

Stimuli-Responsive Surface Ligands for Direct Lithography of Functional Inorganic Nanomaterials

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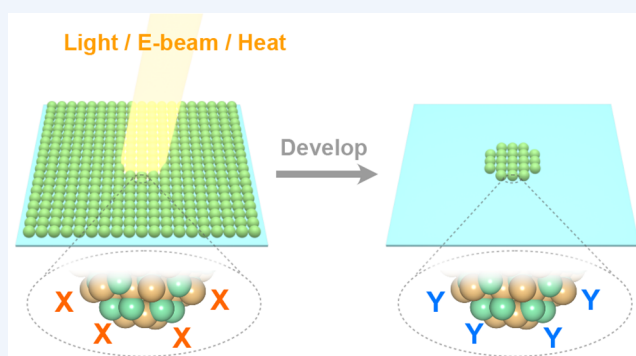


Supporting Information

CONSPECTUS: Colloidal nanocrystals (NCs) have emerged as a diverse class of materials with tunable composition, size, shape, and surface chemistry. From their facile syntheses to unique optoelectronic properties, these solution-processed nanomaterials are a promising alternative to materials grown as bulk crystals or by vapor-phase methods. However, the integration of colloidal nanomaterials in real-world devices is held back by challenges in making patterned NC films with the resolution, throughput, and cost demanded by device components and applications. Therefore, suitable approaches to pattern NCs need to be established to aid the transition from individual proof-of-concept NC devices to integrated and multiplexed technological systems.

In this Account, we discuss the development of stimuli-sensitive surface ligands that enable NCs to be patterned directly with good pattern fidelity while retaining desirable properties. We focus on rationally selected ligands that enable changes in the NC dispersibility by responding to light, electron beam, and/or heat. First, we summarize the fundamental forces between colloidal NCs and discuss the principles behind NC stabilization/destabilization. These principles are applied to understanding the mechanisms of the NC dispersibility change upon stimuli-induced ligand modifications. Six ligand-based patterning mechanisms are introduced: ligand cross-linking, ligand decomposition, ligand desorption, *in situ* ligand exchange, ion/ligand binding, and ligand-aided increase of ionic strength. We discuss examples of stimuli-sensitive ligands that fall under each mechanism, including their chemical transformations, and address how these ligands are used to pattern either sterically or electrostatically stabilized colloidal NCs. Following that, we explain the rationale behind the exploration of different types of stimuli, as well as the advantages and disadvantages of each stimulus.

We then discuss relevant figures-of-merit that should be considered when choosing a particular ligand chemistry or stimulus for patterning NCs. These figures-of-merit pertain to either the pattern quality (e.g., resolution, edge and surface roughness, layer thickness), or to the NC material quality (e.g., photo/electro-luminescence, electrical conductivity, inorganic fraction). We outline the importance of these properties and provide insights on optimizing them. Both the pattern quality and NC quality impact the performance of patterned NC devices such as field-effect transistors, light-emitting diodes, color-conversion pixels, photodetectors, and diffractive optical elements. We also give examples of proof-of-concept patterned NC devices and evaluate their performance. Finally, we provide an outlook on further expanding the chemistry of stimuli-sensitive ligands, improving the NC pattern quality, progress toward 3D printing, and other potential research directions. Ultimately, we hope that the development of a patterning toolbox for NCs will expedite their implementation in a broad range of applications.



KEY REFERENCES

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- Wang, Y.; Pan, J.-A.; Wu, H.; Talapin, D. V. Direct Wavelength-Selective Optical and Electron-Beam Lith-

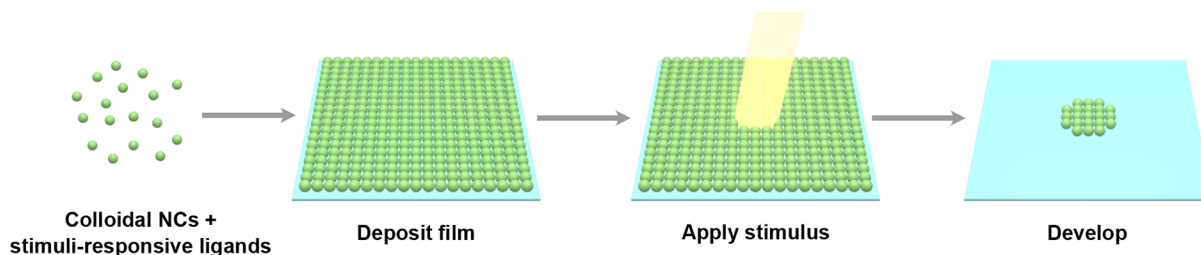
ography of Functional Inorganic Nanomaterials. *ACS Nano* **2019**, 13, 13917–13931.² This work reports the

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Scheme 1. Direct Patterning of Nanocrystals (NCs) with Stimuli-Responsive Ligands



direct electron-beam lithography of colloidal nanocrystals and establishes different families of light sensitive ligands that enable wavelength-selective direct patterning.

- Cho, H.; Pan, J.-A.; Wu, H.; Lan, X.; Coropceanu, I.; Wang, Y.; Cho, W.; Hill, E. A.; Anderson, J. S.; Talapin, D. V. Direct Optical Patterning of Quantum Dot Light-Emitting Diodes via *In Situ* Ligand Exchange. *Adv. Mater.* **2020**, *32*, 2003805.³ In this report, highly emissive quantum dots were directly patterned to make multicolor light-emitting diode arrays.
- Wu, H.; Wang, Y.; Yu, J.; Pan, J.-A.; Cho, H.; Gupta, A.; Coropceanu, I.; Zhou, C.; Park, J.; Talapin, D. V. Direct Heat-Induced Patterning of Inorganic Nanomaterials. *J. Am. Chem. Soc.* **2022**, *144*, 10495–10506.⁴ The patterning of nanocrystals with heat is enabled through the development of several chemical families of heat-sensitive ligands.

■ INTRODUCTION

The ability to place colloidal nanocrystals (NCs) at specific locations with nano/microscale precision has been investigated as early as 1996.^{5,6} These early attempts involved an indirect optical lithography approach through the photodeprotection of self-assembled monolayers on a substrate, resulting in the formation of spatially patterned surface groups that bound colloidal NCs in the subsequent step. One of the earliest direct patterning of NCs was the irradiation of oleate-capped CdSeS NCs with UV light that cross-linked the oleate ligands, rendering the irradiated NCs nondispersible in toluene.⁷ Since then, various direct and indirect approaches have been explored to form patterns of NCs. This includes stimuli-based approaches (e.g., photolithography,⁷ electron-beam lithography,⁸ thermal lithography⁴) as well as physical-based approaches (e.g., inkjet printing,⁹ transfer printing,¹⁰ nano-imprinting¹¹).

The direct lithography of stimuli-sensitive NCs involves using a particular stimulus (e.g., light, heat, electron beam) to induce a change in dispersibility of NCs (Scheme 1). In this process, a solution of stimuli-sensitive NCs is first formulated by functionalizing the NCs with stimuli-responsive ligands or additives. This NC solution is then deposited as a film, e.g., by spin-coating. The stimulus is then applied to specific parts of the film, usually reducing the dispersibility of NCs in those regions. During the development step, the film is immersed in a developer solvent which redisperses the unexposed NCs, leaving behind a patterned NC film. Alternatively, the exposure step can make NCs dispersible in the developer solvent, while the unexposed regions of NC film remain intact.

The direct patterning of NCs relies upon changes in the NC dispersibility which is primarily dependent on the surface and ligand chemistry of the NCs. This has led to the exploration of

various types of stimuli-sensitive ligands for patterning NCs. This Account focuses on the recent studies on the development of such stimuli-responsive ligands.

■ FORCES ACTING BETWEEN COLLOIDAL NCS

The stimuli-induced patterning of NCs relies on the ability to modulate the dispersibility of NCs in a particular solvent using an appropriate stimulus. The NC dispersibility is governed by several types of colloidal interactions: van der Waals attraction, steric interaction, and electrostatic double layer repulsion. A brief description of these interactions is provided here, while a more extensive discussion (including analytical expressions and numerical approaches) is provided in the [Supporting Information](#) and [Figures S1 and S2](#).

van der Waals Attraction

The van der Waals dispersion force is a ubiquitous force acting between all atoms and molecules due to the interaction of instantaneous dipoles that arise from the distortion of the electron cloud within an atom or molecule. For nanoscale materials, the van der Waals interaction can be approximately calculated using the Hamaker approach, which assumes that the interatomic forces are pairwise additive and not retarded.^{12–14} Since this interaction is attractive, NCs will aggregate in the absence of any additional interactions.

Steric Interaction

NCs synthesized with long-chain organic surfactants are stabilized through repulsive steric interactions. In the presence of a “good” solvent, there is a negative free energy of mixing between the NC surface ligands and solvent molecules, making it a favorable interaction. When two NCs approach each other, these ligands overlap and exclude solvent molecules within this region, leading to a repulsive osmotic pressure that drives the NCs apart. The “goodness” of a solvent for a particular ligand can be qualitatively evaluated on the basis that “like dissolves like” or quantitatively through the Hildebrand and Hansen solubility parameters.¹⁵ Hence, the goodness of a particular solvent depends on the chemical nature of both the ligand and the solvent. For instance, a nonpolar solvent like toluene would be a good solvent for NCs with nonpolar hydrocarbon ligands like oleate but would not be a good solvent for NCs with more polar ligands like chalcogenidometalate ions.¹⁶

Electrostatic Double Layer Repulsion

NCs can also repel one another due to an electrostatic double layer (EDL) interaction arising from changes in local ionic concentrations around a charged NC surface in a polar solvent. The EDL interaction is determined by several parameters including the surface charge/potential, the ionic concentration, and the solvent permittivity. These parameters can serve as chemical handles that change the dispersibility of NCs using an appropriate stimuli-sensitive ligand.

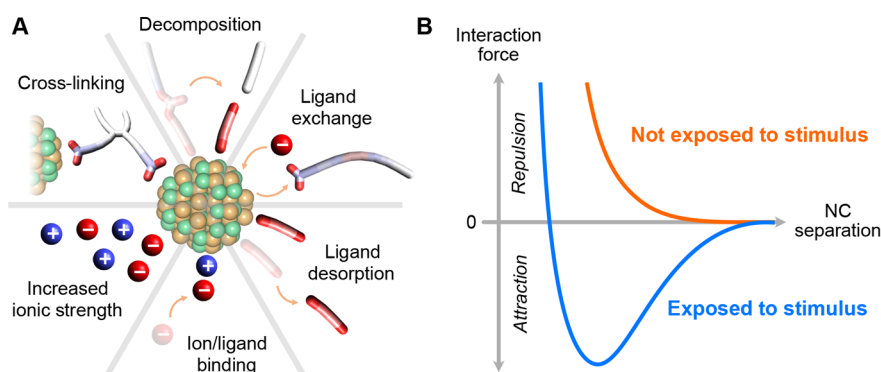


Figure 1. (A) Patterning mechanisms that enable a stimuli-induced change in the dispersibility of colloidal NCs. (B) Interaction force profiles during postexposure development for NCs exposed or not exposed to stimulus.

PATTERNING MECHANISMS

The working definition that we will use for “patterning mechanism” is the underlying microscopic chemical changes that occur upon exposure of the NCs to a stimulus that changes the NC dispersibility. In other words, what chemical bonds are broken and/or formed upon stimulus exposure and how does this affect the dispersibility of the NCs? Figure 1A visually summarizes the different patterning mechanisms that have been proposed to enable this dispersibility change. These mechanisms include cross-linking, decomposition, exchange, desorption, binding, and increased ionic strength (which reduces the repulsion screening length, κ^{-1}). All these chemical changes ultimately lead to changes in the interaction forces between NCs (Figure 1B), allowing NCs to be patterned.

The chemical transformations for some of these stimuli-sensitive ligands are shown in Schemes 2–4, grouped based on their patterning mechanisms. For ease of implementation, we have also tabulated these ligands based on whether they are used with sterically stabilized NCs (Table 1) or electrostatically stabilized NCs (Table 2).

Cross-linking

Cross-linking occurs when one or more ligands bind two NCs linking them together. If cross-linking is induced by an applied stimulus, it forms a network of cross-linked NCs in the exposed regions that resist redispersion during the development step.

Ligand with an alkene group can be cross-linked upon the stimuli-induced cleavage of the C=C bonds with the formation of new C–C bonds.^{17–21} Even alkanes can be cross-linked with a highly energetic stimulus such as an electron beam, although this requires a relatively high dose.⁸ More recently, more sensitive functional groups, such as bisazides, diazarines, and benzophenone derivatives, have been used to efficiently form cross-links between organic ligands.^{23–28} These ligands form reactive radical species upon application of light or heat, which initiate the formation of new covalent bonds.

Decomposition

The stimuli-induced decomposition of ligands is another way to modulate the dispersibility of NCs. During this process, the stimulus causes the ligands to decompose into two or more fragments, leading to two effects: (1) reducing the interparticle spacing between NCs and (2) forming new chemical species that changes the charge/polarity of the NC surface. For sterically stabilized NCs, the decomposition of oxime sulfonate,⁴² ammonium carbamate,⁴ and *tert*-butoxycarbonyl-

(BOC)-protected amines^{4,31–33} ligands significantly reduces the dispersibility of NCs in nonpolar solvents. This is due to the formation of smaller and more polar ligand fragments (e.g., an amine group) on the NC surface. In some cases, the decomposition of the bound ligands (e.g., ligands with a BOC group) is a secondary process that is initiated by an acid produced from a photoacid generator.^{31,32,34} In another demonstration, the photodecomposition of an *ortho*-nitrobenzyl ester led to a charge reversal that modulated the NC dispersibility.³⁵

For electrostatically stabilized NCs, our group discovered several classes of sulfur-based ligands that can directly stabilize semiconductor/metallic NCs but decompose under light irradiation.^{1,2} This includes the chemical families of thiocarbamate, xanthate, azole, and dithiooxalate ligands, with each ligand having different wavelengths of sensitivity as well as decomposition products. In all cases, these decomposition products are no longer able to stabilize the NCs electrostatically. For example, the ammonium 1,2,3,4-thiatriazole-5-thiolate ligand decomposes into thiocyanate, which only weakly binds to the NC surface. Another study found that the thiostannate ligand ($\text{Sn}_2\text{S}_6^{4-}$) bound to NCs can decompose into SnS_2 , thus reducing the NC dispersibility in polar solvents.³⁷

Ligand Exchange

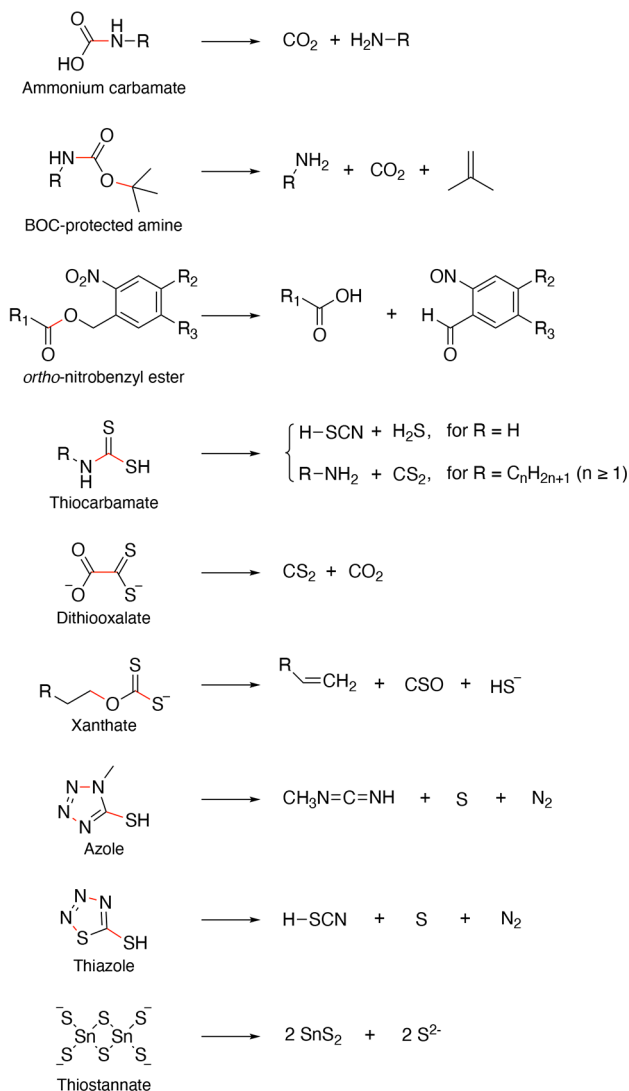
The dispersibility of a sterically stabilized NCs can also be reduced through an *in situ* ligand exchange via stimuli-induced decomposition of an additive, which produces a reactive species that interacts with existing surface ligands. For example, photoacid generators such as 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine or triphenyl aryl sulfonium triflate produce hydrochloric or triflic acid upon photoirradiation which replaces the oleate, oleylamine, or methacrylate ligands on the NC surface, rendering the NCs more hydrophilic.^{1,3,38} If a nonpolar developer solvent is used, only the NCs that have undergone the ligand exchange will remain on the substrate. On the other hand, a polar solvent such as *N*-methyl formamide can be used as a developer to wash away the hydrophilic NCs, resulting in the opposite pattern tone.

Ligand Desorption

A stimulus can also reduce the NC dispersibility via a ligand desorption mechanism. For instance, methacrylate ligands bound to metal oxide NCs were found to detach upon illumination, resulting in NC aggregation.³⁹ Recently, the 3D printing of NCs was achieved using a two-photon lithography

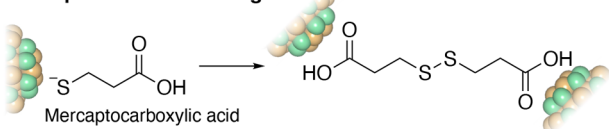
Scheme 3. Chemical Transformation of Some Stimuli-Responsive NC Ligands That Decompose

Decomposition



acts as a loosely associated counterion that photodecomposes into a carboxylic acid which neutralizes positively charged NCs.⁴² Similarly, protons that are realized by photoacid generators can bind and neutralize negatively charged NCs.^{1,2} Recently, photobase generators (PBGs) have been used to pattern semiconductor NCs. Upon light exposure, these PBGs release amines that bind to the surface of the NCs, changing their polarity and reducing the NC dispersibility in DMF.

Desorption + cross-linking

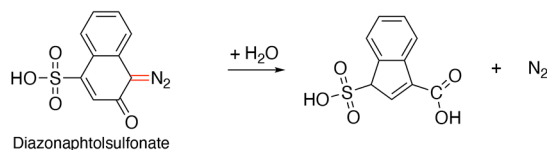
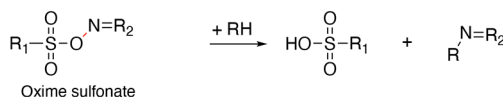
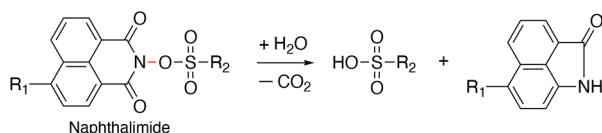
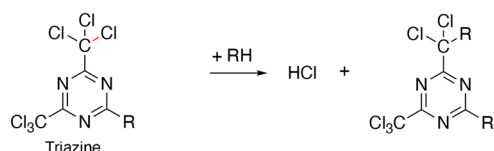
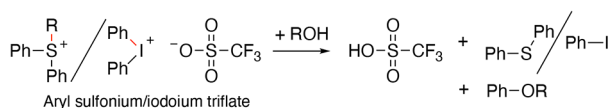


process that involves the photo-oxidation and desorption of mercapto-propionic acid from the NC surface.⁴⁰ This resulted in newly exposed surface sites that enabled cross-linking of NCs through the binding of carboxylate groups to these sites. In our group, we also recently found that the photoinduced surface oxidation of “bare” semiconductor nanocrystals leads to the desorption of surface DMF ligands, leading to reduction in dispersibility.⁴¹

Another method to modulate the dispersibility of electrostatically charged NCs is by changing the ionic strength of its environment. A stimuli-induced increase in the local ionic strength reduces the electrostatic repulsion screening length, κ^{-1} , leading to the selective deposition of NCs. For example, nonionic photoacid generators, such as *N*-hydroxynaphthalimide triflate, are neutral molecules that decompose upon irradiation by light, forming charged ions. The ions screen the electrostatic double layer repulsion between NCs, preventing them from being redispersed during the development step.

Scheme 4. Chemical Transformation of Some Photoacid Generators (PAGs) and Photobase Generators (PBGs) Used for Patterning NCs

Photoacid generators (PAGs)



Photobase generators (PBGs)

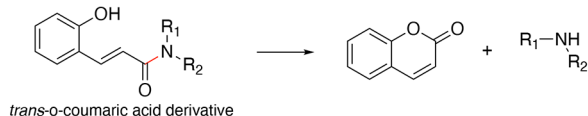


Table 1. Ligands for Patterning Sterically Stabilized NCs Dispersible in Nonpolar Solvents

Patterning mechanism	Ligand family	Stimulus	References
Cross-linking	Alkene	360 nm, 225 nm, 13.5 nm (EUV), e-beam	7,17–22
	Alkane	E-beam	8
	Bisazide	254 nm, 365 nm, heat	23–28
	Diazarine	254 nm	26
	Benzophenone derivatives	254 nm, 365 nm	29
Decomposition	Oxime sulfonate	365 nm, 405 nm	30
	Ammonium carbamate	Heat	4
	BOC-protected amine	Heat, 254 nm (with PAG)	4, 31–34
	ortho-nitrobenzyl ester	365 nm	35
Ligand exchange	Photoacid generator (PAG)	EUV, 254 nm, 365 nm, 405 nm	1, 3, 36

DESIGN OF STIMULI-SELECTIVE LIGANDS FOR NC PATTERNING

In the previous section, we outlined the different mechanisms that have been used for the direct patterning of NCs.

Table 2. Ligands for Patterning Electrostatically Stabilized NCs Dispersible in Polar Solvents

Patterning mechanism	Ligand family	Stimulus	References
Cross-linking	1,3,4-thiadiazole-2,5-dithiol	365 nm	2
Decomposition	Thiocarbamate	254 nm	2
	Xanthate	254 nm	2
	Azole/Thiazole	254 nm, 365 nm	1, 2
	Dithiooxalate	254 nm, 365 nm	2
	Thiostannate	365 nm	37
Ligand exchange	Photoacid generator (PAG)	13.5 nm, 254 nm	38
Ligand desorption	Methacrylate	254 nm, 13.5 nm	39
	Mercaptocarboxylic acid	780 nm (two-photon)	40
Ion/ligand binding	Dimethylformamide ("bare NCs")	254 nm, 365 nm, 405 nm	41
	Diazonaphthosulfonic acid	365 nm, 405 nm	2, 42
	Aryl sulfonium/iodonium triflate	254 nm, e-beam	1, 2
	Photobase generator (PBG)	254 nm	43
Increased ionic strength	Nonionic PAG	254 nm, 365 nm, 405 nm	2

Understanding these mechanisms provides an underlying chemical picture of how these ligands work, which can guide further optimization and exploration of other stimuli-sensitive ligands. However, the development of stimuli-sensitive ligands is often guided by more practical reasons: how can one obtain high quality patterns of specific NCs of interest using a particular stimulus?

The type of stimuli to be used is an important consideration when choosing and developing a stimuli-sensitive ligand. The stimulus used has a big influence on the quality of the patterns, the accessibility of the patterning technique, and the fabrication cost.

A widely used stimulus for lithography is electromagnetic radiation such as UV or visible light. We call this process of patterning NCs with light as Direct Optical Lithography of Functional Inorganic Nanomaterials, or DOLFIN. Ligands that were sensitive to deep UV (254 nm) were the first types of ligands that we explored, mostly due to their commercial availability or ease of synthesis, including photoacid generators and small thiol-based ligands.¹ These ligands allowed the first proof-of-concept for patterning high-quality, functional inorganic NCs (Figure 2A).

We soon realized the need to develop ligands photosensitive at longer wavelengths of light (such as near-UV or blue light) for several important reasons including: (1) the exposure sources (e.g., LED lamps, direct laser writers) at these wavelengths are much less expensive compared to the exposure tools using 254 nm photons; (2) deep UV photons can be more damaging to some NCs compared to the lower energy photons; (3) lower energy photons can penetrate deeper into the NC films and are preferred for patterning thick NC layers. However, the sensitivity to longer wavelength photons typically requires the ligand or additive to have increased molecular conjugation and structural complexity, which limit the number of commercially available options. Still, several chemical compounds including diazonaphthosulfonic acids,^{2,42} oxime sulfonates,^{2,30} and 2-(4-methoxystyryl)-4,6-bis-(trichloromethyl)-1,3,5-triazine³ were successfully used to

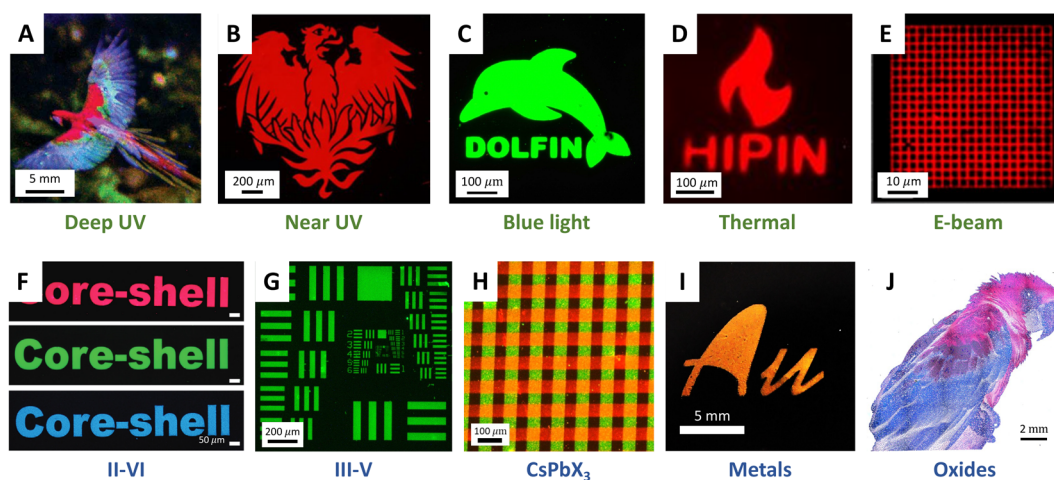


Figure 2. Optical and fluorescent images showing the direct patterning of various types of NCs using a range of stimuli. (A) A multicolored image made by patterning CdSe/ZnS, InP/ZnS, and ZnSe/ZnS NCs with deep UV (254 nm) light. (B) A pattern made of CdSe/ZnS using near-UV (365 nm) light. (C) Patterned CsPbBr₃ NCs with blue (405 nm) light. (D) Patterns of InP/ZnS NCs made by thermal lithography using a 532 nm pulsed laser. (E) CdSe/ZnS NCs patterned with an electron beam. (F–J) Patterns made from the direct patterning of CdSe core-shell NCs (F), InP/ZnS NCs (G), CsPbBr₃ and CsPbBr_{3-x}I_x NCs (H), gold NCs (I), and ZrO₂ nanoparticles (J). (A, I) Adapted with permission from ref 1. Copyright 2017 AAAS. (B, E) Adapted with permission from ref 2. Copyright 2019 American Chemical Society. (C, H) Adapted with permission from ref 30. Copyright 2021 American Chemical Society. (D) Adapted with permission from ref 4. Copyright 2022 American Chemical Society. (F) Adapted with permission from ref 3. Copyright 2020 Wiley. (J) Adapted with permission from ref 42. Copyright 2021 American Chemical Society.

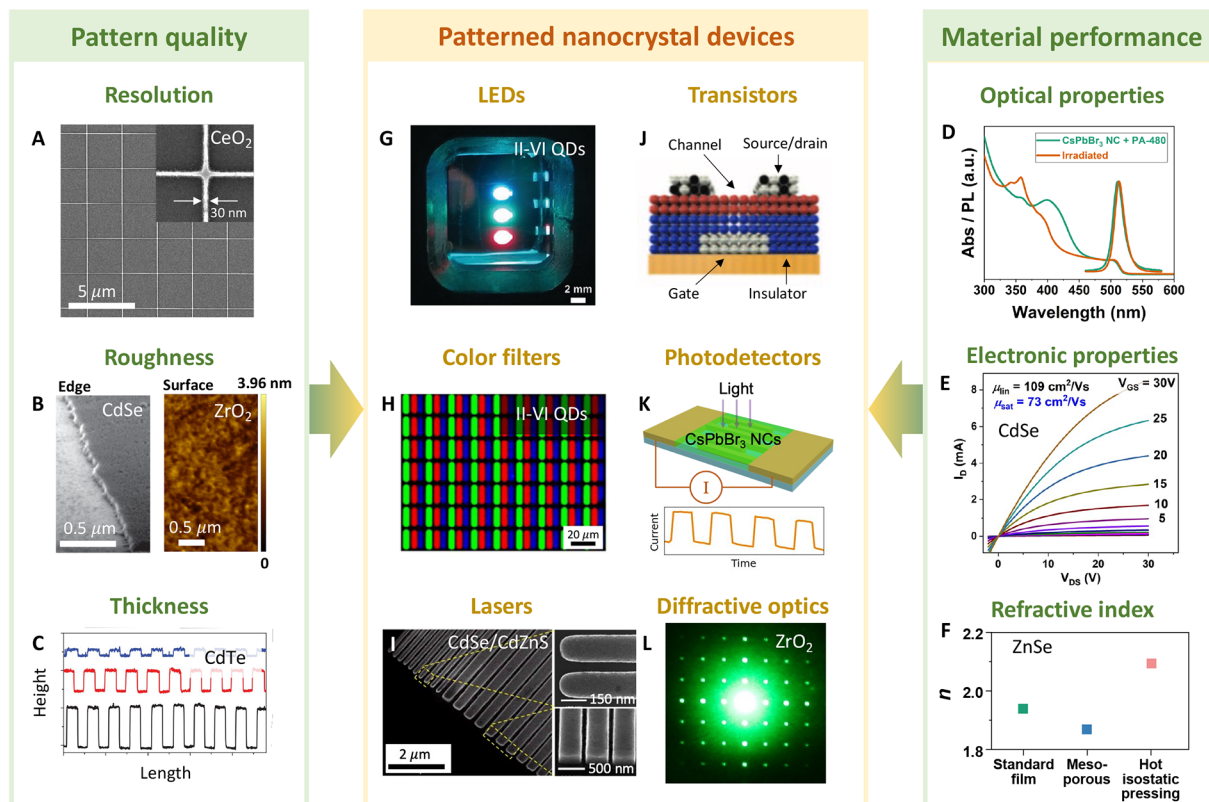


Figure 3. Figures of merits for the NC pattern quality (A–C), material performance (D–F), and their implementation in patterned NC devices (G–L). (A) Adapted with permission from ref 2. Copyright 2019 American Chemical Society. (B-left, C, E) Adapted with permission from ref 1. Copyright 2017 AAAS. (B-right, L) Adapted with permission from ref 42. Copyright 2021 American Chemical Society. (D) Adapted with permission from ref 30. Copyright 2021 American Chemical Society. (F) Adapted with permission from ref 41. Copyright 2022 American Chemical Society. (G) Adapted with permission from ref 3. Copyright 2020 Wiley. (H) Adapted with permission from ref 25. Copyright 2020 The Authors. CC BY 4.0. (I) Adapted with permission from ref 46. Copyright 2021 American Chemical Society. (J) Adapted with permission from ref 47. Copyright 2016 AAAS. (K) Adapted with permission from ref 30. Copyright 2021 American Chemical Society.

pattern various NCs with 365 or 405 nm light (Figure 2B and C). Based on similar motivations, other groups have recently developed highly conjugated cross-linkable ligands that enable NCs with organic hydrocarbon ligands to be patterned efficiently with near-UV light.²⁹

We also did some preliminary exploration of ligands that are sensitive to electron beam irradiation. This process, which we call Direct Electron-beam Lithography of Functional Inorganic Nanomaterials (DELFIN), uses an electron beam to interact and reduce the dispersibility of NCs. One ligand family which worked well for DELFIN was the aryl sulfonium/iodonium triflate ligands, which decompose to release an acid upon an exposure to electron beam (Figure 2E).² We note that many of the other ligand families listed in Tables 1 and 2 may also be sensitive to an electron beam and have not been fully explored in this regard.

Recently, we and the others started exploring the use of heat to directly pattern NCs, which we called the Heat-Induced Patterning of Inorganic Nanomaterials (HIPIN).^{4,24} Although thermal patterning approaches are less developed compared to the photo- and electron-based methods, there are several potential advantages in using heat for patterning. For instance, thermal patterning is not diffraction-limited and has been used to pattern sub-100 nm features with visible light or a heated AFM tip.^{44,45} Also, this method can be used to pattern much thicker (>10 μm) films of NCs since the NCs are usually transparent to the infrared light used for heating.²⁴ Finally, the use of heat as a stimulus could be less invasive than UV-light, which reduces the damage to the NCs. While excessive heat could lead to alloying and grain growth of NCs, this can be minimized by choosing thermally sensitive ligands that react at relatively low temperatures (<200 $^{\circ}\text{C}$), and by using short durations of heating time (e.g., using a ns-pulsed laser).^{4,24}

With these stimuli-sensitive ligands, we have demonstrated the patterning of a variety of NCs including II–VI and III–V quantum dots (QDs), lead halide perovskite NCs, metal NCs, metal oxide nanoparticles (Figure 2F–J). The stimuli-sensitive ligand needs to be catered to each type of NC due to differences in the NC surface chemistry. For instance, ligands with thiol binding groups are suitable for patterning II–VI and III–V QDs and gold NCs but will not bind to metal oxide NCs and will typically decompose lead halide perovskite NCs.

FIGURES OF MERIT

Each stimuli-sensitive ligand can also be evaluated in terms of the quality of the resulting patterned NC film. There are two categories of figures of merit that can be used in this evaluation. First, the quality of the NC patterns can be evaluated and compared through the pattern resolution, exposure dose, edge/surface roughness, and thickness (Figure 3, left panel). At the same time, the material characteristics of the patterned NC film, such as the absorbance, luminescence, refractive index, and charge carrier mobility are the equally important figures of merit (Figure 3, right panel). Both the pattern quality and NC properties should be considered when fabricating a particular patterned NC device (Figure 3, middle panel).

Resolution

The resolution achievable in patterning NCs is affected by both physical and chemical factors. A key physical factor that limits the resolution is the type of stimulus used (and secondarily, the lithography tool). Optical lithography is

fundamentally diffraction limited and hence is ultimately tied to the wavelength and numerical aperture of projection system. In many nanofabrication research cleanrooms, direct laser writers or light projection sources using near-UV (365 nm) or blue light (405 nm) are typically limited to a resolution of about 500 nm. Using deep UV (254 nm) sources can typically push the resolution to a few hundred nanometers, while extreme-UV (EUV, 13.5 nm) sources can be used to pattern features down to tens of nanometers or less. Electron-beam lithography has a much smaller resolution limit due to the shorter wavelength of electrons, with tens of nanometers easily achievable.² The resolution attainable via thermal lithography depends significantly on the method used to provide heat. A pulsed 532 nm laser that directly heats absorbing NCs can achieve submicron resolution.⁴ Using a thermal scanning probe lithography setup can further push the pattern resolution to tens of nanometers but has yet to be demonstrated for patterning NCs.

The resolution may also depend on the dispersibility contrast, which is how steep the dispersibility of the film changes near the required exposure dose. For a well-behaving NC photoresist, we have found that a reasonable dispersibility contrast (enough to pattern 10 μm -sized features) can usually be obtained after a rough optimization of the photosensitive ligand fraction (usually 1–25 wt % relative to the NCs) and the exposure dose. We have generally found that the patterning mechanism (and its effect on contrast) only begins to have a significant impact when trying to achieve a resolution <5 μm .

Edge and Surface Roughness

There are two types of roughness metrics related to the NC patterning: edge roughness and surface roughness. Both edge and surface roughness of NC pattern are, at best, limited by the physical size of the individual NCs, which is on the order of a few nanometers. However, the edge roughness is often found to be tens or hundreds of nanometers, which can be due to NCs aggregating to form larger domains that redisperse or remain deposited as collective units. This can be mitigated by ensuring a well-passivated and well-separated NC surface which minimizes any irreversible aggregation during the NC film formation. However, one needs to consider trade-offs between the NC–NC separation, the density of patterned NC layer, and the efficiency of charge and heat transport between NCs. On the other hand, surface roughness depends on the drying forces during deposition, which can be controlled using the type of solvent, deposition method, and additives.

Thickness

Controlling the thickness of the NC pattern is important for several applications. For instance, a thicker QD film would have a larger absorbance that enables more efficient color conversion. In contrast, the NC film should not be too thick for some device applications such as LEDs due to limitations in charge transport. The thickness of a spin-coated NC film can be controlled through several parameters such as the NC concentration and deposition speed. However, there is a maximum thickness (usually a few hundred nanometers), above which the spin-coating of thicker films becomes much more challenging, due to the formation of cracks.⁴⁸ This effect can be reduced by the addition of plasticizers or avoided by using a different deposition technique such as doctor-blading.

Another limiting factor in patterning thick films of highly absorbing NCs is the ability of the stimulus (light, electron beam, or heat) to penetrate all the way through the thickness

of the NC layer. For photolithography, this penetration depth can be extended using longer wavelengths photons that have a weaker absorption by NCs.

Optical Properties

Luminescent QDs are actively explored for optoelectronic device applications due to their unique optical properties. Ideally, the absorption and emission spectra of the QDs should be preserved after the patterning process, with no significant changes of the absorption and emission spectra. This would mean that the QDs have not been damaged during this process. Retaining a high photoluminescence quantum yield (PLQY) is also highly desirable, although some drop in the PLQY is usually noted for most direct patterning approaches.^{3,4,26} One approach that retained high PLQY for II–VI QDs used a small fraction of stimuli-sensitive ligands combined with a larger fraction of traditional ligands providing colloidal stability, while applying a minimal dose of lower energy light (365 nm instead of 254 nm).²⁹ For lead halide perovskite NCs, the drop in PLQY is more pronounced due to their chemical fragility. However, a postpatterning surface treatment was found to be an effective way to heal the surface and increase the PLQY for these NCs.^{23,30}

The ability to directly pattern NCs while preserving their optical properties enabled the fabrication of color conversion filters, light emitting diodes (LEDs), and microlasers. For example, patterning green and red-emitting QDs directly at the desired position of green or red pixels improves the efficiency of color conversion QD films. A next-generation QD display technology is expected to utilize the electroluminescent QDs in the form of QD LEDs with individually electrically addressable red, green, and blue pixels made with corresponding QDs patterned as part of the device stack. Proof-of-concept devices have already been demonstrated in several reports.^{3,23,29} Patterned NCs are also explored in micro lasers. In a recent report, distributed Bragg reflector QD laser was made by patterning colloidal CdSe/ZnS nanoplatelets as strips with appropriate spacings.⁴⁹

Electronic Properties

Optimizing the electronic properties of the patterned NC film is important for all NC devices that require charge injection or extraction. Often small inorganic or organic ligands are required for reducing the spacing between NCs, facilitating charge transport in the devices.⁵⁰

We have demonstrated the ability to pattern CdSe NCs (capped with metal chalcogenide complexes) that show high electron mobility ($>100 \text{ cm}^2/(\text{V s})$).¹ We also showed patterning of indium gallium zinc oxide (IGZO) for transparent transistors, as well as the patterning of Al_2O_3 NCs for dielectric components of electronic circuits. The solution processability, good electronic properties, and facile patternability should allow these NCs to be used in devices that are complementary to traditional silicon electronics, e.g., large-area flexible substrates.

Photodetectors are yet another class of devices that benefit from the multiplexing capabilities afforded by NC patterning. For instance, the direct patterning of arrays of various QDs with different absorption wavelengths was used to fabricate skin-like, ultraflexible photodetector arrays for bioimaging applications.³⁷ In our group, we showed that patterned CsPbBr_3 NCs can be used as photodetectors, demonstrating good electronic communication between the NCs.³⁰ For efficient light detection, the photoexcited charges need to be

extracted before recombination occurs. This is aided by ligands that are short (allowing for faster charge transport) while also passivating the dangling bonds at NC surface to reduce surface recombination.

Inorganic Fraction

The inorganic fraction (or the packing fraction) of a NC film is the volumetric ratio of the inorganic NC content to other components present (e.g., organic ligands, air, additives, solvent). The inorganic fraction of a NC film is typically higher for electrostatically stabilized NCs compared to NCs that are stabilized by bulkier long-chain organic ligands. A high inorganic fraction of NCs is often desirable since it increases the film extinction coefficient and refractive index, allowing for stronger light absorption and other forms of light-matter interaction. High inorganic fraction also enables higher conductivity and charge mobility. However, there is also a trade-off since increasing the inorganic fraction beyond reasonable level can create surface dangling bonds that trap charge carriers and severely limit carrier lifetimes in semiconductor NC layers.

We have demonstrated the patterning of densely packed NC films with high refractive index. By adding a small fraction of photosensitive ligands to “bare”, ligand-free metal oxide nanoparticles, we fabricated patterned transparent ZrO_2 thin films with refractive indices up to 1.88 (at 633 nm) after a thermal annealing step.⁴² Recently, we also showed that bare, absorbing NCs such as ZnSe and ZnS NCs can be patterned directly without having to add any other photosensitive component.⁴¹ After subjecting the films to a hot isostatic pressing (HIP), a refractive index of up to 2.22 (at 633 nm) was obtained which corresponded to a packing fraction of 0.87. On the other hand, the addition of block copolymer micelles enabled the fabrication of NC patterns with lower inorganic fractions and increased porosity, thus allowing patterning of low- k dielectric components valuable for high-frequency electronic components and antireflective coatings.

Devices that benefit from the optimization of the inorganic fraction include diffractive optical elements, waveguides, and nanophotonic modules. For instance, we demonstrated the 2π phase control of patterned ZrO_2 NC films through a thickness of $1 \mu\text{m}$ and refractive index of 1.61.⁴² Using this platform, we also fabricated and tested a NC diffraction grating that efficiently channeled light into first order diffraction spots.

OUTLOOK

The direct patterning of NCs with stimuli-sensitive ligands continues to be an interesting and rapidly developing area of research as it utilizes fundamental colloidal science to address a very practical need. From a chemical perspective, current findings have only scratched the surface in terms of the diversity of ligands that can be used for direct NC patterning. Many of currently used stimuli-sensitive ligands have been identified due to their commercial availability or ease of synthesis. Future development of stimuli-sensitive ligands would build upon these established ligand families and involve more careful chemical design with specific targets in terms of stimulus, NC type, and pattern properties, followed by custom ligand synthesis.

At the same time, there is room for progress in improving both the pattern quality and material performance of patterned NCs, as well as pursuing new device applications that benefit from NC patterning. For instance, continuous progress is being

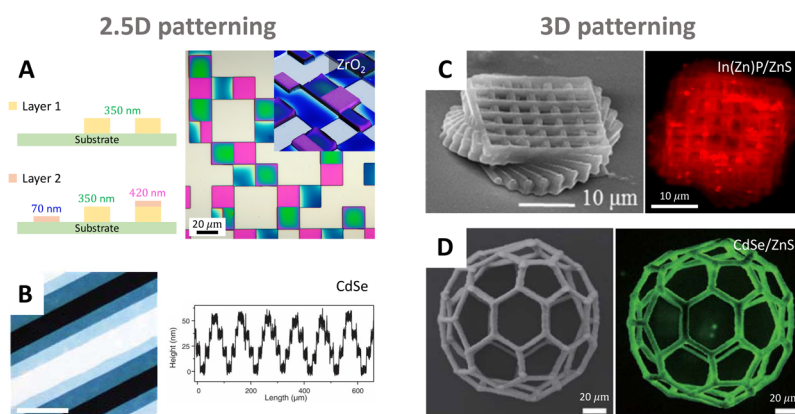


Figure 4. Patterning of NCs beyond two-dimensions (2D). The examples include 2.5D (A, B) and 3D patterning (C, D). (A) Adapted with permission from ref 42. Copyright 2021 American Chemical Society. (B) Adapted with permission from ref 1. Copyright 2017 AAAS. (C) Adapted with permission from ref 21. Copyright 2017 The Optical Society. (D) Adapted with permission from ref 40. Copyright 2022 AAAS.

made in developing stimuli-sensitive ligands that retain the high PLQY of QDs. Pushing the pattern resolution down to tens of nanometers also opens the possibility of integrating NCs with high refractive index into more complex nanophotonic devices such as metasurfaces.

Another exciting area of development is in extending the direct patterning of NCs beyond two-dimensions. One form of this is 2.5D patterning, which involves some degree of thickness control through multiple iterations of 2D patterning (Figure 4A and B). This can allow, for instance, patterning of colored pixels due to thin-film interference.⁴² Ultimately, direct 3D printing of NCs can be approached through two photon lithography or stereolithography. The two-photon lithography of luminescent QDs has been investigated as early as a decade ago, but most early attempts involved mixing the NCs with organic monomers that polymerized during the patterning process (Figure 4C).^{17,21,51} This not only dilutes the inorganic content but often results in nonuniform dispersion of NCs within the patterned structure. Recently, a new approach to 3D patterning NCs was realized with light-sensitive ligands that desorbed from NC surface in the focal point of a 780 nm femtosecond laser, followed by chemical bonding between the NCs. This method allowed the fabrication of highly densified and uniform 3D structures of NCs (Figure 4D).⁴⁰

Moving forward, we believe that research in discovering and understanding stimuli-sensitive ligands will enable colloidal NCs to be a unique and versatile chemical platform for both 2D and 3D lithography. For many practical NC devices, the direct optical lithography approach does a good job in balancing resolution, throughput, fidelity, and tool availability/cost. In fact, the photocurability of NC inks can also be used in conjunction with physical patterning techniques for increased robustness and versatility (e.g., photocuring during nanoimprinting). We believe that achieving a true “Lego-like” control of NC assembly requires a synergistic combination of both bottom-up (e.g., ligand design, self-assembly) and top-down approaches (e.g., lithography, printing).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.accounts.3c00226>.

Discussion and figures on DLVO interaction energies for colloidal nanocrystals (PDF)

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Notes

The authors declare the following competing financial interest(s): Dmitri Talapin is a co-founder of Nanopattern Technologies, Inc, a company that is developing photopatternable nanoparticle inks.

Biographies

Jia-Ahn Pan received his Ph.D. at the University of Chicago in 2022 under the guidance of Prof. Dmitri Talapin. He worked on the ligand and surface chemistry of NCs, focusing on the development of stimuli-sensitive ligands for patterning semiconducting and dielectric NCs. He is currently a postdoctoral scholar at the Molecular Foundry, a nanoscience facility at the Lawrence Berkeley National Laboratory, where he is working on lanthanide-doped upconverting nanoparticles.

Himchan Cho received his bachelor's degree (2012) and Ph.D. (2016) from Pohang University of Science and Technology (POSTECH). After working at Seoul National University (2016–2018) and the University of Chicago (2018–2021) as a postdoctoral scholar, he started his independent career at Korea Advanced Institute of Science and Technology (KAIST) as a faculty member in 2021. He has expertise in halide perovskite materials, colloidal quantum dots, organic/inorganic hybrid light-emitting diodes, and solution-processed optoelectronics.

Igor Coropceanu received his PhD at the Massachusetts Institute of Technology in 2016 under the supervision of Prof. Moungi Bawendi, where he worked on the synthesis and spectroscopy of highly luminescent nanostructures. He then worked as a postdoctoral scholar in the group of Dmitri Talapin at The University of Chicago, working on the self-assembly of metallic and semiconducting nanocrystals. He is currently working as a scientist at Nanosys.

Haoqi Wu is a PhD. Candidate at the University of Chicago under the guidance of Prof. Dmitri Talapin. His research interest is on the development of stimuli-sensitive ligands for direct thermal and optical patterning of inorganic nanomaterials. He is also investigating these patterning techniques for the fabrication of next-generation nanocrystal devices.

Dmitri Talapin received his doctorate degree from the University of Hamburg, Germany, in 2002. He joined the IBM Research Division at the T. J. Watson Research Center in 2003 as a postdoctoral fellow and moved to Lawrence Berkeley National Laboratory in 2005 to be a staff scientist at the Molecular Foundry. Since 2007, he has been a professor in the Department of Chemistry, James Franck Institute and Pritzker School of Molecular Engineering at the University of Chicago and scientist at the Center for Nanoscale Materials at Argonne National Laboratory. His research interests focus on different aspects of chemistry, physics, and applications of inorganic nanomaterials.

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