions (pink and green).⁸¹



Figure 5.1.2 Reversible electro-optical tuning and modulation. a,b, Spectral dependence of changes in transmission T (a) and reflection R (b) induced by applying a static voltage to the reconfigurable photonic metamaterial.⁸¹



Figure 5.1.3 Temporal color control from suspended silicon metasurfaces. (A) Schematic metasurface devices at 0-V (left) and a 2.75-V (right) bias. (B) Finite-element mechanical simulation for a pixel size of 12 μ m. (C) Bright-field light scattering from a metasurface with 100-nm-wide nanowires spaced at 300 nm.⁸⁸

Phase change materials can be used to build the coupling knob. As the temperature changes, the phase change material can transit from one state to another state, along which, the mechanical, electrical or optical properties are also changed. For example, $Ge_3Sb_2Te_6$ is used as the knob to control the chiroplasmonic resonances⁸³ (Figure 5.1.4). The metallic structures are encapsulated by $Ge_3Sb_2Te_6$. When the temperature changes, the crystal structure of $Ge_3Sb_2Te_6$ transits from amorphous to crystalline, which leads to a change of dielectric function, on the other hand, the plasmonic resonance of the metallic structures is very sensitive to the dielectric function of their environment, therefore, this phase transition can induce the shift of the plasmonic resonance.



Figure 5.1.4 Tunable chirality concept. (a) Active chiral plasmonic dimer stack consisting of 50 nm GST-326 (red) with two protective10 nm ZnS/SiO₂ layers (gray) sandwiched between vertically displaced, corner-stacked, orthogonal gold nanorods embedded in PC403 (light red). For better visibility of the nanorods, a cut-away is included at the edge of the stack. (b) Thermal actuation of the phase change layer leads to a CD signal ΔT that is shifted to longer wavelengths.⁸³

In the previous sections, we discussed the possibility of using thermal annealing to control the shape morphing of the metamaterials. However, in our cases, the thermal annealing permanently changes the structure of the NC layer, therefore, this shape morphing process is irreversible. In the next several sections, I would like to propose several methods that can build multiple "coupling knobs" into current systems.

5.2 Acoustic Field Driven Assembly and Disassembly of 3D Superstructures

An acoustic field is the mechanical oscillation of a system. In solids, the oscillation of atoms constitutes the acoustic waves and in liquids and gases, the oscillation of molecules supports the acoustic waves. As the mechanical oscillation, the acoustic wave can interact

with objects and exert forces on them. The effects can be easily identified when the objects are immersed into liquids and acoustic waves are then generated in liquids through a transducer. For example, a liquid cell with matched dimensions to the wavelength of the acoustic wave can support standing acoustic waves. Low-pressure regions are built up at the nodes of the standing wave, therefore, objects with proper parameters can be levitated at these nodal positions, a phenomenon called acoustic levitation.

There are many other forces derived from the interaction between the acoustic wave and objects. By designing a proper shape, composition and size of the object, it is possible to manipulate the motion of the objects in a liquid. By further integrating a magnetic field, more complicated motion control can be achieved⁸⁹ (Figure 5.2.1). In this case, the acoustic wave contributes to three different forces: the primary Bjerknes force, the streaming propulsive force and the secondary Bjerknes force and the shape of the objects determines the directions and magnitudes of these forces. Therefore, the controlled motion is possible through the optimization of the design of the objects.



Figure 5.2.1 Theoretical analysis and experimental demonstrations of microswimmers' responding to an acoustic field and a magnetic field. (A) Schematic of the primary Bjerknes force FPB (blue solid arrow), secondary Bjerknes force FSB (red solid arrow), and streaming propulsive force FSP (black solid arrow) on a microswimmer at the moment that an acoustic field is applied (T = 0). The yellow dot indicates the center of mass of the microswimmer, and black dashed arrows indicate the streaming flow pattern. The total force (yellow dashed arrow) generates a torque to rotate the axis of the microswimmer into the z direction. When the magnetic field is on (blue dashed arrows), the microswimmer is tilted at an angle a and starts to translate. (B) Experimental demonstrations (top view) of the self-rotation of microswimmers when the acoustic field is on and the translation of microswimmers over 2 s when both acoustic and magnetic fields are applied.⁸⁹

Given the 3D superstructures we have fabricated, it is interesting to see how the acoustic wave can couple to them. Instead of symmetric structures presented in Figure 5.2.1, the superstructures we fabricated don't have mirror symmetry, so it is expected that not only

forces will be exerted on them, but also the torques will also be present. Experimentally, we successfully monitored the rotation of the 3D chiral superstructures.

From the video we recorded (Figure 5.2.2), it is observed that the rotation can be either clockwise and counterclockwise, even though all the structures have the same chirality, in addition, the rotation of the superstructures doesn't only happen in one plane, but in different planes; another prominent effect is the superstructures undergoing clockwise rotation form a domain while the superstructures undergoing counterclockwise rotation form another domain, in other words, superstructures having different rotating directions separate into two phases.



Figure 5.2.2 Image captured from a recorded video showing the chiral structures rotating in the liquid under the acoustic field. The structures in this image are undergoing clockwise rotation.

An earlier theoretic work illustrates a similar idea where rotating small balls with different directions separate into different rotation phases, and the phase also shares the same rotating direction as a whole.⁹⁰ However, in their models, they only consider the

interactions from the collisions among the rotating structures. In our cases, the spinning of the superstructures also generates perturbations in the liquid, and through the perturbations, long-range interactions among the rotating superstructures are possible.



Figure 5.2.3 (a) Clockwise (A) and counterclockwise (B) spinners. (b) The ratio of translational to total kinetic energy κ indicates the presence of a phase transition (ω_0 =1). Error bars are smaller than the symbols. The inset shows the critical density ϕ_c as a function of noise T. (c) Nonequilibrium phase diagram based on simulation data at T=0. Lines indicate phase boundaries. Insets show representative snapshots as the system approaches steady state. A and B spinners in the fluid (crystal) phase are shown in dark (light) blue and orange (red) colors. Fifty:fifty mixtures are used in (b),(c).⁹⁰

Therefore, to thoroughly study the interactions, the next step, 2D structures will be used to see the spinning behavior. Furthermore, it is crucial to understand the underlying physics that driving the rotating directions. For now, it seems the rotating direction is random for one specific superstructure, however, as the superstructures possess a certain chirality, it is hard to say which factor predominantly determines the rotating direction. In the future, superstructures with non-chiral shape should be adopted to see the rotation behavior.

As mentioned in chapter 2, 3 and 4, the chiral structures respond to different CPLs differently. Therefore, it is possible to couple the CPLs to the free-standing superstructures to see whether the CPLs can trigger the spinning of the superstructures. A possible route is to take advantage of is the absorption difference between LCP and RCP for chiral superstructures. If the superstructures are made of TiO_2/NCs , then the chiroplasmonic effect will selectively transfer the energy of CPLs to the superstructures, and then electron transfer from the NCs to TiO_2 can be utilized to catalyze a liquid environment, like H_2O_2 . This chemical reaction can potentially drive the spinning of the superstructures.

5.3 Light-Induced Phase Transition of 3D Superstructures

In chapter 2, we demonstrate how we couple the superstructures to an external magnetic field by using superparamagnetic NCs to fabricate the bilayer structures. It is also possible to mix the Au NCs and Zn-ferrite NCs, and then spin-cast the mixture to fabricate the bilayer structures. In this architecture, the gold NCs provide the plasmonic knob that can couple to light. The plasmonic resonance generate heat, which can then couple to the superparamagnetic NCs. Through the heat transfer, it is possible to tune the temperature of the structures so that the magnetic NCs undergo a ferromagnetic state to superparamagnetic

state phase transition. In the ferromagnetic state, NCs link together to form a self-assembly lattice, while in the superparamagnetic state, they disassemble (Figure 5.3.1).



Figure 5.3. Schematics showing the mechanism of light-induced assembly of 3D superstructures.

5.4 Electrostatically Reconfigurable Metamaterials

Electrostatic force can be used to actively control the deformation of structures, which has been extensively studied in MEMS. In general, the structures consist of parts that are separated by air and also suspended. The separation enables a voltage to be applied between different parts and the suspension enables the deformation of the parts. As we have demonstrated in the previous chapters, the fabrication process we developed can also achieve these requirements.

We therefore design a "table" structure as a proof of concept. This structure is composed of a small middle pad, connected with four long arms which are bonded to even larger pads. The etching process is used to release the small middle pad and all the arms, while the larger pads are still anchored on the substrate. Through the bending of the arms, the small middle pad can be lifted up, creating an air gap between the substrate and the small pad. Therefore, by applying a voltage difference between the structure and the substrate, we anticipate the electrostatic force can reversibly modulate the air gap distance, if an AC signal is applied, the vibration of the middle pad can be generated.

As shown in the Figure 5.4, after etching, the small middle pad lifts up a little bit due to the bending of the arms. However, as the arms are bounded on both ends, the bending is restricted and only a small air gap can be generated from this design. We further propose an improved design of the table structure as shown on the right of the Figure 5.4. In this pattern, the middle pad is no longer directly connected to the long arms. The long arms and the middle pad are connected through short segments. Therefore, one end of the long arms is now free, so after etching, they can bend up without restraint, and the middle pad is expected to be lifted up to a higher position.



Figure 5.4. Left: Fabricated table structures showing a small air gap. Right: Schematics of proposed table structure which is expected to create a large air gap.

5.5 Suspended CdSe QDs Thin Film Transistor (TFT) for Probing Intrinsic Carriers' Transport

In this final section, I would like to discuss a research topic that is different from the topics covered above. I spent around one year on this research topic and hope to address questions: how does the intrinsic transport of carriers in CdSe QDs based TFT look like? How many factors do affect the transport?

The story comes from the typical architecture of the TFTs used in research (Figure 5.5.1). Unlike MOSFETs where PN junctions serve as the building blocks of the transistor, the TFTs consist of heavily doped Si serving as the gate electrode, a thin oxide serving as the gate oxide, the active semiconductor layer and the source and drain electrode patterned on top of the semiconductor. If the semiconductor is n (p) type, then the TFT is n (p) type.



Figure 5.5.1 (a) Architecture of MOSFET (b) Typical architecture of TFTs used in research.

TFTs typically use glass as the substrate. Therefore, from the perspective of fabrication, the processing temperature should be below the strain point of the glass; also, as the substrate is amorphous, the semiconductor that deposited onto it is amorphous or polycrystalline. To meet these requirements, only a handful materials are available, one of the widely used materials is hydrogenated amorphous silicon. More recently, the development of QDs provides another possibility. This is because QDs are solution processible, so the deposition can be spin-coating at room temperature, and other than rigid substrate like glass, they are compatible with soft substrate materials like plastics.

The development of QD based TFTs undergoes several stages. At first, ligand exchange methods are heavily explored to optimize the electronic coupling between the QDs. Many ligand chemistries have been discovered that can improve the lifetime, mobility of the carriers and passivate the traps. Then the doping methods are studied to actively control the carrier number in QDs layers. Certain ligands and impurities can serve as n or p-type dopants. More recently, the engineering of traps in the system attracts a lot of attention. Traps come from various origins and play a key role in determining the transport of carriers including mobility, subthreshold swing, threshold voltage, etc. The interface between the QDs layer and oxide contribute to a majority of the traps. For example, the hydroxyl group that exists on the surface of SiO_2 has been identified as a source of traps and can contribute to large hysteresis and lowered mobility, in addition, the surface of QDs can also contribute to traps due to non-passivated sites. However, as the interface is a complex containing both the oxide and QDs, it is not clear which factor contribute the most traps. In addition, phonon modes in oxides can also couple to the carriers' transport, which adds extra factors that impact the mobilities of the carriers.

To address these questions, it is necessary to study the traps from different origins independently. Therefore, we design a new measurement platform for QDs based TFTs (Figure 5.5.2). In this architecture, the CdSe QDs film is suspended over the oxide so that there is an air gap between them. This architecture contains two parts, the bottom part contains the heavily doped Si and oxide, and an electrode pair with wider separation distance is patterned onto it through photolithography; the top part contains the sapphire as another substrate, onto which the CdSe QDs can be deposited. As the sapphire is an insulator, there is no floating gate effect associated with it. Another electrode pair with short separation distance is patterned onto the semiconductor through shadow evaporation. Then the two parts are clamped by magnets. The distance of the air gap is determined by the thickness of the electrode, the surface roughness of the two substrates, the attractive force between the magnets and more importantly, the bowing effect of the two substrates.



Figure 5.5.2 (a) Architecture of suspended CdSe QDs TFT. (b) Optical images of the structure from (a), containing top part and bottom part. (c) Optical image of the assembled structures from (b), clamped by the magnets.

Two methods can be used to quantify the distance of the air gap. Firstly, it is possible to inject the resist into the air gap and then cure the resist by heating. By detaching the two parts, it is possible to use SEM to measure the thickness of the resist to get the distance of

the air gap; in a second method, ellipsometry can measure the distance directly by building a proper model.

We used the electric probestation to characterize the electric performances of both suspended and typical TFTs (Figure 5.5.3). From the transfer characteristics, it can be concluded: suspended transistors have smaller hysteresis and smaller threshold voltage than those with a gate oxide. To quantify the results, we used the square-law model of transistors to describe our system:

$$I_{D} = \frac{Z\mu_{n}C_{0}}{L} ((V_{G} - V_{T})V_{D} - \frac{V_{D}^{2}}{2}) \quad (V_{G} \ge V_{T} \& 0 \le V_{D} \le V_{Dsat})$$
$$I_{D} = \frac{Z\mu_{n}C_{0}}{L} (V_{G} - V_{T})^{2} \quad (V_{D} \ge V_{Dsat})$$

In our experiment, for the typical architecture of TFTs, the operation is within the saturation regime, where $V_D = +80$ V and V_G is scanned from -80 V to +80 V, therefore, $\sqrt{I_D} \sim V_G - V_T$, the slope of the experimental curve gives the carrier mobility, which we extract in control samples as 2 cm²/(V·s). The intersection of the slope to the x-axis give the information about the V_G , so we can calculate it as 54.1 V. By plotting the log (I_D) vs V_G , it is also possible to extract the subthreshold swing as 10 V/dec.



Figure 5.5.3 (a) Transfer characteristics of suspended TFTs. (b) Transfer characteristics of traditional TFTs

However, the operation mode is changed when the suspended architecture TFTs are used. From the square-law model, the condition for the saturation regime is: $V_G - V_T < V_D$. This condition can be easily satisfied by experimentally setting the $V_D = \max(V_G)$, so long as V_T is positive. In terms of the suspended TFTs, it should be noted that V_T becomes negative (Figure 5.5.3 (a)). In this situation, $\max(V_G) - V_T > V_D$, where $V_D = +80$ V and V_G is scanned from -80 V to +80 V. So TFTs in this scenario are no longer in saturation regime. In addition, the large V_D applied to the drain side doesn't qualify TFTs to be in linear regime, so it is hard to extract the mobility information by only using the square-law model. While from the slope information given by the transfer characteristics in Figure 5.5.3 (a), it is still able to give the estimates that the threshold voltage is -39.8 V and the subthreshold swing is 12 V/dec.

The slightly larger subthreshold swing is due to the capacitance contribution from the air gap. From the definition of subthreshold swing, $S = (\ln 10) \frac{kT}{q} (1 + \frac{C_{dep}+C_{it}}{C_{die}})$, where C_{dep} represents the capacitance coming from the depletion region, C_{it} represents the capacitance coming from the interfacial traps, and C_{die} is the capacitance coming from the dielectric stack between the semiconductor and the heavily doped substrate. For traditional TFTs, C_{die} is the capacitance of the oxide, however, for suspended TFTs, C_{die} is the capacitance of the oxide, however, the C_{die} is much smaller in suspended TFTs compared to that in traditional one, leading to a large S. In addition,

subthreshold swing provides a way to evaluate the interfacial density by evaluating the capacitance due to the traps.

We know the Debye length $L_D = \sqrt{\frac{kT\varepsilon_s\varepsilon_0}{q^2N_D}}$. Plugging in the parameters we can get the L_D is ~45 nm, which is larger than the thickness of the film. Therefore, $C_{dep} = \frac{\varepsilon_s\varepsilon_0}{T_{film}} = 1.77 * 10^{-3} F/m^2$, combining the equation for subthreshold swing, we can calculate the:

 $N_T = \frac{C_{it}}{q} = 1.23 * 10^{11} / cm^2$. As a comparison, the table below showing the interfacial trap density coming from various oxides.

	SiO ₂	Al ₂ O ₃	Air
N _T (cm ⁻²)	1.36*10 ¹³	8.97*10 ¹²	1.23*10 ¹¹
Mobility(cm ² /Vs)	2	27	NA
Threshold voltage(V)	54	12	-40

Table 5.5: Comparison of electronic parameters caused by different semiconductor-dielectric interface.

For future reference, low-temperature electronic characterization is needed to map the relationship between mobility and temperature to study the transport mechanism.

5.6 Reference

- Ou, J. Y.; Plum, E.; Zhang, J.; Zheludev, N. I. An Electromechanically Reconfigurable Plasmonic Metamaterial Operating in the Near-Infrared. *Nat. Nanotechnol.* 2013, 8 (4), 252–255. https://doi.org/10.1038/nnano.2013.25.
- Holsteen, A. L.; Cihan, A. F.; Brongersma, M. L. Temporal Color Mixing and Dynamic Beam Shaping with Silicon Metasurfaces. *Science (80-.).* 2019, No. July, 2–6.
- (3) Yin, X.; Schäferling, M.; Michel, A. K. U.; Tittl, A.; Wuttig, M.; Taubner, T.;
 Giessen, H. Active Chiral Plasmonics. *Nano Lett.* 2015, *15* (7), 4255–4260.
 https://doi.org/10.1021/nl5042325.
- (4) Ren, L.; Nama, N.; McNeill, J. M.; Soto, F.; Yan, Z.; Liu, W.; Wang, W.; Wang, J.; Mallouk, T. E. 3D Steerable, Acoustically Powered Microswimmers for Single-Particle Manipulation. *Sci. Adv.* 2019, *5* (10). https://doi.org/10.1126/sciadv.aax3084.
- Nguyen, N. H. P.; Klotsa, D.; Engel, M.; Glotzer, S. C. Emergent Collective Phenomena in a Mixture of Hard Shapes through Active Rotation. *Phys. Rev. Lett.* **2014**, *112* (7), 1–5. https://doi.org/10.1103/PhysRevLett.112.075701.