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Bottom-up approach to fabricate nanostructured thin films from colloidal nanocrystal precursors

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Bottom-up approach to fabricate nanostructured thin films from colloidal nanocrystal precursors

by

Santosh Shaw

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

Program of Study Committee:
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The student author and the program of study committee are solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2017

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DEDICATION

I dedicate this dissertation to my parents for their constant support and believing in me, and to my special friend Varsha for always being there with me, without her constant moral support this journey was unimaginable.
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ABSTRACT

Control over microstructures at the nanoscale (<100nm) still seems challenging due to, among other things, the stochastic nature of nucleation in the bulk phase. The densification of assemblies of ligand-capped nanocrystals (colloidal nanocrystal assemblies, CNAs) could bypass this challenge that limits our control over the nanostructure and, therefore, the properties of materials. However, the removal of the ligands and the cracking that follows it are the two critical hurdles that have been stymieing this approach.

We show that low-pressure plasma processing can effectively remove ligands from CNAs (down to 0.6 at.% of carbon which can be accounted for adventitious carbon) without harming the properties of the inorganic cores of the nanoparticles and the structure of CNAs. The cracking of CNAs is correlated with the structure of the CNAs, which can be controlled and easily predicted by Hansen solubility parameters of solvent in which the nanoparticles are dispersed. While a fully solvated ligand shell leads to the formation of close-packed ordered CNAs – which cracked after self-assembly or ligand removal – a partially solvated one results in interdigitation of the ligand shell yielding disordered CNAs, which remained crack-free after ligand removal and sintering up to a critical cracking thickness of 440nm. The process is demonstrated with particles of different compositions, ligands, sizes, shapes, as well as with binary systems. These findings allowed for the fabrication of cm² crack-free, phase-pure polycrystalline films with tunable, near-monodisperse grain sizes using CNAs as precursors. We observed electrical conductivities of PbS films produced by this
approach over 1 cm to be 1.370 S/cm which is comparable to those of bulk crystal. This conductivity value is remarkable considering the fact that the typical porosity in fully processed CNAs is around 40%.

We simultaneously answered the fundamental question that how microstructure of CNAs evolves during ligand removal and studied its effect on microstructure related physical properties, e.g., mechanical properties. We further demonstrated that our bottom-up approach can control the grain boundary composition in the final materials by controlling the chemical structure and composition of the ligands and the characteristics of the plasma. We show that with our unprecedented control on grain boundary composition, we can selectively modify grain growth mechanisms, control phase transitions, and affect mechanical properties. By understanding the interaction of plasma species with CNAs and the mass transport in the system, we were able to accelerate the plasma etching rate by more than an order of magnitude.

Finally, we demonstrate the applicability of our approach in developing an optics-free lithography in which CNAs are used as resist and as an active material. By selectively masking the interaction of plasma with CNAs with a hard mask we could change the solubility of the exposed regions. This patterning technology can pattern materials which are hard to pattern by traditional inorganic etching based pattern transfer (example, copper, gold).
CHAPTER 1

GENERAL INTRODUCTION

This dissertation describes a facile and scalable bottom-up approach to build thin film materials with programmable nanostructure by using colloidal nanocrystals as precursors. While several approaches are available to control microstructure of materials, this work brings an unprecedented control of the nanostructure and hence the materials properties.

**Research Motivation**

Materials by design is the major objective of materials research. While ideal control in designing, materials would lie in our ability to “program” atoms, this atomic-level control might be fundamentally prohibited by the second law of thermodynamics. Our control on designing materials must therefore reach the nanoscale, where absolute control is still conceivable. By programming materials, we mean to independently control (i) grain composition, (ii) grain phase, (iii) grain size and their distribution, (iv) grain shape, (v) composition of grain boundaries, (vi) porosity. For such a level of control to exist, materials manufacturing might have to change. Most current materials manufacturing approaches rely on nucleation in bulk systems (e.g., cooling of melts, reaction of precursors), which is stochastic and yields broad grain-size distributions.

Creating materials with programmable microstructure/nanostructure is highly sought for by material scientist, because it will help us reliably understand the microstructure-property relationship, but also facilitate creating materials with
predictable properties. Few example, we believe that the lack of materials with fully programmable nanostructure and interfaces is precluding us to reliably conclude the long standing debate on the inverse Hall-Petch effect \cite{1}, to create highly efficient thermoelectric materials \cite{2}, to create magnetic materials with well controlled nanodomains in order to increase the storage densities of our magnetic devices \cite{3}.

**Our Approach**

Material scientists in the early 90’s have shown that independently synthesizing the nano-sized particle (“grain”) and consolidating them into a solid could bypass the fundamental limitations of traditional material manufacturing methods, i.e. the stochastic nature of the nucleation process, and can create materials with predictable nanostructure \cite{4}. They were able to build materials through this approach but with significant limitations. Either they were limited in the initial quality of the precursors (e.g., large grain size distribution, amorphous particles), or by technical complications that arise during processing (e.g., cracks or blister formation during binder burnout, several days of firing schedule), or by the reliability of the final product (e.g., composites instead of phase-pure materials, could not retain the nanoscale size of the grains). Numerous methods exist to synthesize nanoparticles: sol-gel, gas-condensation, electrodeposition, colloidal synthesis, plasmas, and more. However, in terms of reproducible synthesis of crystalline, single-phase, and monodisperse size (polydispersity <5%) particles, the colloidal route is usually unparalleled.

Our approach is to combine bottom-up methods and colloidal nanocrystals to build materials with programmable microstructure. Over the past few decades, colloid chemists have developed synthetic methods to create nanoparticle with up to 1Å
resolution in size and a polydispersity in particle size of less than 5%. Typically, the core of the nanoparticles can be controlled extensively in size (between 2 and 100 nm), shape (from spherical, to polygons, to wires, to platelets), composition (from oxides, to chalcogenides, to pnictides, to metals). An example of such homogeneous size and spherically shaped colloids with polydispersity ~3% are shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** a. Cartoon showing colloidal nanoparticles with an organic ligand shell b. TEM image of ~3nm diameter ZrO$_2$ nanocrystals with oleic acid as organic shell

Colloidal nanocrystals are synthesized by wet chemistry in which precursor(s) are reacted in the presence of organic molecules termed ligand. Ligands usually have a long hydrocarbon tail with a reactive head. The head binds to the surface atoms (typically the metal) through coordination that reduces surface energy and helps controlling the growth of the nanoparticle. The hydrocarbon tail keeps the particles dispersed in solvent and prevents aggregation by steric stabilization. These colloids are often termed as “artificial atoms” because of their typically spherical shape and their ability to assemble in ordered arrays. The assembly can be tuned from close-packed structures (face-centered cubic or body-centered cubic or hexagonal close-
packed structure) to random ones (amorphous). Figure 2 provides a broader perspective of our approach where panel a shows periodic arrangement of gold atoms\(^5\), panel b shows state of the art nanostructure produced in bulk copper after sophisticated post processing\(^6\), panel c shows nanostructure of colloidal PbS nanocrystal (~5nm in diameter) assembly\(^7\) fabricated by drop-casting nanocrystals dispersion, and panel d shows core-shell nanoparticles\(^8\), which can be viewed as a way to control the grain boundary composition.
Figure 2. Electron microscopy images of a. gold atoms, b. nanostructured bulk copper, c. colloidal PbS nanocrystal assemblies, d. showing core-shell nanoparticles of Fe$_3$O$_4$@SiO$_2$ in left, and FePt@SiO$_2$ in right.
Bottlenecks in our Approach

The densification of colloidal nanocrystals into all-inorganic solids has been stymied by two main challenges: (1) cracking of CNAs upon deposition from their dispersion or during removal of ligands, and the (2) efficient removal of ligands from colloidal nanocrystal assemblies (CNAs) without leaving residue.

Making uniform films or coatings from particle-based dispersions can be an engineering challenge. Any volume loss – either during solvent evaporation or post-processing, like ligand removal – can lead to cracking of CNAs. Cracks develop when stress generated by volume loss exceeds the weak bonds between the particles. Apart from compromising the uniformity of the material, cracks also compromise the structural integrity, functionality, reliability, and mechanical durability of nanoparticle-based films. Several approaches are available to avoid cracking in CNAs. The self-assembly of nanoparticles can be performed at liquid interfaces\textsuperscript{[9]}, however, their integration to a substrate is challenging and often produce mechanically poor films. Layer-by-layer deposition can increase the critical cracking thickness, or fill in the cracks formed in the underlying layers\textsuperscript{[10, 11]}. Cracks can still occur beneath the surface of the CNA, where they cannot be backfilled. Another approach is to “glue” the nanoparticles together with a secondary phase, which has either limited functionality\textsuperscript{[12]}, limited diversity of compositions\textsuperscript{[13-17]}, or is organic\textsuperscript{[18]}, and, in each case, yields a composite rather than a phase-pure material. So, there is a need of a facile approach to avoid cracking while consolidating colloidal nanocrystals into all-inorganic films.
Ligands constitute the bulk of the volume fraction of the CNAs and therefore strongly affect their properties, especially those associated with transport (e.g., electrical conductivity). The mechanical properties of CNAs are comparable to those of a hard polymer, even when the inorganic core is a hard oxide, whereas colloidal semiconductor nanocrystal assemblies, e.g., PbSe CNAs, behave as electrical insulators\cite{19}. The typical approaches for organic removal involve heating above the decomposition temperature of ligands\cite{19, 20}, chemical ligand stripping\cite{19, 21, 22}, ligand exchange with smaller molecules\cite{19, 22}, and using inorganic ligands instead of organics ones\cite{15}. However, each of the above approaches have drawbacks or limitations. Calcination can lead to carbonization, nanoparticle growth, and the method is substrate-dependent, i.e., it cannot use heat sensitive substrates like plastic. Ligand exchange or ligand stripping methods are solution based, so they rarely remove all the organic fraction and often compromise the structural integrity of the CNAs due to capillary stresses. The limitation of inorganic ligands is that they lead to the formation of composites instead of phase-pure inorganic solids. On the other hand, plasma etching or Nanocrystal Plasma Polymerization (NPP)\cite{13, 23-25} has proven to be an efficient technique in removing ligands from CNAs. NPP employs low-pressure, room temperature, partially ionized plasma to selectively etch the organics fraction from the CNAs. NPP is a “green” (i.e., solvent-less), environmentally friendly process, yields homogenous processing, is compatible with heat sensitive substrates, is highly reproducible, and does not harm or changes significantly the functional inorganic fraction of the nanocrystals film. However, it is not clear how plasma effectively removes organic from CNAs that are several hundreds of nanometers thick. Without
having a mechanistic understanding of ligand etching from CNAs by plasmas, NPP process optimization is not possible.

**Characterization Challenges**

**Chemical characterization of CNAs**

NPP can etch the organic fraction from CNAs. However, to deduce mechanistic understanding of plasma processing of CNAs one must characterize non-destructively the composition of the film as a function of depth. Techniques like X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and Time-of-flight secondary ion mass spectrometry (TOF-SIMS) obtain elemental analysis (within top 5-10nm of the film) along with depth profiling of thin film. However, they measure profile by etching with physical sputtering whose rate depends on density and composition of the film, which are the variables that we need to determine. Other techniques such as Energy Dispersive X-ray Spectroscopy (EDS) or Electron Energy-Loss Spectroscopy (EELS) are also capable to provide depth profile by doing a line scan across the cross-section of the film. However, they have limitations such as low sensitivity, low effective resolution due to the penetration of electrons, and can deposit carbonaceous materials on the sample surface (these deposits will create additional signals which complicate the accurate determination of carbon concentrations). Ion Beam Analysis (IBA) is a set of techniques that can accurately characterize the concentration of elements in a film without damaging the sample. IBA are ion scattering techniques that are non-destructive, standard-less, and allow the quantification of elements with <1 at% detection limit. A distinguishing feature of IBA is that they can measure hydrogen in the film using Elastic Recoil Detection (ERD) mode. The quantitative evaluation from
spectra collected (counts vs energies) from IBA measurements is done through specialized data fitting software like SIMNRA, MultiSIMNRA, RUMP, or DataFurnace. IBA provides directly accurate areal concentration values - expressed as atom/cm² - without making any assumption about the structure of the material. These concentrations can be used to determine the atomic density, \( N \) (atom/cm³) and then converted to mass density, \( \rho \) (gm/cm³) of a film as follows:

\[
N = \frac{\text{areal concentration (atom/cm²)}}{\text{thickness (cm)}}
\]

where, thicknesses were determined by cross-sectional SEM images of the films

\[
\rho = \frac{\sum N_i \times A_i}{N_{\text{avogadro}}}
\]

where, \( A_i \) = atomic weight of each element.

**Nanoindentation of thin films**

Nanoindentation or instrumented indentation is a technique that can measure mechanical properties of small volumes of materials. The distinguishing feature of nanoindentation is the indirect measurement of contact area created by the indenter into the specimen. In conventional indentation methods, contact area is calculated from direct measurement of residual area after the load has been removed. In nanoindentation, contact area is calculated from penetration depth of indenter into the specimen along with known geometry of the indenter.

While indenting thin films, the substrate influences the mechanical response of the film. Usually sharp, three-sided Berkovich pyramidal indenters are used due to their fast transition from elastic to plastic deformation of the film before the influence of substrate begins. This helps to create fully developed plastic zones within tens of
nanometers below the surface of the film. At fully developed plastic zones, the mean contact pressure is equal to hardness, which can be observed by a plateau region in the hardness profile with indentation depth. However, sharp indenters compromise the modulus measurement. Stress concentration at the tip of a sharp indenter is such that strain field developed in the film is strongly influenced by the substrate.

If the film is thick enough, i.e., $>1\mu$m, then the Oliver and Pharr\cite{26} analysis will be sufficient to extract the film properties while reporting the data from the top 10% of the film thickness (rule of thumb). If the film is thinner, then analytic models are applied to extract intrinsic modulus of the film from the composite data. Hay’s model\cite{27} to extract substrate-independent modulus is a most versatile model: it works for both compliant films on stiff substrates and stiff films on compliant substrates over the domain $0.1 < E_{\text{film}}/E_{\text{substrate}} < 10$. In addition to the above benefits, the model can accurately provide elastic modulus of film until 40% of film thickness, which opens the door to reliable mechanical information to be extracted from films as thin as $\sim 50\text{nm}$.

**Dissertation Organization**

The chapters are organized sequentially, displaying how we can program the materials with our approach, how the microstructure and its related properties evolve with plasma processing, how plasmas interact with colloidal nanocrystal assemblies, and finally the impact of our approach from the point of view of application. In chapter 2 we show the success of our approach in creating polycrystalline materials with predictable nanostructure using colloidal nanocrystals as precursors. We avoided cracking in CNAs during deposition of colloidal nanocrystals on a substrate, during ligand etching and during sintering. This approach appears to be general in nature i.e.
it is applicable to nanoparticles with different composition, shape, and size and even applicable to multicomponent nanocrystals system. This chapter shows that we can control the following microstructural features with our approach: (i) grain size, (ii) grain shape, (iii) grain composition. In chapter 3, we show that a slight modification of our approach can help controlling the grain boundary composition of the particles. We then demonstrated the role of interface composition on the grain growth mechanism and physical properties. Chapter 4 answers the fundamental question of how the microstructure of CNAs evolve during ligand removal and hence its mechanical properties. In chapter 5 we studied the interaction of different plasma species with CNAs, the kinetic of etching and demonstrate how to substantially accelerate etching. Chapter 6 describes an application of our approach. We describe here our ability to form crack-free CNAs and plasma etching to develop an optics-free lithography in which CNAs are used as resist or as an active material.
CHAPTER 2

BUILDING MATERIALS FROM COLLOIDAL NANOCRYSTAL ARRAYS: PREVENTING CRACK FORMATION DURING LIGAND REMOVAL BY CONTROLLING STRUCTURE AND SOLVATION

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Abstract

We report here that cracking of assemblies of ligand-capped colloidal nanocrystal during ligand removal (down to 0.6 at.% of carbon through plasma processing\textsuperscript{[13]}) is correlated with their structure: while close-packed and ordered colloidal nanocrystal assemblies (CNAs) cracked, disordered CNAs up to 440-nm-thick remained free of cracks after ligand removal and sintering. The process is demonstrated with particles of different composition, ligands, size, and shape, as well as with binary systems. The structure of the CNA can be predicted by the Hansen solubility parameter $\delta_P$ of the solvent associated with polar interactions: a narrow range of $\delta_P$ values leads to ordered CNAs. We explain this finding in terms of solvation of a
supersaturated and polarized ligand shell. Better solvation minimizes interdigitation, increases the repulsion between particles, and favors ordering. These findings allowed for the fabrication of cm² crack-free phase-pure polycrystalline films with tunable, near-monodisperse grain sizes using CNAs as precursors. Films produced by this approach have conductivities comparable to those of bulk crystals over more than 1 cm (1.370 S/cm for PbS films).

**Main Text**

Limitations in the control over the nanostructure of solid state materials are slowing or preventing our understanding of structure-property relationships and the development of new materials by design.\[28, 29\] Bottom-up approaches in materials manufacturing could provide such level of control\[4\] (e.g., the densification of CNAs\[17, 23, 24, 30, 31\]), but are stymied by an often unrecognized and yet critical limitation: the cracking that occurs during the densification of the building blocks into a solid state material.\[31-33\] These cracks introduce extended defects that compromise the performance and reproducibility of devices.\[11, 34\]

The inorganic phase occupies a small volume fraction of a typical CNA (e.g., 5-6 vol% of the bulk phase for 1.6 nm particles, capped with oleic acid, and packed as a random close-packed array) because of the ligands separating the particles. The compaction that occurs during the drying of CNAs from residual solvent (during self-assembly) and then during the removal of ligands to form into all-inorganic nanocrystalline polycrystals causes stresses that can overcome the weak forces that hold colloidal nanocrystals together\[35-37\] and cause cracking.\[11, 38, 39\]
Several approaches have been developed to avoid cracking in CNAs. Their deposition can be performed at liquid interfaces, to avoid pinning to the substrate,\textsuperscript{[9]} or in a layer-by-layer fashion, to increase the critical cracking thickness (CCT) or fill in the cracks formed in the underlying layers\textsuperscript{[10, 11, 39]} (cracks can still occur beneath the surface of the CNA where they cannot be backfilled). Another approach is to “glue” the nanoparticles together with a secondary phase, which has either limited functionality,\textsuperscript{[12]} limited diversity of compositions,\textsuperscript{[13-15, 17, 40]} or is organic,\textsuperscript{[18, 33]} and, in each case, yields a composite rather than a phase-pure material.
We find that the structure of the CNAs correlates with its ability to tolerate volume loss and hence avoid cracking. The films shown in Fig. 1 were obtained by spin-coating thoroughly purified dispersions of nanoparticles (Fig. 1a, phase = non-monoclinic ZrO$_2$, diameter = 3.7 ± 0.3 nm, ligand = trioctylphosphine oxide (TOPO), concentration = 114 mg/ml) in toluene (Fig. 1b) and hexane (Fig. 1e) on silicon substrates. Scanning electron microscopy (SEM) of the CNAs self-assembled from a toluene dispersion (~350 nm thick) revealed domains, cracks, and noticeable roughness (29.3 nm RMS, Fig. S1). The most discernible cracks and thickness inhomogeneities lay at the boundaries between domains. The small-angle diffraction of X-rays showed the CNAs to be ordered (Fig. S3). The removal of the ligands from the CNA with O$_2$ plasma (carbon concentration [C] dropped from 23.9 at.% to 3.9 at.%, Fig. S5) further cracked the film between and within the domains (Fig. 1c and Fig. S4). The CNAs remained ordered despite shrinking by ~15% perpendicularly to the substrate (Fig. S4 shows hexagonal symmetry consistent with an fcc structure). Sintering (700 °C, 24 hrs) further shrank and cracked the film and increased the Scherrer grain size from 3.53 nm to 4.62 nm (Fig. 1d and Fig. S7)
By comparison, the CNAs obtained from a hexane dispersion revealed no evidence of domains, cracks, or roughness (1.0 nm RMS, Fig. S2). The structure of the CNAs was disordered (see Fig. S3). Remarkably, as shown in Figs. 1f and 1g, the films did not crack even after removal of the ligands ([C] decreased from 21.7 at.% to 4.1 at.% - see Fig. S4 and S6 – longer processing can reduce [C] to 0.6 at% without causing cracking[42]) and sintering (700 °C, 24 hrs), leading to a total vertical shrinkage as large as ~40%. The result of the process is a crack-free, phase-pure material whose microstructure (Fig. 1h) – i.e., the size, size distribution, and shape of the grains – is “encoded” in the building blocks, thereby circumventing the limited control over nucleation sites in traditional material processing that causes broad grain size distributions and uneven grain shapes.

The formation of cracks in ordered close-packed films can be tentatively attributed to accelerated ligand etching at the domain boundaries that could facilitate crack nucleation similarly to stress corrosion cracking.[43]. Ligands are more rapidly removed from ordered CNAs than from disordered ones in spite of their theoretically higher packing density (Figs. S5 and S6). This counterintuitive result can be explained if the boundaries between domains, due to their lower density, are subjected to faster ligand etching.

The formation of cracks during material fabrication process is affected by several interdependent variables, e.g., the entity, kinetics, homogeneity of volume loss, and the thickness of the film. Fig. 2a shows how cracking depends on the hexane/toluene ratio of the dispersion and, therefore, on the order of the film (see also Fig. S3). The diagram in Fig. 2b shows how CNAs crack as a function of their
thickness, order, and extent of compaction. Analysis of the data concluded that (i) removing the ligands cracked all close-packed ordered CNAs, (ii) the critical cracking thickness (CCT) – the maximum thickness a film can be produced without cracking – increased with the disorder of the CNA (see also Fig. S3), and (iii) the CCT decreased with increased densification for all CNAs (solid line versus dashed line in Fig. 2b). Films as thick as ~70 particle layers were obtained free of cracks after sintering at 700 °C for 24 hrs (thicker films can be obtained easily by layer-by-layer processing – see Fig. S8).

Since the structure of the CNA determines their resilience to cracking, it is important to understand what parameters govern the assembly of different CNA structures during spin-coating. Typically, the formation of ordered structures by self-assembly is affected by the geometry of the building blocks (e.g., shape, polydispersity, presence of impurities\(^{[44]}\)), kinetics\(^{[45]}\) (e.g., growth rate\(^{[46]}\)), and the thermodynamics of the system (i.e., interactions\(^{[35]}\) and entropy\(^{[37]}\)). Poor colloidal stability can affect the kinetic of assembly and result in disordered structures.\(^{[47]}\) Yet, dynamic light scattering (DLS, see Fig. S10) measurements indicate that our highly purified ZrO\(_2\) dispersions had low polydispersity (7.5%) and were devoid of aggregates even after long times (>18 hrs) at very high concentrations (457 mg/ml) in both hexane and toluene: toluene and hexane are excellent solvents for these colloids.

If colloidal instability is not responsible for the different structures observed with toluene and hexane, what is then the cause? Slower kinetics during the deposition process typically favor the assembly of a typically ordered thermodynamic structure.
Surface tension of the solvent was also suggested to be an important parameter in the assembly of ordered nanoparticle films from drying dispersion.[48]

The plot in Fig. 2b shows how good solvents with different surface tensions, boiling points, and ligand solubilities lead to ordered (filled circles) or disordered (open circles) CNAs during spin-coating. The solubility of the ligand was the only correlated variable: high solubilities leading to ordered CNA and vice versa. Other variables – dielectric constants, viscosities, etc... – did not show any correlation.

The solubility of the ligand in the solvent is an approximate, but easily measurable proxy for the energetic cost of interdigitation. The concentration of ligands in most ligand shells (0.13 g/ml on our ZrO₂ particles, accounting for 33% coverage) is higher than the solubility limit (e.g., 0.07 g/ml for TOPO in hexane): therefore, the ligand shell should not be fully solvated even in many good solvents.[49] All else being equal, a more solvated ligand shell will be more stable towards interdigitation than a less solvated one since it exhibits more favorable ligand-solvent interactions and a larger conformational entropy.[50]
Figure 2. Characterization of the influence of deposition and processing parameters on cracking and ordering of CNAs. 
a, Cracking suppression as a function of the hexane/toluene ratio of the dispersion. b, Chart summarizing the observation of cracks in colloidal nanocrystal assemblies (CNAs) of ZrO₂ nanoparticles as a function of film thickness, the toluene: hexane volumetric ratio of the colloid dispersion, and the processing of the film. The round scatters indicate disordered CNAs, while rhombi indicate ordered CNAs. The empty scatters indicate CNAs that cracked after deposition, grey-filled
scatters indicate CNAs that cracked after ligand removal, while black-filled scatters indicate films that were crack-free after ligand removal and sintering. The continuous line indicates the estimated critical cracking thickness (CCT) of as-deposited CNAs, while the dashed line indicates the CCT for sintered CNAs. c. Chart summarizing the influence of the solvent’s boiling point, surface tension, and solubility of the ligand (TOPO) on the order of the CNA (circles indicate disordered CNAs while rhombi indicate ordered CNAs). d. Hansen plot of solvents categorized by their ability to form ordered or disordered CNAs (circles indicate disordered CNAs while rhombi indicate ordered CNAs). e. TEM images of ZrO₂ nanoparticles dried from toluene and hexane showing in red the size of the TOPO ligands. f. histogram showing the significant difference in average interparticle distance observed in CNAs deposited from toluene (blue, three different particle batches) and hexane (red, two different particle batches), indicating different degrees of interdigitation.

Nonetheless, solvation is a complex process: e.g., some bad solvents (e.g., solvents that do not disperse the particles, like acetone) showed high solubilities for TOPO. Solvation of molecules is often understood and modeled in first approximation by quantifying the separate molecular interactions (dispersive, dipolar, and H-bonding) through the Hansen solubility parameters (δ_D, δ_P, and δ_H respectively).[^51] Figure 2d shows the Hansen plot of the solvents that lead to ordered (rhombi) and disordered (circles) CNAs. The discerning parameter appears to be the dipolar parameter δ_P: only a narrow range of values of δ_P were found to lead to ordered CNAs in these assembly conditions. Bad solvents that showed high solubility for TOPO were all characterized by high δ_H (e.g., 1,4-dioxane) that indicate H-bonding with the ligand head.

The crucial role of δ_P can be understood as follows. TOPO, like other ligands, is a polar molecule. Therefore, packed TOPO molecules bound to the same surface will repel each other through dipole-dipole interactions. This repulsion (and the associated destabilization of the ligand shell) can be screened by polar solvent molecules between the ligands, i.e., by solvation. It is also plausible that the dipole of
the solvent should be similar to the dipole of the ligands: if the solvent has a much larger dipole than the ligand, the solvent/solvent interactions should be more favorable than solvent/ligand and therefore lead instead to poor solvation of the ligand shell.

Improved solvation of the ligand shell should manifest as a decreased tendency towards interdigitation of the ligand shells in packed arrays. This prediction is verified in Figure 2e-f, which shows the separation of TOPO-capped ZrO₂ particles dried from toluene and hexane dispersions. The average distance obtained from particles dried from toluene dispersions was equivalent to the distance between the O and the terminal methyl of the TOPO molecule (~1 nm) taken twice, suggesting little interdigitation and a fully solvated ligand shell that effectively repelled neighbouring particles until drying, favoring ordering. In hexane the average interparticle distance was half than in toluene, suggesting poor solvation resulting in interdigitation and the formation of “sticky” surfaces[52] that can (i) hamper 3D ordered assembly by yielding kinetically trapped assemblies, and (ii) yield more cohesive arrays. Cyclohexane showed similar interparticle distances to hexane.
Figure 3. Compositional and microstructural diversity. a-i, 9.3 nm Fe₃O₄ nanoparticles (top row), 5.3 nm PbS nanoparticles (second row), and 5 × 2.5 nm HfO₂ nanorods (third row) shown as synthesized (left column), after deposition from toluene and ligand removal (middle column), and after deposition from
hexane and ligand removal (right column). j-m, Characterization of crack-free, ligand-free, sintered binary CNAs of Fe₃O₄ nanoparticles and ZrO₂ nanoparticles showing the homogeneously mixed microstructure, j, the crack-free morphology, k, and the lack of segregation as evidenced by EDS mapping, l-m, showing Fe in green and Zr in purple.

The spin-coating of disordered CNAs and their plasma-processing and sintering appears to be a general approach for the formation of crack-free polycrystals with a programmed microstructure. Fig. 3 shows crack-free, ligand-free CNAs obtained from particles of different composition, size, ligands, and shape: Fig. 3a-c shows spherical 9.3 nm Fe₃O₄ nanoparticles capped with oleic acid, Fig. 3d-f shows spherical 5.3 nm PbS nanoparticles capped with oleylamine, Fig. 3g-i shows 5 × 2.5 nm HfO₂ nanorods capped with TOPO, and Fig. 3 j-m shows binaries of 9.3 nm Fe₃O₄ and 3.7 nm ZrO₂ spherical nanoparticles capped with oleic acid and TOPO respectively. Toluene-based dispersions of these nanoparticles favored the formation of close-packed ordered, cracked CNAs (Fig. 3b and 3e). Particles deposited from hexane, remained disordered and crack-free after sintering. Building blocks with larger entropies – HfO₂ nanorods and the binary system – remained disordered even when assembled from toluene and did not crack when the ligands were removed. The TEM images and elemental mapping with energy dispersive X-ray spectroscopy (EDS) (Figs. 3j, 3l, 3m) shows that microscale segregation in binary systems can be avoided even if the CNA is disordered.
Figure 4. Characterization of charge transport. a, Scheme of the Van der Pauw measurement setup used to determine conductivities in He-plasma-processed PbS CNAs. b–c, Cross-sectional and top view of a PbS CNA after 48hrs He plasma processing. d, Conductivity for different PbS CNAs depending on the processing, compared to the reported range of single crystal conductivities.

To demonstrate the impact of controlling cracks has on function, we characterized charge transport in PbS CNAs deposited on glass from toluene and hexane dispersions, before and after ligand removal by He plasma for 48hrs. Charge
transport is especially relevant to some of the most compelling applications of nanostructured solids in energy science and technology (e.g., solar cells, batteries, capacitors, catalysts) and is diagnostic of material uniformity due to its sensitivity to defects. The measurements were performed in a van der Pauw geometry with electrodes spaced ~1.3 cm apart (Fig. 4a). The as-deposited CNAs were found to be fully insulating, as expected (conductivities $\sigma < 1 \cdot 10^{-6}$ S/cm, Fig. 4d). After plasma processing, the conductivity of the CNA obtained from the toluene dispersion was also insulating ($\sigma$ ranged between $2 \cdot 10^{-6}$ S/cm and $8 \cdot 10^{-5}$ S/cm), whereas, for the CNA obtained from the hexane dispersion (Fig. 4, b to c) instead was 5 orders of magnitude larger (1.370 S/cm). For reference, the conductivity of bulk PbS ranges between 0.11 and 1800 S/cm (Fig. 4d), even though it is important to notice that our material, given its nanostructuring, could exhibit doping way beyond that of the typical bulk crystal.

In summary, we have demonstrated a facile and scalable approach to fabricate crack-free solids by ligand-removal and densification of colloidal nanocrystal arrays. Low-pressure dilute plasmas remove ligands completely and cracking is avoided by tuning the structure of the assemblies through the solvation of surface-bound ligands. Our approach works with nanoparticles of different sizes, shapes, composition, and ligands, as well as with mixtures of different nanoparticles. The use of non-oxidizing plasmas allows for the creation of films of ligand-free nanoparticles with bulk-like conductivity (1.370 S/cm for PbS CNAs) over cm-scale distances. We believe the precision with which the microstructure can be controlled by this approach will be
useful in applications (e.g., photovoltaics, catalysis, energy storage) and potentially necessary in clarifying structure/property relationships in nanostructured materials.

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Materials and Method

Particle synthesis

All the reactions were performed in a 3-neck round bottom flask, with septum in the side necks and condenser attached to the central neck.

ZrO₂ nanoparticles

Synthetic procedure: The reaction for ~3.7 nm diameter zirconia nanoparticles synthesis has been adapted from a prior report.\(^{[41]}\) 80 g of trioctylphosphine oxide (TOPO, Strem Chemical – 90%) was liquefied under an argon blanket and degassed at 80 °C for 30 mins under vacuum. 16 mmol of zirconium (IV) isopropoxide isopropanol complex (Aldrich – 99.9%) and 20 mmol of zirconium (IV) chloride (Aldrich – 99.5%) were then added to TOPO under stirring (IKA® C-MAG MS 4 magnetic stirrer, speed control set to 3, glass-coated stir bar – Teflon covered stir bar degraded in the reaction conditions). The temperature of the reaction mixture was...
increased to 340 °C under Ar flow (flow was allowed by inserting syringe needle in one of the septa) and held there for 2.5 hrs under Ar blanket. Reaction mixture was then cooled down to 80 °C and diluted with toluene until achieving a 1:1 volume ratio. At this stage the solution has a blue-green color.

*Cleaning procedure:* The mixture was first centrifuged at 1000g for 3 mins to remove any collooidally unstable products. Particles were destabilized by adding acetone (~10 ml of diluted reaction mixture requires ~15 ml of acetone), and then precipitated out by centrifugation at 112g for 1 min. The white precipitate was further washed with pure acetone for three times, to remove any excess TOPO. The particles were then redispersed in the solvent of interest, and centrifuged at 1790g for 10 mins to remove collooidally unstable particles. The supernatant was filtered through 0.2 µm nylon filter to obtain a dust-free product ready for spin coating. The scale reported above produced 2.2 g of particles (measured by TGA).

HfO₂ nanoparticles

*Synthetic procedure:* The reaction to obtain 5 nm × 2.5 nm hafnia nanorods was a slight modification of a previously published procedure. The reaction was performed similarly to ZrO₂ nanoparticles procedure, except for the reaction temperature. 4 mmol of hafnium (IV) isopropoxide isopropanol adduct (Alfa Aesar – 99%) and 4 mmol of hafnium (IV) chloride (Alfa Aesar – 99.9%) were added to degassed TOPO under stirring. The reaction mixture was first heated to 300 °C, held at this temperature for 30 mins, and then raised to 320 °C and held there for 20 mins.

*Cleaning procedure:* Similar to what was mentioned above for ZrO₂ nanoparticles.
Fe$_3$O$_4$ nanoparticles

*Synthetic procedure:* Synthesis of ~9 nm diameter Fe$_3$O$_4$ nanoparticles was a slight modification of a previously published procedure.$^{[54]}$ A mixture of 6 mmol of iron (III) oxide (Aldrich – catalyst grade, hydrated, grounded to fine powder using mortar and pestle - slightly shiny granular material, transformed into fine brown colored powder with little grinding; 5-7 mins will be enough), 24 mmol of oleic acid (Aldrich – 90%), and 60 mmol of 1-octadecene (Aldrich – 90%) was heated, while stirring, in argon atmosphere to 150 °C, and held there for 1 hr. The temperature of the reaction was then raised to 320 °C, and held there for 2 hrs. There will be bubbling at temperatures >300 °C, so condenser attachment is important for safety. The reaction mixture was then cooled down to 60 °C, and diluted with toluene to a 1:1 volume ratio.

*Cleaning procedure:* The reaction mixture was first centrifuged at 1000g for 3 mins to remove any colloidally unstable products. To the supernatant, 1:4 volume ratio of solvent of interest and acetone was added, until particles were destabilized (~10 ml of diluted reaction mixture requires ~20 ml of solvent mixture to destabilize the particles), and then centrifuged at 161g for 1 min. Supernatant was discarded, and particles were washed three more times with the solvent mixture. Particles were then redispersed in the solvent of interest and centrifuged at 1000g for 5 mins. The supernatant was filtered through 0.2 µm nylon filter to obtain a dust-free product ready for spin coating. Nanoparticles cleaned from ~25 ml reaction volume were dispersed in ~10 ml of solvent. This concentration of dispersion produced >200 nm-thick CNAs (spin coated at 1000 rpm).
PbS nanoparticles

Synthetic procedure: The ~5 nm diameter PbS nanoparticles were prepared according to a slight modification of a previously published procedure.\(^{[55]}\) 20 g of lead (II) chloride (Aldrich − 98%) added to 38.6 g of stirring oleylamine (Acros Organics − C-18 content − 80-90%) under nitrogen flow. The mixture was heated to 120 °C and degassed for 5 min. The mixture was heated to 160 °C and held there for 30 mins to form a homogeneous dispersion of lead (II) chloride in oleylamine. There should be no visible clumps in the stirring mixture. In the meantime, sulfur was dispersed in oleylamine by simultaneously sonicating and heating the dispersion at 80 °C. The temperature of the reaction was lowered to 120 °C, and the sulfur solution was injected. The temperature was stabilized to 100 °C and held there for 12 mins. The reaction was then rapidly quenched in hexane to produce a 1:2 mixture (product: hexane).

Cleaning procedure: Particles were cleaned following the reported procedure.\(^{[56]}\) Once the particles were separated from excess lead chloride and sulfur, they were further cleaned following the procedure mentioned above for Fe\(_3\)O\(_4\) nanoparticles.

Film deposition

Unary CNAs

All the CNAs were deposited on a substrate by spin coating (Laurell Technologies Model: WS-650MZ-23NPP). Nanoparticles dispersion was placed on the substrate until complete coverage. Then the substrate was accelerated at 330 rpm/sec to 1000 rpm, which uniformly spreaded the dispersion and left a thin film of dispersion on the substrate. It was then held at 1000 rpm for 25 secs, for the layer of dispersion to dry. Based on solvent, these spinning parameters will produce defined and
reproducible thickness of CNAs. We kept the spin coating condition constant for all the CNAs prepared in this study, for better comparison. Different thicknesses were obtained by changing the concentration of the dispersion.

**Binary CNAs**

Solution for binary CNAs were prepared by dispersing nearly equal amount of ZrO₂ and Fe₃O₄ nanoparticles in hexane. CNAs were made with similar spin coating condition used for Unary CNAs.

**Plasma processing**

Plasma processing was performed in a Harrick’s plasma etcher (PDC-001) with PlasmaFlo gas flow mixer at plasma power of 7 W and pressure of 500 mTorr. The gases (ultra-high purity) used for plasma exposure were oxygen and helium. All CNAs (both unary and binary) were processed for 24 hrs or 48 hrs.

Oxides CNAs were treated with oxygen plasma whereas PbS CNAs were treated with helium plasma.

**Sintering**

Plasma processed CNAs were sintered in a furnace, either in air or in an inert atmosphere (argon). The heating rate was maintained at 20°C/min. After the sintering time, the samples were left in the furnace to cool. ZrO₂ CNAs were sintered at 700°C in air for 24 hrs. Binary CNAs of Fe₃O₄ and ZrO₂ were annealed under argon environment at 250°C for 6 hrs.

**Layer-by-layer processing**

Crack-free thicker (>200 nm) consolidated CNAs were prepared by layer-by-layer deposition and processing according to the following protocol: (i) deposit a layer
(~200 nm); (ii) plasma process it; (iii) deposit the subsequent layer, (iv) plasma process; (iv) finally consolidate the layers by sintering. We have coated 190 nm thick layer of ZrO₂ CNAs and followed the above steps until second layer. Finally, layers were sintered at 700 °C for 24 hrs in air to form a crack-free nanocrystalline solid.

**Ion beam analysis**

The elemental analysis of the samples throughout the film’s depth was determined by combining non-Rutherford elastic backscattering spectrometry (EBS) and elastic recoil detection (ERD) ion beam analysis techniques at the Surrey Ion Beam Centre. The samples were mounted on a sample plate on the 6-axis goniometer of the 2 MV Tandem accelerator. Two particle detectors were used at backscattering angles of 172.4° (DetA) and 147.7° (DetB), measured with an accuracy of 0.2° using the goniometer with an in-line laser. The solid angles of detection were 2.6 ± 0.1 and 3.1 ± 0.3 msr for DetA and DetB, respectively. A third particle detector (ERD; DetC) was mounted at a scattering angle of 30.8° with a foil of 31.0 µm of Kapton (C₂₂H₁₆O₅N₂; density of 1.42 g/cm³). Its solid angle of detection was 0.8 ± 0.1 msr.

Each sample was analyzed in three different locations and each location was measured in two different geometries of detection: namely, spectra were collected from the DetA & B using a 4He beam at 3.05 MeV for sensitivity to the oxygen signal through the EBS resonance at 3038.1 keV; then the samples were analyzed using a 4He beam at 4.3 MeV for sensitivity to the carbon signal through the EBS resonance at 4265 keV and recording the spectra from the DetA, B & C. The samples were relocated at the same positions for both analyses. The incident beam direction was close to the normal at the sample at 3 MeV, while the sample was titled by 70 degrees
toward the DetC for the analysis carried out at 4.3 MeV. For both analyses, the beam spot size was about $1.5 \times 1.5 \text{ mm}^2$ and the beam intensity was between 10 and 30 nA.

For each measurement point, the set of 5 spectra was self-consistently analyzed using DataFurnace\textsuperscript{[60]} to take advantage of the synergy between EBS and ERD techniques\textsuperscript{[61]}. The elemental analysis presented in this work are the average of the three measurement points performed on each sample.

**X-ray diffraction (low angle and wide angle)**

Powder X-ray diffraction was performed with Siemens D500 X-ray diffractometer at Materials Analysis and Research Laboratory (MARL) at Iowa State University. The instrument is equipped with a diffracted beam monochromator and sample spinner. No special sample preparation was done for XRD characterization. The CNAs spin coated on silicon substrate were used for XRD measurements. Low angle XRD patterns were collected in 2θ range 0.8-5° by using 0.05DS, 0.02° steps, and 5s per step. Similarly, wide angle XRD patterns were collected in 2θ range 20-60° by using 0.15DS, 0.05° steps, and 3s per step. For nanoparticle size analysis, diffraction pattern was collected in slow scan mode (0.03° steps and 10s integration) to improve peak-to-noise ratio. Accurate measurement of nanoparticles size using Scherrer equation was done following the procedure reported\textsuperscript{[7]}.

**Scanning electron microscopy**

Scanning electron microscopy was performed with FEI quanta 250 field-emission SEM at MARL at Iowa State University. The instrument is equipped with field emission gun with maximum resolution on the order of 1 nm and Oxford EDS microanalysis system. It is capable of variable and extended (i.e. environmental)
pressure modes for non-conductive and moist samples. It has a Peltier stage for heating (~1000 °C) and cooling samples (~-25 °C). Imaging was done in secondary electrons mode at 10 keV with beam spot size of 3.

**Transmission electron microscopy/Scanning transmission electron microscopy**

Transmission electron microscopy (TEM) and high resolution TEM images were obtained using 2007 JEOL 2100 200kV STEM in TEM mode, operating at 200 kV. This STEM is located at Microscopy and NanoImaging facility, Iowa State University and equipped with a Thermo Fisher Noran System 6 X-ray microanalysis system. Samples for TEM analysis were prepared by evaporating drops of dilute nanocrystals dispersion at room temperature, on a carbon-coated copper grid. EDX measurements were performed in STEM mode. Samples for EDX characterization were prepared by scraping off flakes of CNAs from the substrate using a sharp blade, and then attaching them on a carbon-coated TEM grid.

**Atomic force microscopy**

Topographic measurements of assemblies of ZrO$_2$ nanocrystals were done using Bruker Icon AFM at Roy J. Carver Laboratory for Ultrahigh Resolution Biological Microscopy of the Institute for Combinatorial Discovery at Iowa State University. All of the images were captured in ScanAsyst® mode in air with SCANASYST-AIR tips with scan rate of 1Hz. Images were flattened after capture using NanoScope Analysis v1.20. Imaging and analysis were done on samples before and after 24 hrs of oxygen plasma treatment.
Dynamic light scattering

Dynamic Light Scattering (DLS) measurements were performed using Malvern Zetasizer Nano ZS90 (Model: ZEN3690). DLS measurements were done on ZrO₂ nanoparticles dispersion in hexane and toluene. The measurements were done on highly concentrated dispersion (457 mg/ml), 1 hr and 18 hrs after their redispersion in the solvent.

Electrical characterization

Film conductivity was measured using the Van der Pauw method1 using a thin PbS QD films of known thickness in a square geometry with corner contacts. The corners were contacted with silver print (Pelco Conductive Liquid Silver) and probed using micromanipulated probes on a home-build probe station. A Keithley 2400 in four-wire source-sense mode was used to simultaneously source current and measure voltages. Sheet resistances were determined by numerical integration. Reported values are the average of several measurements ranging over several orders of magnitude of source current (10⁻⁶ to 10⁻³ A) was used. The as-prepared thin films of two kinds of PbS samples were then processed with helium plasma for 48 hrs at the power of 7 W and pressure of 500 mTorr.
Figure S1. AFM images and height profile of ZrO₂ CNAs prepared from dispersions in toluene. a and c, As deposited. b and d, After exposure to oxygen plasma for 24 hrs; root mean square (RMS) roughness data shows some surface smoothing after plasma exposure. Height scale bar range is 600 nm.
Figure S2. AFM images and height profile of ZrO$_2$ CNAs prepared from dispersion in hexane. a and c, As deposited. b and d, After exposure to oxygen plasma for 24 hrs; root mean square (RMS) roughness data shows similar smoothing effect after plasma exposure, as shown above for ordered CNAs. Height scale bar range is 100 nm.
Figure S3. Low angle XRD (LAXRD). LAXRD showing transition from ordered CNAs to disordered ZrO$_2$ CNAs with increasing hexane content (vol.%) in ZrO$_2$ nanocrystals dispersion in different fractions of hexane.

Figure S4. Z-contrast STEM images of ZrO$_2$ CNAs, after exposure to oxygen plasma for 48 hrs. a, Ordered CNA – arrows indicate cracks within the grains. b, Disordered CNA; insets show FFT analysis of the images, which confirm that ordering in toluene sample is preserved, even after ligand removal.
Figure S5. Non-Rutherford elastic backscattering spectrometry (EBS) spectra of ordered ZrO$_2$ CNAs. a, As deposited. b, After exposure to oxygen plasma for 24 hrs. The continuous lines indicate the best fit obtained by DataFurnace.
Figure S6. EBS spectra obtained from disordered ZrO$_2$ CNAs. a, As deposited; after exposure to oxygen plasma for, b, 24 hrs; c, 48 hrs. The continuous lines indicate the best fit obtained by DataFurnace.
Figure S7. XRD spectra of disordered ZrO₂ CNAs at different stages of processing. Left panels show no effect of processing steps on the crystallinity of ZrO₂; right panels show that plasma etching has no effect on particle size, but sintering at 700 °C for 24 hrs in air leads to an increase in nanocrystals size from 3.53 nm to 4.62 nm (on average).
Figure S8. SEM images of crack-free ZrO₂ CNAs prepared by layer-by-layer deposition and processing. a, First layer after deposition. b, Second layer deposited on the plasma processed first layer. c, Fully processed, crack-free, 360 nm thick film (after 2 layers of deposition and processing).
Figure S9. SEM images showing rate of self-assembly has no effect on ordering of ZrO$_2$ CNAs. a, Hexane (bp = 69 °C). b, Heptane (bp = 98 °C). c, Octane (bp = 126 °C). They all formed disordered CNAs.
Figure S10. Hydrodynamic diameters of concentrated ZrO$_2$ nanoparticles in different solvent as a function of time, measured by DLS. a, Toluene. b, Hexane. Highly concentrated (concentration = 457 mg/ml) ZrO$_2$ nanoparticles are colloidally stable even after 18 hrs, in both toluene and hexane.
CHAPTER 3

BUILDING MATERIALS FROM COLLOIDAL NANOCRYSTAL ARRAYS: MOLECULAR TUNING OF INTERFACES BY PLASMA PROCESSING OF LIGANDS

A paper in preparation to be submitted

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Introduction

As the characteristic length scales of materials and devices shrink in size to the nanoscale, the influence of their surfaces on their properties becomes increasingly dominant. For most lattices, a radius of curvature of ~1-2 nm indicates the threshold at which more than half of the atoms are effectively at the surface. While the
modification of exposed surfaces has been a subject of intense interest and remarkable success in the past decades \[62\], the modification, control, and characterization of solid/solid interfaces within a material has been a much more difficult problem.

While the control of exposed surfaces is essential in controlling the interaction of the material with its environment – with exceptional consequences on its wetting, catalytic, optical, chemical, tribological, and electrical properties – the control over the interfaces within a polycrystalline material can dominate the thermal, mechanical, and bulk transport properties. Interfaces can make thermodynamically unstable phases stable \[63\], can make soft metals hard \[64\], brittle ceramics ductile \[65\], weak composites tough \[66\], and metallic conductors insulating \[67\]. Furthermore, interfaces are at the heart of some of the most exciting recent discoveries in solid state physics: e.g., topological insulators \[68\], and interface superconductivity \[69\]. From a more fundamental standpoint, interfaces in a solid material represent a departure from equilibrium conditions: controlling interfaces would expand the canvas of materials design outside of equilibrium and into metastability and new properties.

The ability to engineer the grain boundary composition from the bottom-up will give us unprecedented control on the interface-dependent properties. By interface engineering from the bottom-up we mean the modification or addition of an homogenous interface layer to the initial building blocks before they are integrated/consolidated into a solid material. Homogeneous control of the interfaces after consolidation of the materials is a complex problem. Techniques like atomic layer deposition (ALD) can deposit/coat exposed surfaces, thereby filling up the pores. Uniform coating of the surfaces can become more complicated when the pore sizes are
<5nm. Adhesion and wetting of the coating can also be questionable unless strong chemical bonds are formed with the underlying surface.

There are several approaches with which we can control the interface composition of nanoparticles from the bottom-up. It has been shown that during post-synthesis, an outer shell layer can be grown on the starting nanoparticles e.g., creating a SiO₂ encapsulation. Typically, these shell layer are thick and could dominate the properties of the core, especially when particle size are <5nm. In an another elegant work where Talapin and coworkers[15] demonstrated the capping of colloidal nanocrystals with inorganic ligands which after post-processing form an outer coating layer of different composition to the core's composition. With this approach, it will be difficult to form a phase-pure material and we are always left with a composite.

We have shown in our earlier chapters [70] that plasma processing of colloidal nanocrystals assemblies etches the alkyl tail of the ligands, leaving behind the phosphorus of the functional group (P=O) homogenously in the film. We further demonstrated that we can model very well the mechanical properties of the fully etched film with a granular model, only when we considered the surface energy to be that of common phosphates (i.e. hydroxyapatite). The discrepancy in modulus was close to 64% if we instead considered the hydrated ZrO₂’s surface energy i.e. 1.02 J/m² [70]. In this chapter, we show that systematic modifications of the ligands, together with plasma processing allow for systematic tuning of the interfaces of the material, leading to a fine control over the thermal and mechanical properties.
Experimental Design

We have shown in the supporting information in the form of TEM images and FT-IR spectra that we have successfully replaced the TOPO-capped ZrO$_2$ with Oleic Acid, without change of size and shape of particles.

The next and final step in the process is to etch away all the organics from the colloidal nanoparticles layer. To do so we exposed the nanocrystal films to oxygen plasma, which homogenously etches the organics, as described in our earlier work $^{[70, 71]}$ and selectively modifies the boundary composition of colloidal nanocrystals $^{[70]}$. We have processed these nanoparticles assemblies (320 nm thickness) with oxygen plasma at plasma power of 30W, with chamber pressure of 500mTorr, and exposure duration of 48hr. From our earlier studies these conditions are sufficient to etch all the ligands from such films.

The chemical analysis of the films both before and after plasma exposure was performed by Rutherford Backscattering Spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS). RBS is a non-destructive, standard-less analytical technique, which provides accurate composition of the layer and more importantly depth information of elements. With depth profile, we can gauge the homogeneity of phosphorous in the film. On the other hand, XPS will provide us with the chemical composition and chemical state of the interface layer.

Finally, we characterized the effect of the interfacial layer on the physical behavior of ZrO$_2$ nanoparticles layer. We have estimated the interfacial energy of the particles through fitting the elastic modulus of films by Kendall’s model $^{[72]}$ and compared the effect of the interface layer on their collective mechanical properties.
measure by substrate-corrected nanoindentation \cite{26, 27}. The most noted application of zirconia is their stability to high temperatures. The response to heat of these nanoparticles film is also important from densification perspective. We heat treated our plasma-modified nanoparticles film in static air from temperature range of 300-900°C. We then assessed the presence of interface layer at the particle boundary on their grain growth behavior and studied their growth kinetics, and compared with same sized tetragonal and cubic YSZ nanoparticles \cite{73}. 
Figure 1. Schematic of bottom-up approach to control the grain boundary composition of nanoparticles. First step is the synthesis of initial nanoparticles, then through ligand exchange alter the chemical composition of ligands and finally though plasma exposure control the formation of interface layer.
Results and Discussion

Ligand Exchange

We followed the route of ligand exchange to change the molecular composition of the ligands because ligand exchange typically maintains the size and shape of the initial nanocrystals. ZrO₂ is chemically stable and so will be resilient to any modification even in the presence of excess ligands like oleic acid.

Fourier transform infrared spectroscopy (FT-IR) spectra in the Supporting Information confirms the ligand exchange of TOPO-capped ZrO₂ by Oleic Acid. Absence of P=O peak at ~1100 cm⁻¹ in the oleic acid-capped ZrO₂ nanocrystals confirms the ligand exchange. X-ray diffraction (XRD) and Transmission electron microscopy (TEM) data in the Supporting Information shows no change in size and phase of ZrO₂ nanocrystals after ligand exchange. The average distance between TOPO-capped particles surface calculated from TEM images is ~0.9nm whereas distance between particles after ligand exchange with oleic acid is ~2nm, consistent with when oleic acid ligand is fully interdigitated. The complete interdigitation of ligand deposited from ZrO₂ dispersion in hexane has been explained elsewhere \[71\].
Figure 2. Chemical analysis of plasma-processed nanoparticles films. (a) & (b) Elemental profile from Ion Beam Analysis (IBA) showing the complete removal of carbon and homogenous distribution of non-etched functional group of the ligands, (c) XPS showing the change in chemical state of the non-etched component of the ligands after plasma processing, (d) XPS showing the shift in the Zr 3d core-line towards higher bending energies for the fully processed TOPO-capped ZrO$_2$ films in comparison to Oleic Acid. Thin film unit (TFU) = 10$^{15}$ atoms/cm$^2$

Chemical analysis of plasma-processed nanoparticles films

Exposure of ZrO$_2$ nanocrystals films to plasma serve two purposes, (i) conversion of colloidal nanocrystal assemblies (inorganic core + organic ligands shell) into all-inorganic solids, and (ii) “program” the interface composition of the nanocrystals.
Complete removal of ligand can be seen from the Figure 2 (a) & (b) where [C] etched down to ~1at.% from ~21at.% for both Oleic acid and TOPO-capped ZrO$_2$ films. ~1at.% is also the detection limit of the IBA for carbon so possibly we have much lower carbon content than 1at.% in the films. The steep increase in the carbon concentration towards the surface of the films is from the adventitious carbon which shows up only in the first few TFUs. Depth profile confirms uniform composition of phosphorus in the TOPO-capped ZrO$_2$ films. IBA do not show any presence of phosphorus in the oleic acid-capped ZrO$_2$ films which corroborate the efficiency of our ligand exchange.

The XPS peak at 132.5eV in the unprocessed TOPO-capped ZrO$_2$ films in Figure 2(c) corresponds to peak position of Ph$_3$PO$^{[74]}$ (132.5±0.2 eV from the NIST XPS Database). TOPO molecule has P=O as a functional group that binds to the surface of ZrO$_2$ nanocrystal. In the fully-processed films, oxygen plasma etches the hydrocarbon tail of the ligands, and simultaneously alters the composition of the complex formed between functional group of ligand and the ZrO$_2$ surface. The peak shift of the fully-processed film to higher binding energy (~133.9 eV) is consistent with a conversion to zirconium hydrogen phosphate Zr(HPO$_4$)$_2$ (133.4±0.5 eV from the NIST XPS Database)$^{[74]}$.

In Figure 2(d) we show the comparative Zr 3d core-line of the TOPO and Oleic acid capped, fully-processed ZrO$_2$ films. The binding energies are consistent with the TOPO sample (182.9 eV) being capped with hydrogen phosphate groups (183.9±0.9 eV from the NIST XPS Database), and the OA sample (182.4 eV) being bare (183.1±0.7 eV from the NIST XPS Database). Furthermore, it has been demonstrated
that the full width at half maximum (FWHM) of the XPS peaks for oxides like ZrO₂ are influenced by the metal-oxygen bond length or the metal-oxygen coordination number. From the calculation of the FWHM of the Zr 3d₅/₂ peak of OA- and TOPO-capped ZrO₂ films we found that FWHM of the core-line of TOPO film is ~0.2eV narrower than the oleic acid film. Similar difference have been found between γ-Zr phosphate and yttria stabilized zirconia (YSZ) [75].

**Interfacial energies of ZrO₂ CNAs with and without phosphate layer**

Interfaces play a dominant role in defining the physical properties of polycrystalline materials. In earlier work [70] we demonstrated that TOPO-capped ZrO₂ CNAs behave as a granular system both before and after complete ligand removal by plasma processing. More specifically they obey quantitatively an equation by Kendall[72] that predicts the elastic modulus of a granular system on the basis of its bulk modulus $E_0$, its filling fraction $\phi$, its grain size $d$, and its surface energy $\gamma$. We here apply the Kendall's granular model to estimate the surface energy $\gamma$ of the interfaces in the samples after plasma processing, as a function of the starting ligand. The fit values of $\gamma$ for fully-processed TOPO-capped and OA-capped ZrO₂ films are 0.18 J/m² and 1.06 J/m² respectively (shown in Supporting Information). The value of 0.18 J/m² is smaller than the value for hydroxyapatite (0.33 J/m²) [76] but higher than the value reported for amorphous calcium phosphate (0.1 J/m²) [77]. The $\gamma$ value of hydrated and anhydrous ZrO₂ are 1.02 J/m² and 1.23 J/m² respectively[78] showing remarkable agreement with the $\gamma$ obtained for our plasma-processed OA-capped ZrO₂ samples.
Figure 3. Role of interface composition on the thermal stability of ZrO$_2$ particles. Thermal stabilization of plasma-modified particles towards grain growth calculated by doing Scherrer analysis on their respective XRD spectra. Comparing the particle growth as function of temperature for (a) TOPO-capped particles with OA-capped ones, (b) TOPO-capped particles with YSZ (with similar initial particles size)

Thermal stabilization of plasma-modified ZrO$_2$ nanocrystals

Zirconium oxide is a high temperature ceramic and due to their low thermal conductivity applied as thermal barrier coating in gas turbines and jet engines and because of its excellent conduction of oxygen ion at high temperatures used as solid
electrolyte in solid oxide fuel cell and as oxygen sensors to determine oxygen content in exhaust gases.

Both for the application at high temperature environments and the heat treatment involved during densification of the nanocrystals, the understanding of the thermal behaviors of plasma-modified ZrO₂ nanocrystals film is important. In Figure 3(a) we present the normalized particle size \( \frac{d}{d_0} \) as a function of sintering temperature (held for 24 hrs). Stabilization towards grain growth is clearly seen in the plasma-modified TOPO-capped ZrO₂ nanocrystals when compared to OA ones at all temperatures. The onset temperature for grain growth in OA samples is \( \sim 400 \)C, whereas for TOPO samples is \( \sim 700 \)C. More on the growth mechanism of these particles in the following sections.

To understand what could possibly be the reason for such difference in particle growth in relation to temperatures, we have dissected the temperature range into three section of interest, (1) zone 1 – 300-500°C, (2) zone 2 – 500-700°C, and (3) zone 3 – beyond 700°C.

In zone 1, what we see is the desorption of physisorbed and chemisorbed water on ZrO₂ nanocrystals surface. Adsorbed water lowers the surface energy of particles. Physisorbed water adsorbed on the hydroxide (chemisorbed) layer on the nanoparticles surface\(^{[79]}\) is likely to desorb when heated >300°C. When the temperature is increased to 500°C, chemisorbed water starts to desorb too, decreasing the surface energy of particles. These changes in surface energy of particles will be stronger for OA-capped ZrO₂ film due to the higher overall surface energy than TOPO films. Higher surface energy initiates the particle growth in OA films below 500°C.
In zone 2 & 3, significant grain growth occurs in OA films (~1.1 at 500C to ~3 at 700C). TOPO films resist grain growth until ~700C. In zone 3, the grains continue to grow however growth is severe at >800C. At 900C, particle grow nearly the 2 times of that at 800C for both TOPO and OA films. More on the increased growth rate at 900C in our grain growth kinetics study below.

We further compared the thermal stability of our plasma-processed TOPO-capped particles with yttria-stabilized zirconia particles in both tetragonal and cubic phases (t-YSZ and c-YSZ, prepared by a modified protocol of the original synthesis of ZrO$_2$ nanocrystals[41]). The size of the as-synthesized YSZ particles is comparable with our TOPO-capped particles (2.70nm vs 2.82nm). From Figure 3(b) we can see that plasma-processed TOPO particles show a superior thermal stability to t-YSZ and comparable or better than c-YSZ particles, while our OA particles (from figure 3(a)) show comparable or better thermal stability compared to t-YSZ. On the other hand, plasma.modified “TOPO” particles show similar growth behavior to c-YSZ particles. These results suggest that the stabilization obtained in our system is not only due to the kinetic barrier at the grain boundary (the phosphate layer), but is also thermodynamically motivated. The surface energy of phases of ZrO$_2$ is ranked as monoclinic>tetragonal>cubic. Our results validate the calculations that demonstrate that t-ZrO$_2$ is indeed the thermodynamically stable phase, when the grain size is smaller than ~10 nm due to the lower contribution of surface energy of the tetragonal phase.
Figure 4. Grain growth kinetics with and without phosphate layer. (a) grain growth comparison as function of sintering time in the temperature range of 600-800°C, (b), grain growth kinetic of plasma-modified “TOPO” particles of our study comparing with cubic YSZ from literature (c) & (d) showing good fits of our grain growth kinetics with Ostwald’s ripening model, Arrhenius plot of (e) TOPO and (f) Oleic Acid capped ZrO₂ particle growth analyzed through Ostwald’s ripening model (with exclusion of the 900°C data)
Grain growth kinetics of plasma-modified ZrO$_2$ nanocrystals

Kinetic study of polycrystalline materials with nanosized grains will help us to mechanism of grain growth and will answer the question whether the grain growth mechanism is similar or different than micrometer-sized grains. The grain growth kinetic study in Figure 4(a) reveals that with sintering time, particles initially grow to certain particle size (depending on the sintering temperature) and grain growth stagnates more or less after longer sintering times.

In the plasma-modified “TOPO” particles, phosphorous at the particle boundary lowers the grain boundary energy, hinders grain growth, and extends the coarsening to higher temperatures, which is desirable from high-temperature application point of view. We then compared grain growth kinetics of plasma-modified “TOPO” particles and c-YSZ from Goto et.al. [73] to show their difference in growth behavior in time. As can be seen from Figure 4(b), the study by Goto et.al. for c-YSZ was performed for very short sintering times (1-5 hr). c-YSZ nanocrystals grew to 1.5 times at 600C and 700C, which is higher than our plasma processed TOPO-capped ZrO$_2$. Extrapolating the slope of c-YSZ at 800C, the particle will grow further with sintering time. The particle size at 800C for 5hr is already greater than any time treatment of plasma processed TOPO-capped ZrO$_2$ at 800C.

The grain growth in polycrystalline materials is controlled by the atomic diffusion at the grain boundary. We therefore have fitted our grain growth data using the equation for Ostwald’s ripening [80, 81],

$$D = D_0 + k \cdot t^{\frac{1}{n}}$$
where $D_0$ is the diameter of the particle at $t=0$, $D$ is diameter of particle at time $t$, $k$ is the temperature dependent rate constant, and $n$ is grain growth exponent. Ostwald’s ripening model has been primarily studied for dilute conditions however applicable to concentrated system, but with different rate limiting step to growth. Our grain growth data for both plasma-processed OA and TOPO capped particles can be described relatively well with the equation (as shown in Figure 4(c) & (d)). From the fit we got a grain growth exponent of 2.1 and 2.8 respectively for TOPO and OA particles respectively.

The value of $n$ contains information on the kinetically limiting step of growth. It has been shown that for $n = 2$ the growth is controlled by the diffusion of ions along the matrix-particle boundary, whereas for $n = 3$ the growth is controlled by the volume diffusion of ions\cite{81}. 33% of the Zr sites on the particle’s surface are capped with phosphorus so that two surfaces facing each other would create a nearly continuous layer of phosphate comparable to a matrix. The presence of this phosphate layer explains the exponent value of 2 whereas due to absence of interface layer, volume diffusion will likely to happen between the plasma-modified OA particles.

Activation energies help us determine the kinetic barriers to growth. The rate constants for both the TOPO and OA samples follow closely an Arrhenius dependence on temperature (only when excluding the 900C rate constants) with activation energies of 53kJ/mol and 32kJ/mol respectively. In OA particles the activation energy of grain growth is remarkably similar to the molar $\Delta G$ of melting of the particles, considering the size-dependent contribution of surface energy. The increased activation energy of
grain growth for TOPO particles could be explained by a kinetic hindrance to growth caused by the presence of phosphate at the grain boundaries.

The 900°C rate constant does not follow the Arrhenius trend that the previous temperatures show (shown in Supporting Information), which indicates that a change in behavior could be associated with a transition to the monoclinic phase. We observed evidence of monoclinic phase for 900°C TOPO films and the peaks only emerge after heating for 48hrs, which suggests nucleation and then growth of monoclinic phase after prolonged heat treatment (XRD spectra are in Supporting Information). The change of phase from tetragonal to monoclinic is accompanied by a 4-5% volume change which might disrupt the phosphate layer and accelerate grain growth in “TOPO” films. Zr(HPO₄)₂ and ZrO₂ exist as separate phases at these temperatures.

Mechanical properties of plasma-modified ZrO₂ nanocrystals

The presence of a secondary phase typically affects the mechanical strength of a material. But it seems that phosphates layer does not have much effect on the modulus of the films but clearly has an effect on hardness as seen in Figure 5 (b) & (c). However, TOPO-capped ZrO₂ films have shown higher modulus compared to OA-capped ZrO₂ films for the fully processed samples (53GPa vs. 35GPa). It suggests that clean ZrO₂ surfaces in the OA sample are more prone to be saturated by atmospheric contaminants (e.g., water) due to their higher surface energy. Moduli of OA-capped ZrO₂ films reach similar values to TOPO-capped ZrO₂ films when all the chemisorbed water has been removed (>500°C). It has been demonstrated that the modulus of SiO₂ nanoparticles increased by a factor of 2 when the surface energy of the particles
Figure 5. Mechanical properties of ZrO$_2$ CNAs with and without phosphate layer. (a) elastic modulus & (b) hardness of ZrO$_2$ films measured by nanoindentation to observe the effect of the interface composition on their mechanical properties.

Increased after removal of water at 700°C [72]. It can be argued that this might be due to difference in porosity of these samples as hardness and elastic modulus of films composed of oxide nanoparticles are strongly correlated with porosity. On the contrary, TOPO sample is more porous than oleic acid (∼40% vs. ∼34%).
On the other hand, the hardness of OA-capped ZrO\textsubscript{2} films starts to increase only when the sample is heat treated above 400°C. OA films are significantly more porous compared to TOPO films (porosity data in Supporting Information), which can easily explain the difference in hardness values: in a granular model such as Kendall’s the dependence of modulus on porosity is very strong (4\textsuperscript{th} power). The high porosity of the OA sample is simply explained by the fact that OA ligands are much longer (~1.8 nm) than TOPO ligands (~0.8 nm), thereby establishing much larger distances between the particles in the assembled CNA. The removal of the ligand leads to a homogeneous collapse of the film along the vertical direction thereby preserving the low density of the films. Compaction could be also limited in OA samples due to their higher interfacial energies \cite{72, 84}.

**Conclusions**

We have demonstrated a simple and scalable bottom-up approach to control the grain boundary composition of colloidal nanoparticles through combination of chemical composition of ligands and plasma processing. The role of plasma is to selectively etch the ligands and modify the interface composition at the molecular level. We confirmed through RBS and XPS the complete removal of ligands and homogenous distribution of interface composition in the film. Using Kendall’s granular model, we can extract the effect of phosphate layer on the interfacial energy of the particles. With and without phosphate layer, the value of surface energies remarkably matches with hydrated common phosphates and hydrated t-ZrO\textsubscript{2}. The interface changes the mechanical properties of the particles layer (especially the hardness), and the thermal properties. By engineering t-ZrO\textsubscript{2} nanoparticles to have a phosphate layer
we obtained a stabilization comparable to that obtained by yttria doping. The growth kinetic could be easily modeled by a simple Ostwald’s ripening model with grain growth exponent of $\sim 2$ and $\sim 3$ for particles with and without phosphate layer. With our unprecedented control on grain boundary composition, we can selectively alter the grain growth mechanism of same particles.

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Supporting Information

Particle synthesis and ligand exchange

The synthesis of TOPO-capped ZrO$_2$ nanocrystals as described in our earlier paper [71]. Ligand exchange (LE) was performed in solution and in the presence of excess ligands.

LE with Oleic Acid

*Experimental Condition:* Oleic Acid in the ratio of 10:1 to ZrO$_2$ solution was put under vacuum at 120C for 30mins. Argon flow was restored and temperature was lowered to 50C and then nanoparticles dispersion in hexane is injected into the Oleic Acid. Hexane was pumped of the solution and the mixture was heated to 300C and hold there for 1hr. Solution was then cooled down to room temperature and purification was performed without diluting the solution.
Purification: Purification of the particles should be taken seriously to achieve high quality of nanoparticles dispersion. To 12.5ml of reaction mixture 37.5ml of acetone was added and centrifuged at 5000rpm for 2hr. Supernatant was discarded and precipitates was washed with 10ml of acetone for 3 more times and then dispersed in hexane. The dispersion was centrifuged at 4000rpm for 10mins to remove any junk or colloidally unstable particles and finally filtered through 0.2µm nylon filter.

Characterization Techniques

X-ray Diffraction: Powder X-ray diffraction (XRD) was performed with Siemens D500 X-ray diffractometer at Materials Analysis and Research Laboratory (MARL) at Iowa State University. The diffraction pattern of as-synthesized ZrO$_2$ nanoparticles was collected from drop casted film on a zero-diffraction plate, whereas, pattern from plasma processed sample was collected from CNA spincoated on silicon substrate. XRD patterns were collected in 2θ range 20-60° by using 0.15DS, 0.05° steps, and 3s per step. For nanoparticle size analysis, diffraction pattern was collected in slow scan mode (0.03° steps and 20s integration) to improve peak-to-noise ratio. Accurate measurement of nanoparticles size using Scherrer equation was done following the procedure reported.[7]

Ellipsometry: The optical properties of nanocrystal films were characterized via spectroscopic ellipsometry that had a spectral range between 200 nm and 1600 nm. Ellipsometry spectra were obtained at three angles of incidence (65°, 70° and 75°) using a VASE ellipsometer (J. A. Woollam). The experimental spectra were fitted using a three-layer model, consisting of Si-substrate, native oxide and nanocrystal film. In
order to obtain the porosity of the nanocrystal film, an effective medium approximation (Bruggeman’s method) was used to represent the film as a composite material with two constituents (i.e., zirconia and air). The optical properties of zirconia were taken from Synowicki et al. The best fits were obtained when a thickness non-uniformity of around 8% was included for the nanocrystal film.

**Raman Spectroscopy**: Raman spectra of ZrO₂ films were collected using XploRA Plus confocal Raman microscope (Horiba Scientific, Edison, NJ) with a 25 mW 532-nm excitation source. A 50× (Numerical Aperture 0.50) long working distance objective (Olympus, Waltham, MA) and a 1200 gr/mm grating with a spectral range of approximately 900 to 3300 cm⁻¹ were used. The spectra were collected from the center of each film for 600 seconds with 2 accumulations. Two accumulations facilitate the removal of cosmic spikes. The spectrum of a bare silicon substrate was collected to background correct the ZrO₂ spectra.

**X-ray Photoelectron Spectroscopy**: The XPS measurements were performed using a Kratos Amicus/ESCA 3400 instrument. The sample was irradiated with 240W unmonochromated Mg Kα x-rays, and photoelectrons emitted at 0° from the surface normal were energy analyzed using a DuPont type analyzer. The pass energy was set at 150 eV and a Shirley baseline was removed from all reported spectra. CasaXPS was used to process raw data files. All spectra were energy calibrated with measured C 1s peak position at 284.6 eV.
**Scanning Electron Microscopy:** Scanning electron microscopy was performed with FEI quanta 250 field-emission SEM at MARL at Iowa State University. Imaging was done in secondary electrons mode at 10 keV with beam spot size of 3.

**Transmission Electron Microscopy/Scanning Transmission Electron Microscopy:** Transmission electron microscopy (TEM) and high resolution TEM images were obtained using 2007 JEOL 2100 200kV STEM in TEM mode, operating at 200 kV. This STEM is located at Microscopy and NanoImaging facility, Iowa State University and equipped with a Thermo Fisher Noran System 6 X-ray microanalysis system. Samples for TEM analysis were prepared by evaporating drops of dilute nanocrystals dispersion at room temperature, on a carbon-coated copper grid. Energy Dispersive X-ray (EDX) analysis were performed in STEM mode. Samples for EDX characterization were prepared by scraping off flakes of CNAs from the substrate using a sharp blade, and then attaching them on a carbon-coated TEM grid.

**Fourier transform infrared spectroscopy (FT-IR):** FT-IR spectra was collected using a spectrometer from Bruker Tensor 37 with a maximum resolution of 0.5 cm\(^{-1}\). A droplet of the nanoparticles dispersion was drop-casted on a polished salt plate. The plate was then mounted into the FT-IR chamber consequently flushing out the CO\(_2\) with N\(_2\) gas. The spectra were then collected in transmission mode with accumulation time of 3 mins.
**Ion Beam Analysis:** All ion beam analysis measurements were carried out at the Michigan Ion Beam Laboratory\[^{[87]}\] at the University of Michigan with the 1.7 MV Tandetron accelerator.

The elemental analysis of the samples throughout the film depth was determined by combining non-Rutherford elastic backscattering spectrometry (EBS) and elastic recoil detection (ERD) using a helium beam.

The EBS and ERD spectra were taken simultaneously at two different energies for each sample. A 3040-keV He\(^{++}\) beam was used for sensitivity to the oxygen signal through the EBS resonance at 3038.1 keV\[^{[88]}\]. Similarly, a 4290-keV He\(^{++}\) beam was used for sensitivity to the carbon signal through the EBS resonance at 4265 keV\[^{[89]}\].

The samples were mounted on a sample plate on the 5-axis goniometer of the 2 MV Tandem accelerator. The scattering angle of the EBS detector was 170° and of the ERD detector 30°. For each measurement, the beam incident angle was 70°. The filter in front of the ERD detector was a 24 µm thick foil of Kapton (C\(_{22}\)H\(_{10}\)O\(_5\)N\(_2\); density of 1.42 g/cm\(^3\)). The beam current on the samples during these measurements was ~20 nA with a beam spot of 1.5 mm by 1.5 mm.

The spectra were analyzed using Multi-SimNRA\[^{[90]}\] to get the depth profiles of the elements present in the film.
Figure S1. Altering the chemical composition of ligands through ligand exchange (LE). a. TEM image showing TOPO-capped ZrO₂ particles, b. TEM image showing Oleic acid-capped ZrO₂ particles after LE, c. No change in size of the nanoparticles after ligand exchange, d. FT-IR confirms the replacement of TOPO with Oleic Acid
Figure S2. XRD of the TOPO-capped and Oleic Acid capped ZrO$_2$ nanocrystals collected by depositing the nanocrystals solution on zero diffraction plate.
Figure S3. Full XPS spectrum of (a) TOPO-capped ZrO2 before and after ligand removal by plasma, (b) Oleic Acid-capped ZrO2 before and after ligand removal by plasma.
Figure S4. Calculated surface energies of plasma-processed particles through Kendall’s granular model
Figure S5. Deviation from the Arrhenius behavior of the rate constants when rate constant of 900°C is included for both (a) TOPO, (b) Oleic Acid particles.
Figure S6. XRD of plasma-modified TOPO-capped ZrO$_2$ nanocrystals films on silicon substrate. (a) showing monoclinic peak in the film sintered at 900°C for 48hrs, (b) showing monoclinic peak at 28° 2θ “pops out” only after prolonged heating at 900°C
Figure S7. Porosity data measured from Ellipsometry for the sintered film with (TOPO) and without (Oleic acid) phosphate layer.
Figure S8. Mechanical properties of sintered ZrO$_2$ nanocrystals films with and without phosphate layer at the interface. In abscissa, we have replaced the sintering temperatures with corresponding relative density.
CHAPTER 4

BUILDING MATERIALS FROM COLLOIDAL NANOCRYSTAL ARRAYS: EVOLUTION OF THE STRUCTURE, COMPOSITION, AND MECHANICAL PROPERTIES UPON REMOVAL OF LIGANDS BY O₂ PLASMA

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Abstract

This paper explains the structural, chemical, and mechanical evolution of films of colloidal nanoparticles (non-monoclinic ZrO₂, 3.7 nm diameter, disordered superstructure) upon exposure to an O₂ plasma (500 mTorr, 7 W, 6 h to 168 h of exposure). The particles in the arrays are initially separated by organic ligands (trioctylyphosphine oxide, TOPO) that bind to the particle’s surface through the phosphine oxide group. The plasma removes the alkyl tails of the ligands over the course of several hours (carbon concentration is 1.3 ± 0.5 at. % after 168 hrs). Before finally settling into an all-inorganic polycrystal, the arrays go through an intermediate,
highly porous state (~0.5 void fraction) where the particles are joined by necks of ligand molecules. Characterization of the mechanical properties through substrate-corrected nanoindentation\textsuperscript{[26, 27]} and the subsequent analysis through the mechanical model of Kendall et al.\textsuperscript{[72]} indicate that the arrays behave as granular matter before processing as well as after the complete removal of the ligands, albeit with radically different moduli and hardnesses (modulus, $E$: 2.2 ± 0.3 vs 44.5 ± 2.6 GPa; hardness, $H$: 0.1 ± 0.02 vs 2.2 ± 0.1 GPa). This intermediate state displays non-granular behavior with ~4 times the strength of a granular system of same porosity. The highly porous state obtained after ligand removal result in high surface area materials with 100% crystallinity, good mechanical properties, and bare inorganic surfaces that could be very attractive for any application involving interface processes (e.g., energy storage, photovoltaics, catalysis) and the study of these processes as a function of material structure.

Main Text

The design of materials is the goal of materials engineering and the purpose of materials science. We\textsuperscript{[91]}, and others,\textsuperscript{[29, 37, 92]} believe that this goal must ultimately reach the nanoscale, where absolute control is still conceivable (atomic-level control might be fundamentally prohibited by the second law of thermodynamics). By “designing materials” at the nanoscale, we mean the ability to program independently the (i) composition (unary, binary, etc...), (ii) grain size distributions (<5 % polydispersity), (iii) grain shape, (iv) arrangement of grains, (v) composition of grain boundaries, and (vi) defect distribution. To attain such a level of control, materials manufacturing might have to fundamentally change. Most current materials manufacturing
approaches rely on nucleation in bulk systems (e.g., cooling of melts, reaction of precursors), which is stochastic and yields broad grain-size distributions. We reported an approach to produce nanostructured polycrystals in the form of films\cite{13,23,24,93,94} by first crystallizing the “grains” first as ligand-capped nanocrystals synthesized in solution as colloids, then depositing them by self-assembly, and finally removing the ligands by plasma processing (i.e., “nanocrystal plasma polymerization”, NPP\cite{13,23,24,93}). In comparison to plasma processing, thermal processing to convert colloidal nanoparticle arrays into all-inorganic solids is limited by well-known issues associated with kinetics (e.g., the carbonization of ligands due to insufficiently rapid diffusion of oxygen into the system or due to pores becoming occluded by sintering\cite{95}) as well as thermodynamics (e.g., particle growth due to the melting point depression expected through the Gibbs-Thompson equation,\cite{95-97} and deterioration of particle morphology due to sintering). Plasma processing operates instead far from equilibrium and is therefore not bound to push the material towards its equilibrium state (i.e., large grains, fewer interfaces). The issues associated with thermal processing affect the applicability of the products\cite{96,98} (e.g., limiting the deployment on organic substrates\cite{96}) and their relevance for the study of interface-mediated and grain-size-mediated processes (e.g., products are composite with black carbon, and control over grain size is compromised).

Since our approach bypasses stochastic bulk nucleation and prevents grain growth by operating close to room temperature (\textdegree{}40-60C), it can form polycrystals with uniform, nanoscale grain sizes,\cite{94} but the evolution of the structure, composition, and cohesiveness of the films during the removal of the ligands is unclear. For example,
it is not known whether trace amounts of carbon remain behind between the particles, whether bonds are formed between the particles, and how the plasma successfully removes organics from the inside of these films. In this work we answer these questions by an integrated analysis of the morphology, composition, and mechanical properties of colloidal nanocrystal assemblies during the removal of the ligands by O₂ plasma.

We used ZrO₂ nanoparticles (Figure 1a, diameter = 3.7 ± 0.3 nm, ligand = trioctylphosphine oxide (TOPO), concentration = 114 mg/ml) as our building blocks due to the interesting mechanical properties of their bulk phase (elastic modulus = 200 GPa for 3Y-TZP\textsuperscript{[99]}, hardness = 8-10 GPa\textsuperscript{[100]}), the remarkable colloidal stability of their dispersions, the high yield of the reaction that produce them (\textasciitilde47 \%),\textsuperscript{[41]} and the high dissociation energy of the Zr-O bond (\(\Delta H_{f,298} = 760 \text{ kJ/mol}\textsuperscript{[101]}) which would make the material resistant to sputtering by plasmas. The films were spin-coated from a hexane dispersion to form disordered, crack-free, 350-nm-thick (\textasciitilde74 particle layers) CNAs (Figure 1b). The films were then processed by a dilute plasma (O₂ feed gas, 500 mTorr, 7 W) for 6, 12, 24, 48 and 168 hrs (replicates = 4). The chemical composition was characterized by ion beam analysis (IBA) to yield compositional profiles throughout the thickness of the films, while the mechanical characterization was performed by nanoindentation.
Figure 1. Plasma processing (NPP) of disordered colloidal nanocrystal assemblies (CNAs). a) Colloidal nanocrystals are synthesized in solution. The TEM image shows 3.7 nm ZrO$_2$ nanoparticles used in this work. b) The colloids are self-assembled by spin-coating from hexane, leading to a disordered assembly that prevents cracking. Cross-sectional SEM display uniform, and smooth film and TEM imaging shows the nanostructure of the CNA. c) The ligands separating the nanoparticles are removed by plasma etching, leading to a crack-free all-inorganic polycrystal. Cross-sectional SEM display the reduction in thickness after ligand removal and TEM imaging shows the homogeneous grain size of the CNA.

The exposure of materials to plasma leads to four types of processes:\[102]\ (i) sputtering, by which active species in the plasma remove atoms from the surface, which can then redeposit on the film or be removed in the gas phase, (ii) bond cleavage,
which can cause the crosslinking of organic backbones and the formation of volatile species, which are then removed in the vacuum, (iii) plasma polymerization of volatile species in the plasmas, which can then redeposit on the material, and (iv) chemical reaction of active species in the plasma with the exposed surfaces.

Figure 2a shows the change in the total amounts of C, Zr, O, P, and Cl (from the ZrCl$_4$ precursor), expressed as atoms/cm$^2$ of films, as a function of the duration of the exposure to the plasma. The error bars indicate 95% confidence interval on the average value of three separate locations on each sample. These data show that (i) carbon (and H, not shown) is selectively removed from the film down to ~1 at.% (which can be accounted for by adventitious carbon), (ii) the nanoparticle cores are not ablated from the films (Zr and O are not decreasing), and (iii) phosphorus from the ligands is unaffected by the plasma.

A deeper look into the data provides substantial information on the structural and chemical transformation of the system during plasma processing. The ratio between O and Zr changes from 2.71 to 2.47 during the processing, indicating the presence of a significant amount of oxygen not associated with ZrO$_2$, which is attributed to H$_2$O in the ligand shells (TOPO is hygroscopic$^{[103]}$) and on the surface of the nanoparticles (ZrO$_2$ has a large surface energy of 1.02 J/m$^2$ $^{[78]}$). The processing and characterization of the samples by IBA were separated by ~90 days in atmosphere. For the fully processed sample there is less than one carbon for each phosphorus in the film: some of the excess oxygen is expected to be bound to phosphorus as the carbon is etched, since O$_2$ is the feed gas.
The amount of phosphorus in the system corresponds to a capping fraction (i.e., fraction of surface Zr atoms coordinated by ligands) of 34 ± 2%.

The removal of carbon is homogeneous throughout the thickness of the film. The reconstructed [C] profiles in Figure 2b show [C] in units of atom% as a function of the thickness of the films expressed in TFUs (thin film units, or 10^{15} atoms/cm^2; IBA cannot detect voids directly, so the thickness information from Figure 2b is not quantitative). The plot shows that (i) the concentration of carbon is remarkably constant between the substrate (bottom of the plot, TFU = 0) and the top surface (straight black line at the top of each colored region), (ii) the thickness of the film decreases during processing.

Somewhat counterintuitively, while the films compact during processing, they also get more porous. The loss of film volume (Figure 2c, black open circles) shows that the films lose up to 46% of their volume, without cracking. On the other hand, the pore volume (Figure 2c, grey open squares) increases from 25% to about 54% after 48 hrs to then decrease again to 36% for the fully processed film. The fraction of volume occupied by air was calculated as the difference between the volume determined by microscopy and the volume of the condensed phases (i.e., ZrO_2, ligands, H_2O) detected by IBA, assuming bulk densities for ZrO_2 and water, and estimating the density of the ligands as intermediate between that of TOPO and that of phosphate, depending on the fraction of carbon left on the ligands. The calculated volume fraction of the particles (i.e., ZrO_2 + ligands) for the fully processed material (62% after 168hrs) is remarkably consistent with that of a random close packed solid (64%)[104]. The filling fraction of the 168hrs film was confirmed by ellipsometry at 59%.
The increase in porosity during compaction can be understood by considering the effect of plasma processing on arrays of larger polymer colloids. In the unprocessed CNAs the porosity is relatively low because the ligands effectively fill the space between the particles. If the ligands are preferentially etched from the larger interstices, the etching results in the creation of pore space (Figure 2d). The substantial decrease in pore volume (~20 %) between the 48 hrs sample and the 168 hrs sample is only accompanied by a drop in carbon concentration of 4%, suggesting that this last bit of carbon is associated with “necks” between particles. Plasma processing of larger spherical colloids showed precisely this increase in porosity due to the formation of “necks”. Particle sintering is not responsible for film compaction in these late stages of plasma processing. Scherrer analysis of the X-ray diffraction data demonstrates that the nanoparticle do not grow in size even after 48 hrs of plasma processing, consistently with the low temperatures (<60 °C) experienced by the sample (cf. Supporting Information). The persistence of porosity during ligand removal might explain the ability of plasma to etch the ligands hundreds of nanometers deep into the film.
Figure 2. Chemical and structural characterization of the nanocrystal assemblies during plasma processing. a) Areal concentrations of Zr, O, P, C and
Cl as a function of processing time. b) Thickness dependence of the C concentration in the film for four different processing times. c) Graph of the total volume loss of the film (black open circles) and pore volume (grey open squares) as a function of the processing time. d) Schematic of the proposed structural changes caused by plasma.

Mechanical characterizations of CNAs have always been performed in the presence of the surface-bound ligands, where they largely dominate the mechanical properties.\textsuperscript{[106, 107]} Our ability to selectively etch or modify the surface-bound ligands by plasma processing provides us the opportunity to systematically characterize the evolution of the interaction between nanoparticles in the CNA as the ligands are progressively polymerized and removed by plasma etching. The modulus E and hardness H of the unprocessed and fully processed films are shown in Figure 3a, and 3b respectively, as a function of the indentation depth (cf. the Supporting Information for the data at the intermediate processing times). The contribution of the substrate was accounted for through a previously reported analytical model.\textsuperscript{[27]} Both modulus and hardness increase by over an order of magnitude as a result of the removal of the ligands (Figure 3c). The observed E (blue) and H (red) are compared with those of relevant materials (e.g., several polymers,\textsuperscript{[108, 109]} colloidal nanoparticle superlattices,\textsuperscript{[106]} and bulk 3Y-TZP\textsuperscript{[99, 100]}). The modulus of the ZrO$_2$ CNAs increases from $2.2 \pm 0.3$ GPa (similar to hyperbranched polyester, $2.2$ GPa\textsuperscript{[109]}) to $44.5 \pm 2.6$ GPa (22 % of bulk 3Y-TZP\textsuperscript{[99]}) and the hardness increases from $0.1 \pm 0.02$ GPa (again, similar to hyperbranched polyester, $0.13$ GPa) to $2.2 \pm 0.1$ GPa (22 % of bulk 3Y-TZP\textsuperscript{[109]}). The adhesion of the films to the substrate is very good as demonstrated by scratch testing (cf. Supporting Information).
Several models have been proposed and tested for describing the mechanical properties of granular films. In a very elegant work, Kendall et al. reported a model that describes the modulus of granular systems as a function of the average particle size $d$, the interfacial energy $\Gamma$ (where, for identical solids in contact $\Gamma = 2\gamma$ where $\gamma$ is surface energy in J/m$^2$), the particle filling fraction $\phi$, and the bulk modulus $E_b$ as

$$E = 17.1\phi^4 \left[ \frac{\Gamma E_b^2}{d} \right]^{\frac{1}{3}}$$

The model was primarily developed to calculate the surface energy of solids by measuring the enlargement of the Hertz elastic contact circle due to the adhesive force between lightly loaded, uniform, and smooth spherical particles. Kendall assumed that the model would be valid for particle sizes less than 1µm since those particle sizes show a tendency to adhere. Due to the large power dependence, the model’s applicability is largely limited by the accuracy with which the filling fraction is determined. In our case the filling fraction was calculated from a thickness measurement (by SEM of film cross-sections, error of 5%) and from IBA data (which are remarkably accurate to 1% - 10% of the obtained TFUs depending on the element).
Figure 3. Mechanical characterization of CNAs during ligand removal. Substrate-independent modulus (a) and hardness (b) of the films as a function of indentation depth for the unprocessed and fully processed films. The thin grey curves show the result of each indentation experiment. The thick curves are the averages over the replicates. c) Modulus (blue circles) and hardness (red squares) of the films as a function of processing time. The straight lines indicate the
modulus (blue) and hardness (red) of representative materials (polymers, straight lines; bulk crystals, dotted lines; nanocrystal superlattices, dashed lines).

The model was applied with the following assumptions. There are three types of samples: unprocessed (0hrs), partially processed (6-48hrs), and fully processed (168hrs). In the unprocessed case, the bulk modulus $E_b$ was assumed to be that of an entangled polymer (hyperbranched polyester, 2.2 GPa \[^{[109]}\]), the surface energy $\gamma$ to be that of TOPO (0.035 J/m\(^2\) \[^{[110]}\]), and the particle size $d$ to be that of the core and two half lengths of the TOPO molecule (3.7 nm + 1 nm; our previous work shows the distance between these particles in the film is \(\sim 1\)nm\[^{[94]}\]). The agreement between model and experiment is very good (2.1 GPa vs 2.2 GPa) as shown in Figure 4a. In the fully processed case, $E_b$ was assumed to be that of 3Y-TZP (200 GPa \[^{[99]}\]), $\gamma$ to be that of a common phosphate (hydroxyapatite, 0.33 J/m\(^2\) \[^{[76]}\], 33% of the Zr sites on the surface are capped with phosphorus so that two surfaces facing each other would create a near-continuous layer of phosphate), and $d$ to be that of the ZrO\(_2\) core (3.7 nm). The agreement for these samples is still remarkably good (49.5 GPa vs 44.5 GPa). It is worth noticing that using ZrO\(_2\)’s surface energy (1.02 J/m\(^2\) \[^{[78]}\]) instead of phosphate’s yields a significant (64 %) discrepancy from the observed results.

The granular model instead fails to describe the partially processed films (Figure 4a) and underestimates the modulus of the films by up to \(\sim 4\) times even when the bulk modulus $E_b$ is overestimated to be that of 3Y-TZP (200 GPa \[^{[99]}\]), and the surface energy and the particle size are assumed to lie in between those of unprocessed and fully processed cases, depending on the fraction of carbon left in the film.
Since $\gamma$ is the main unknown in the model’s equation, it is instructive to plot the values of surface energy that provide agreement between modeled and experimental moduli (Figure 4b). The fitted value for $\gamma$ in the unprocessed film is 0.03 J/m$^2$, which is remarkably close to the values of several polymers as well as to the surface energy of TOPO. The fit value for the fully processed film is 0.18 J/m$^2$, which is about half the value of hydroxyapatite (this 50% discrepancy can be accounted for by surface water as described in the original work of Kendall et al.$^{[72]}$). The surface energies obtained for the partially processed films (>30 J/m$^2$) are significantly larger than the highest known surface energy for common materials (tungsten, 3.68 J/m$^2$$^{[111]}$).

The discrepancy between model and experiment in the partially processed films is significant. Kendall’s model considers the particle’s interactions to be mainly due to interfacial energy (i.e., adhesion). The presence of bonds between the particles, like those that are likely formed by crosslinking of the ligands by the plasma (crosslinking of organic substrates by plasma exposure precedes etching$^{[102]}$) would significantly increase the modulus of the system beyond what expected from a granular system. Furthermore, Kendall’s model uses geometric arguments that imply that the particles are convex, while the presence of necks in the partially processed CNAs would yield much higher porosities for the same contact areas between particles, therefore leading to an underestimation of the modulus.
Figure 4. Granular model of mechanical properties of CNAs. a) Graph of the observed (filled circles) vs modeled (empty squares) moduli for the CNAs as a function of the processing time. The modeled data was obtained by making assumptions about the interface energies in the films. b) Graph of the surface energy calculated from the model of Kendall et al. to justify the observed moduli.

In summary, we have demonstrated that the mechanical properties of assemblies of ligand-capped colloidal nanoparticles can be understood by a granular model in which the surface energy is the major source of interaction, thereby suggesting
that ligand interdigitation does not play a dominant role, at least in the plastic deformation regime. These assemblies can be entirely stripped of their ligands by plasma processing, leaving behind porous assemblies of bare nanoparticles interacting exclusively by adhesion. Also in this case the mechanical properties are predicted quantitatively by a granular model and are found to be sensitive to the specific composition of the interfaces. Intermediate stages of ligand etching by plasmas yield open composites with strengths that are much superior (4 times) to those expected from granular systems, consistently with the formation of necks of crosslinked ligands separating the particle cores. The quantitative agreement between Kendall’s model and our measurements on fully ligand-etched CNAs suggests that a combination of IBA and substrate-corrected nanoindentation experiments on plasma-processed CNAs can also be a valuable and maybe unique tool for the characterization of surface energies of bare nanocrystal surface. The resulting highly porous, high surface area, fully crystalline films are highly attractive for application in energy storage, photovoltaics, and catalysis.

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Materials and Method

Ellipsometry

The optical properties of nanocrystal films were characterized via spectroscopic ellipsometry that had a spectral range between 200 nm and 1600 nm. Ellipsometry spectra were obtained at three angles of incidence (65°, 70° and 75°) using a VASE ellipsometer (J. A. Woollam). The experimental spectra were fitted using a three-layer model, consisting of Si-substrate, native oxide and nanocrystal film. In order to obtain the porosity of the nanocrystal film, an effective medium approximation (Bruggeman’s method \cite{85}) was used to represent the film as a composite material with two constituents (i.e., zirconia and air). The optical properties of zirconia were taken from Synowicki et al.\cite{86}. The best fits were obtained when a thickness non-uniformity of around 8% was included for the nanocrystal film.

Nanoindentation

All nanoindentation testing was done with a Keysight G200 Nanoindenter, configured with the continuous-stiffness-measurement (CSM) option, a DCM II head, and a Berkovich indenter. The CSM option superimposes an oscillation (75Hz, 1nm) on the semi-static loading profile, so that every indentation test returns a complete depth profile of Young’s modulus and hardness. Ten indentation tests were performed on each sample. Loading was controlled such that the loading rate divided by the load (P’/P) remained constant at 0.1/sec; loading was terminated when the indenter reached a penetration depth of 125 nm.

Upon completion of testing, the depth profile of Young’s modulus was corrected for the influence of the silicon substrate in accordance with the Hay-Crawford
model\textsuperscript{[27]}. From the depth profiles of corrected Young’s modulus and hardness, scalar values were reported using measurements made when the indenter penetration was 20\% of the film thickness.

**Scratch Test**

Scratch testing was done with an MTS Nanoindenter XP, fit with a conical indenter having an included angle of 90° and an apical radius of 2\µm. Five controlled scratches were performed on the sample. Scratch test consisted of three steps:

1) The indenter was used to perform a line profile of the scratch path.

2) The tip returned to the origin (of the scratch path) and the controlled scratch was performed along the same path.

3) The indenter returned to the origin and again profiled the scratch path to evaluate residual deformation.

The effect of the scratch is evaluated by the residual deformation measured in the second and third steps of the test and by visual inspection of the scratch, post-test, under an optical microscope (10X magnification).

The entire length of the scratch path was 420\µm long; thus, steps 1 and 3 were profiles of this length. The profiling force was 10mN, and the profiling velocity was 10\µm/sec. The controlled scratch (step 2) consisted of three segments: a 60\µm profile, followed by a 300\µm ramp-load scratch, followed by a 60\µm profile. The profiling segments on either end of the proper scratch are for the purpose of leveling the displacement data measured during the scratch. Over the distance of the proper scratch (300 \µm), the load on the indenter was linearly increased from the profiling
force to the peak force (80mN) while the indenter traversed the surface at a velocity of 10µm/sec.

**Ion beam analysis**

The elemental analysis of the samples throughout the film’s depth was determined by combining non-Rutherford elastic backscattering spectrometry (EBS) and elastic recoil detection (ERD) ion beam analysis techniques at the Surrey Ion Beam Centre. The samples were mounted on a sample plate on the 6-axis goniometer of the 2 MV Tandem accelerator\[57\]. Two particle detectors were used at backscattering angles of 172.4° (DetA) and 147.7° (DetB), measured with an accuracy of 0.2° using the goniometer with an in-line laser. The solid angles of detection were 2.6 ± 0.1 and 3.1 ± 0.3 msr for DetA and DetB, respectively. A third particle detector (ERD; DetC) was mounted at a scattering angle of 30.8° with a foil of 31.0 µm of Kapton (C\(_{22}\)H\(_{10}\)O\(_5\)N\(_2\); density of 1.42 g/cm\(^3\)). Its solid angle of detection was 0.8 ± 0.1 msr.

Each sample was analyzed in three different locations and each location was measured in two different geometries of detection: namely, spectra were collected from the DetA & B using a 4He beam at 3.05 MeV for sensitivity to the oxygen signal through the EBS resonance at 3038.1 keV\[58\]; then the samples were analyzed using a 4He beam at 4.3 MeV for sensitivity to the carbon signal through the EBS resonance at 4265 keV\[59\] and recording the spectra from the DetA, B & C. The samples were relocated at the same positions for both analyses. The incident beam direction was close to the normal at the sample at 3 MeV, while the sample was titled by 70 degrees toward the DetC for the analysis carried out at 4.3 MeV. For both analyses, the beam spot size was about 1.5 × 1.5 mm\(^2\) and the beam intensity was between 10 and 30 nA.
For each measurement point, the set of 5 spectra was self-consistently analyzed using DataFurnace\textsuperscript{[60]} to take advantage of the synergy between EBS and ERD techniques\textsuperscript{[61]}. The elemental analysis presented in this work are the average of the three measurement points performed on each sample.

Ion Beam Analysis provides accurate areal concentration values - expressed as \(\text{atom/cm}^2\) - without making any assumption. These concentrations has been used to determine the atomic density, \(N\,\text{(atom/cm}^3\text{)}\) and then conversion to mass density, \(\rho\,\text{(gm/cm}^3\text{)}\) of a film as follows:

\[
N = \frac{\text{areal concentration(\text{atom/cm}^2)}}{\text{thickness(cm)}}
\]

where, thicknesses of the films were determined by cross-sectional SEM images

\[
\rho = \frac{\sum N_i \times A_i}{Na_{\text{vogadro}}}
\]

where, \(A_i\) = atomic weight of each element

**X-ray diffraction**

Powder X-ray diffraction (XRD) was performed with Siemens D500 X-ray diffractometer at Materials Analysis and Research Laboratory (MARL) at Iowa State University. The diffraction pattern of as-synthesized \(\text{ZrO}_2\) nanoparticles was collected from drop casted film on a zero diffraction plate, whereas, pattern from plasma processed sample was collected from CNA spin coated on silicon substrate. XRD patterns were collected in \(2\theta\) range 20-60° by using 0.15DS, 0.05° steps, and 3s per step. For nanoparticle size analysis, diffraction pattern was collected in slow scan mode (0.03° steps and 20s integration) to improve peak-to-noise ratio. Accurate measurement
of nanoparticles size using Scherrer equation was done following the procedure reported\[7\].

**Scanning electron microscopy**

Scanning electron microscopy was performed with FEI quanta 250 field-emission SEM at MARL at Iowa State University. Imaging was done in secondary electrons mode at 10 keV with beam spot size of 3.

**Transmission electron microscopy**

High resolution Transmission electron microscopy (TEM) images were obtained using 2007 JEOL 2100 200kV STEM in TEM mode, operating at 200 kV. This STEM is located at Microscopy and NanoImaging facility, Iowa State University and equipped with a Thermo Fisher Noran System 6 X-ray microanalysis system. Samples were prepared by scraping off flakes of CNAs from the substrate using a sharp blade, and then attaching them on a carbon-coated TEM grid.

**Supporting Figures**

![X-ray diffraction (XRD) pattern of ZrO₂ nanocrystals film](image)

**Figure S1.** X-ray diffraction (XRD) pattern of ZrO₂ nanocrystals film. a. as-synthesized ZrO₂ nanocrystals showing non-monoclinic phase, b. High resolution XRD spectrum shows no discernible effect on particle size after
exposure to oxygen plasma for 48hrs (peak position changes from 30.16±0.02 to 30.14±0.02 and peak width from 2.90±0.05 to 2.86±0.05).

**Figure S2.** Nanindentation results of plasma processed ZrO$_2$ CNAs. Showing indentation load as a function of indentation depth after different exposure to oxygen plasma.
Figure S3. Substrate-independent modulus and hardness profile of plasma processed ZrO$_2$ CNAs. Profile of intermediate stages of plasma treatment a. 6 hrs, b. 12 hrs, c. 24 hrs, d. 48hrs. n denotes the number of indentation measurements made on the samples.

Figure S4. Scratch test to assess the adhesion of 48hrs plasma processed ZrO$_2$ CNA. a. Optical micrograph of 5 scratches made on the film forming channels, showing no optical evidence of delamination along the scratch track, b. Normal force and penetration depth as function of scratch length, does not show any change in the slope of penetration depth which are indicator for coating failures.
Figure S5. Top-view and cross-sectional SEM images of CNAs showing no evidence of either cracks or delamination. Cross-sectional imaging was performed by fracturing the silicon substrate, even after that CNAs remains remarkably adherent to the substrate. a & c. Unprocessed, b & d. After plasma processing.
Introduction

Creation of materials with a controlled microstructure is hindered by a fundamental limitation that is the stochastic process of nucleation. We have demonstrated in our earlier chapters that processing colloidal nanocrystal assemblies (CNAs) with plasmas allows to create materials with a designed nanostructure. Colloidal nanocrystals are ligand-capped nanocrystals synthesized in solution, and deposited by self-assembly on a substrate/template of choice. Ligands are typically...
composed of a long hydrocarbon chain (similar to polyethylene) with a functional group that binds to the particle’s surface.

Plasma can etch ligands to several hundreds of nanometers deep into the CNAs, but the process requires days to reduce the concentration of carbon, [C], from \( \sim 20 \text{ at.}\% \) to \(<1 \text{ at.}\% \) \cite{70}. Scaling our process to bulk materials will need a drastic improvement in the etching rates.

In order to figure out the kinetically limiting mechanisms, we first need to understand how the plasma etches the ligands from the CNAs, which are typically microporous/mesoporous materials (pore size between \( \sim 1 \) and \( \sim 5 \) nm, depending on particle size and arrangement). The plasma etching of CNAs is fundamentally different from the plasma processing of nonporous solids. In nonporous solids, etching occurs by a combination of chemical (e.g., by radicals) and physical (e.g., bombardment, UV) mechanisms. CNAs are instead porous systems (\( \sim 20-40\% \) porosity) with a connected porosity (most nanocrystal shapes cannot fill space), so that active species can diffuse throughout the film to etch the ligands.

Our earlier work showed that the etching of ligands from CNAs of ZrO\(_2\) nanocrystals (spherical shape, 3.1 nm diameter, capped with trioctylphosphine oxide) with O\(_2\) plasmas is an homogeneous process that yields no compositional gradients across the thickness of the CNA (between 190 nm and 230 nm). This result suggested that the etching of the ligands occurs at the same rate throughout the volume of the CNA. The pore volume of the nanocrystal arrays increases to 54\% (in a partially-processed film) from 25\% (unprocessed film) and then decreases to 38\% in the fully processed film. The increase in porosity is associated with the formation of “necks”
between the particles \[^{70}\]. While the increase and persistence of the porosity could explain the homogenous etching of ligands deep into the films, it did not elucidate the kinetics of etching and its rate limiting step.

Plasma is a complex system. It contains various species i.e. electrons, ions, photons, radicals, excited molecules, and atoms. In order to draw conclusion on the etching mechanism, we need to first isolate and study the role of each species on carbon etching. Ions will be typically neutralized on the particle surfaces, converting to their neutral form \[^{112}\]. Their penetration depth is typically less than 1nm and their effect is mostly restricted to the top surface of a film \[^{113}\]. Energetic electrons will be blocked at the top surface of ZrO₂ CNAs, typically due to the ion-electron recombination at the surface \[^{114}\]. Radicals/excited species and photons can penetrate deep into the material through diffusion and transmission. Vacuum ultraviolet (VUV) are known to cause chemical modification of organics: they can cause C-C bond scission, but requires reactive gases to yield volatile species. \[^{112, 113}\] Radicals/excited species are the longest-lived species in the plasma, but must diffuse into the CNAs to react.

Here, we have isolated and investigated the role of different possible mechanisms on etching kinetics, and use that information to demonstrate a vastly accelerated etching. We find that radicals/excited species and UV (especially VUV) are responsible for etching of ligands. In He plasmas, the etching appears to be especially driven by UV degradation. Etching kinetics was limited by the depletion of radicals/excited species in the CNAs caused by the saturation of the pores with etching by-products. Similar decrease in the etch rate at narrow trenches has been seen in reactive ion etching (RIE) which is termed as micro-loading \[^{115}\]. Among other strategies
(increasing the chamber size to increase the residence time of active plasma species or add nitrogen or fluorine containing gases to increase the oxygen atom density in plasma), we have dealt the problem of depletion of radicals/excited species simply by charging fresh reactants inside the plasma chamber and, most importantly, into the pores of the CNA by employing pressure oscillations.

**Figure 1.** Cartoon showing the species present in plasma but the question is which of these species etches the ligands deep down into the CNAs and how can we control them. Bottom right is non-Rutherford elastic backscattering spectrometry (EBS) spectra of as deposited and oxygen plasma treated ZrO₂ CNAs, showing complete removal of carbon and film thickness reduction due to carbon loss seen inferred from reduction in channel width of zirconium peak.
Experimental Design

In order to understand the role of plasma species in ligand etching, we decided to approach the problem by selectively removing the influence of certain species in control experiments and then comparing the extent of ligand etching as measured by RBS. The species allowed to interact with the CNA can be controlled by appropriately chosen and placed masks\(^{[116]}\). The representation of the set-up is shown in the Figure 2 (a). We used Mylar sheets (50 μm thick, placed at the four corner of the 1.4x1.4 cm samples) to create a known gap between the CNA and the mask. The gap is required to allow the etching byproducts to escape from the CNA. We found the minimum gap size by using films of rhodamine B dye on glass as test samples. We have placed an Al\(_2\)O\(_3\) substrate to block all the plasma generated species except radicals/excited molecules. We have kept all the plasma condition same and adjusted the gap distance by varying the thicknesses of the Mylar sheets which are placed at the four corners of glass substrate. We have found that 6μm and 25μm gap created by Mylar sheets prevented complete etching of dye whereas with 50μm Mylar sheet no sign of film on the substrate. That’s how we decided to have a gap of 50μm between the window and film as shown in Figure 2(a).

Saturated polymers like polyethylene or polypropylene typically absorb strongly in VUV (1-200nm)\(^{[117]}\). The energy of the photons in VUV spectral range (1230eV–6eV) is sufficient to break C-C bonds\(^{[118]}\). At wavelength <120nm, the photons energy (~10eV) is sufficient to ionize organic molecules\(^{[117]}\). We have used MgF\(_2\) (25mm Ø by 2mm, Crystran Ltd., transmit wavelength >120nm) and quartz (25mm Ø by 2mm,
Crystran Ltd., transmit wavelength >180nm) windows, to understand the effect of VUV on ligand etching.

To understand the rate limiting step in the etching kinetics we characterized the carbon etching rate as a function of the composition, concentration, and energy of the species in the plasma. To do so, we used pressure, power, and feed gas as experimental parameters. We varied the pressure from 100mTorr to 2000mTorr, power from 7W to 30W, exposure time from as low as 60s to 48hr, and helium and oxygen as feed gases.

Plasma power linearly affects the energy and density of plasma species \([112, 117, 119]\). Increase in plasma power can translate directly into faster carbon etching rate\([112]\). The density of plasma species is also controlled by pressure in the chamber which is manipulated by the flow rate of feed gas \([120, 121]\). Pressure also affects the mean free path of the electrons \([119, 120]\): at lower pressures (<100mTorr or lower flow rate) the mean free path is larger (less recombination sites in the form of gaseous molecules) but there are fewer reactive species; at higher pressures, mean free path of electron is shorter, which leads to lower kinetic energies (i.e. reduced electron temperature), and fewer reactive species. So, it is expected that the density of active species is maximized at some intermediate pressure. Photon density typically decreases at higher pressures due to the lower kinetic energy of electrons, and the increased rate of absorption (due to higher concentration of the gas) \([113]\).

Feed gas defines composition, density, and energy of the active species. \(O_2\) plasma aggressively etches organics through chemical reactions, whereas \(He\) has much stronger emission in the UV and VUV range, especially when compared to \(O_2\) plasma.
Some nanoparticles compositions may not allow the processing though O₂ plasma due to their propensity to oxidation, hence non-oxidative plasmas like He plasmas are highly interesting. Furthermore, since He is a very light element, damage on the top surface of the CNA from ablation can be excluded even on softer materials. The onset of ablation is the one most significant issue that prevents increasing the power of plasmas to increase etching rates. We can also apply higher power during He processing to accelerate etching rate without being concerned about ablation.

The plasma study is done on ZrO₂ CNAs (~3nm diameter, ligand: trioctylphosphine oxide – TOPO, CNA thickness: ~320nm). The synthesis of tetragonal ZrO₂ (t-ZrO₂) nanocrystals was conducted as previously reported [71]. t- ZrO₂ (metastable phase) is an important and extensively studied functional oxide material for its mechanical, thermal, and catalytic properties. ZrO₂ is fairly transparent in the UV range of 220-250nm with an expected penetration depth for 200nm photons to be ~10µm.
Results and Discussion

Role of plasma species on the processing of CNAs

Figure 2. Role of plasma species in ligand etching. (a) Schematic showing the cross-sectional view of how we isolated the plasma species to study their effect, (b) Histogram showing the carbon concentration in thin film units (TFUs) after processed under various window conditions for oxygen and helium feed gas respectively. $\text{TFU} = 10^{15} \text{ atoms/cm}^2$

Figure 2(b) shows carbon concentration in TFUs extracted from Ion Beam Analysis (IBA) of the CNAs. We can see from the data that there is no discernible effect of VUV on ligand etching during $O_2$ exposure, whereas VUV has significant effect on etching during He exposure. This is attributed to strong emission of VUV in He plasma compare to $O_2$ plasma $^{[122]}$. With quartz window, we can nearly prevent etching in He processing. These results also point us that etching mechanism is entirely different in these plasmas. Most likely, helium etching proceed by demethylation of organic molecules mostly by VUV, but it appears to be dominated by radicals/excited species for oxygen plasma.
Effect of plasma composition and density on etching kinetics

Figure 3. Effect of plasma composition and density on etching kinetics. (a) Effect of power and gas composition can be clearly seen in carbon etching rate only until 1hr of processing, (b) pressure do have effect on carbon etching but only until first few minutes of etching, (c) & (d) etching rate differential
showing carbon etching rate continuously decreases nearly at same rate irrespective of power, pressure or gas composition, (e) etch rate differential at different plasma pressure calculated as $|\text{ABS}(2000\text{mTorr-500mTorr})+\text{ABS}(500\text{mTorr-100mTorr})+$ $\text{ABS}(2000\text{mTorr-100mTorr})$

Complete removal of the ligands from ~350nm thick CNAs can be obtained in 6hrs instead of 7 days with proper optimization of the processing parameters. The corresponding RBS spectra are shown in Figure 1. Over time scales of hours, the etching rate was found to be faster in oxygen rather than in helium as can be seen in Figure 3(a) & (b). [C] after oxygen and helium plasma was 1.5 at.% and 6.8 at.% respectively with similar plasma processing conditions (30W, 500mTorr, 6hr). The etching of ligands by O$_2$ plasma possibly proceeds by radical site generation by abstraction process by oxygen radicals and photons, formation of oxidative derivatives by reactions with oxygen atom/molecules/radicals, and finally scission to form low molecular weight products like CO, CO$_2$, ROOH, ROH, ROO, etc. $^{[117, 122]}$. He plasma etching of ligands proceeds most likely by interaction of helium metastable species and VUV with ligands, that leads to hydrocarbon and hydrogen radicals generation, which then reacts to form H$_2$ (which can then become the part of the plasma) or a lower molecular weight species, that can evaporate from the system $^{[123]}$. The presence of H$_2$ in the plasma can then have a disproportionate effect on VUV emission $^{[122]}$ as well as on the etching chemistry$^{[112]}$.

Figure 3a and 3b illustrate vividly the drastic decrease in etching rates (from $10^3$ TFU/hr to $10^1$ TFU/hr) over the course of few hours. Obviously, if the initial etch rates could be maintained, complete ligand removal could be obtained well within an hour. An initial hypothesis is that the drop in etch rates could be attributed to the
depth dependence of the etch rates, i.e., that the ligands close to the exposed surface of the CNA will etch faster than those close to the substrate. This hypothesis is not supported by our analysis of the depth profile of carbon concentration in partially processed CNA, which shows that the removal of carbon is remarkably uniform throughout the thickness of the CNA. Another hypothesis is that the rate is decreasing due to the decreasing amounts of ligands to be etched. The decrease in etch rate is grossly outpacing the decrease in carbon concentration: e.g., over 1 hr, the carbon concentration for He processing at 30W decreased from 550 TFU to 350 TFU, while the etching rate decreased from 3450 TFU/hr to ~250 TFU/hr, while over 6hrs, the carbon concentration for He processing at 30W decreased from 550 TFU to 100 TFU, while the etching rate decreased from 3450 TFU/hr to ~100 TFU/hr. Lastly, the decreased etching rate can be hypothesized to originate from a decrease in the concentration of plasma active species in the film.

To test this hypothesis, we plotted how the difference in etching rates between different plasma conditions varies over time. Figure 3(c) shows the difference in etching rates between 30W plasmas and 7W plasmas at different stages of the process: until 1hr of exposure, the 30W plasmas outpace the 7W plasmas for both O₂ and He, as expected. Remarkably, as time goes by, the initially large difference in etch rates between the two powers (650 TFU/hr for He and nearly 800 TFU/hr for O₂) decreases and vanishes after 1hr: after 1hr of processing, the ligand etch rate becomes independent of the power of the plasma, and therefore of the concentration of active species in the plasma chamber.
The difference in etching rates between different feed gases is even more interesting. Figure 3 (a) & (d) show that He plasma is more effective than O₂ plasma in the first few minutes of processing. This could possibly be explained by the rapid action of the especially strong VUV radiation produced by He plasma, compared to diffusion of radicals/excited species into the CNAs in the initial minute of processing. This explanation is consistent with the fact that the difference between O₂ plasma etch rates and He plasma etch rates at 30W is smaller than at 7W: at higher power the density of oxygen radicals/excited species or energetic photons available to etch ligands is higher. After 10 minutes, the scenario is reversed with O₂ plasma etching much faster than He plasma at both 7W and 30W. This inversion suggests that higher rates of etching leads a faster decline of the same. Also in this case, the etch rates become independent of feed gas after one hr of plasma processing.

Lastly, the role of pressure leads to similar conclusions. Figure 3 (b) & (e) suggests that pressure has a different effect on the etch rate from different feed gases, with O₂ plasmas being highly active at 2000mTorr, while He plasmas are much more active at intermediate pressures. As discussed above the concentration of active species and high energy photons will be maximized at some intermediate pressures. But most remarkably, the sum of the absolute differences in etch rates for different pressures also vanishes after 1hr of processing.

The conclusions of this analysis are that the effect of plasma parameters on ligand etching rate are only observed in the first few minutes of processing, and that the ligand etching rate is essentially independent of the plasma conditions after 1hr of processing. These surprising observations can indicate (i) a collapse of the accessible
porosity, (ii) the crosslinking and redeposition of volatile etching byproducts (e.g., CH₃) that have become part of the plasma, and (iii) the saturation of the nanoscale pores of the CNA with etching byproducts.

The first hypothesis is inconsistent with the prior observations of highly uniform etching rates across the thickness of the film: a collapse of the structure is most likely to happen first at the exposed surface, therefore leading to a gradient in carbon concentration. The second hypothesis is also inconsistent with the homogeneity of processing: while we do observe a higher concentration of carbon at the surface of the CNAs, we can attribute it to adventitious carbon. Furthermore, crosslinked plasma polymerized species are unlikely to diffuse deeply into the micropores of the CNA and to do so uniformly.

The third hypothesis is more consistent with the available data and is also consistent with existing literature in the processing of powder-binder mixtures by calcination. The production of volatile etching byproducts in the pores of the CNA can lead to the development of an overpressure inside the CNA that (i) prevents the active species of the plasma from entering the pores of the CNA, and (ii) increases the concentration of volatile radicals in the pores therefore leading to higher rates of recombination. The fact that the rate of etching becomes independent of the feed gas, strongly suggests that the rate observed after 1 hr is determined by the structure of the film and therefore by mass transport limitations. While a decrease in pressure in the chamber might suggest a higher flow of byproducts out of the CNA, it also reduces the amount of active species that can diffuse in.
Improving etching kinetics with flushing

**Figure 4.** Effect of flushing of plasma chamber on etching kinetics. (a) Byproducts of the plasma etching will be purged out during lower chamber pressure cycle, (b) Fresh plasma species along with feed gas will be charged in CNAs at high pressure cycle, (c) Combination of the above two steps lead to faster etching of the ligands
The best way to test this hypothesis is to apply the same solution that was implemented by Cima and others to increase mass transport between powder/binder porous media and a reactive gas phase. The solution was to apply oscillations of pressure during processing, therefore causing the sequential removal of byproducts during the low-pressure phases and the input of fresh reactive species during the high-pressure phases.

We ran the oscillatory pressure experiments (Figure 4(a) & (b)) with a cycle of 30mins: after every 30mins of processing we reduce the pressure to 100 mTorr and flush the chamber with fresh feed gas. We kept the final duration of exposure to be fixed at 6hrs and ran 0, 1, 2, and 11 cycles respectively.

In Figure 4 (c) we can see that with oscillations, [C] comes down to \(~2\) at.% from 4.5 at.% with a 15% increase in etching rate. This flushing results nearly matches up the carbon etching with that of high density plasma (2 at.% at 7W vs 1.5 at.% at 30W). 1 or 2 cycles of flushing already etched down the [C] to \(~2\)at%, which means most of the depletion of reactive species happened in the first 30mins. This correspond with our earlier conclusion about fast and rapid ligand etching taking place within the first few minutes of the plasma exposure.

**Conclusions**

We have isolated and investigated the interaction of plasma species with CNAs and found that radicals/excited species and VUV are responsible for ligands etching. VUV was found to be the dominant species in He plasma etching (to some extent may be H generated as byproducts of ligand etching), and in case of O₂ plasma its predominantly radicals/excited species. Plasma etching rate becomes independent of
plasma composition or density beyond 1hr of processing which suggests etching rate is limited by structure of material. Similar decrease in the etch rate at narrow trenches have been seen in reactive ion etching (RIE) termed as micro-loading. Either reactive species find it hard to reach at the point of interest or they are less in amount to do any etching. We have enhanced the kinetics of plasma etching by following an approach similar to what was found effective for binder burnout i.e. pressure oscillation during firing. By regular flushing of the chamber, we were able to achieve 15% enhancement in etching rate. More rigorous study is underway to fine tune the flushing experiments and explore other approaches. Nitrogen or helium plasma have high density emission spectra in VUV range and also aid in enhancing the oxygen radicals/atomic density. Exposing our CNAs to plasma created by mixture of oxygen and nitrogen or helium gases, could possibly etch ligands at faster rate. Our approach could be a possible pathway to etch the carbon residue in the binder burnout process, this will eliminate heat based approaches and hence prevent grain growth. This could be more beneficial for binder burnout from metal compacts.

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CHAPTER 6

OPTICS-FREE, PLASMA-BASED LITHOGRAPHY IN INORGANIC RESISTS MADE UP OF NANOPARTICLES

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Abstract

We describe a lithographic approach – Nanocrystal Plasma Polymerization (NPP)-based lithography (Figure 1) – where colloidal nanocrystal assemblies (CNAs) are used as the resist and, potentially, the active material. The patterning process is based on a change in the dispersibility of the CNAs in solvents as a result of the exposure to plasmas. Plasmas can etch the capping ligands from the exposed area. During the development step, the unexposed area of CNAs are redispersed leaving behind the patterned area.

Introduction

Demands for smaller and faster electronics is pushing the length-scale of devices to nanometers. Photolithography is reaching its physical limits, whereas X-ray and e-
beam lithographies are currently impractical for manufacturing\textsuperscript{[124]}. Extreme ultraviolet (EUV) lithography at 13.5nm is seriously being considered as a next-generation lithography process but, among other challenges, it requires high performance photoresists with 22-nm half-pitch resolution and beyond\textsuperscript{[125]}. Above all, cost is a key consideration in the development of technologies for the high-volume manufacturing of chips. This scenario demands for novel patterning materials and technologies to propel the $200 billion/year semiconductor industry and achieve a 5 nm node by 2020\textsuperscript{[126]}.

We report here a non-conventional lithography on colloidal nanocrystal assemblies\textsuperscript{[127]} using Nanocrystal Plasma Polymerization (NPP)\textsuperscript{[13]}. Colloidal nanocrystal assemblies (CNAs) are used as inorganic resists, and potentially may be the active materials. Since the process is plasma-driven, it is not bound by the diffraction limit on the resolution of photolithography. In principle, the smallest feature size that can be achieved is ideally defined by the size of the nanoparticles (which can be below 3nm). NPP-based lithography is low-cost, facile, rapid, scalable, versatile, and relies on plasma processing which is already scaled to chip-manufacturing scale, facilitating potential integration in the current semiconductor manufacturing.

Beside integrated electronics the ability to pattern nanocrystal superlattices composed of functional nanoparticles, and their conversion into all-inorganic functional and high-surface-area patterns could be useful in a range of other applications that are not as severely resolution-driven, e.g., energy storage, photovoltaics, catalysis. Therefore, even if this technology won’t be able to achieve the desired resolution by
the time it is required, we believe its development could still benefit other industries
or other aspects of the integrated electronics manufacturing stream.

What is a colloidal nanocrystal? Colloidal nanocrystals are synthesized by wet
chemistry and are stably dispersed in a solvent as colloids (i.e., they do not settle over
time), so that they can be processed as a solution. Their colloidal stability derives from
a coating of organic molecules on their surface. These molecules, called ligands, are
typically amphiphilic with a polar, reactive head, and an apolar, unreactive tail. The
reactive head binds the surface of the nanocrystals, reducing its surface energy, while
the tail is solvated by the solvent and repels other particles, preventing aggregation.
Typically, the core of the nanoparticles can be controlled precisely in size (between 2
and 20 nm), shape (from spherical, to rod, to wire, to branched), composition (from
oxides, to semiconductors, to metals). The control over the size, and therefore over
the properties of the material is interesting for applications in electronics \cite{22}. On the
other hand, the integration of these colloids in electronics has been hampered by three
main challenges: (i) lack of reproducibility and scalability in the synthesis of
nanoparticles, (ii) the removal of the ligands from the deposited nanoparticles \cite{22}, and
(iii) the cracking of the nanoparticle-based films upon deposition or removal of the
ligands \cite{22, 34}.

The ligands on the nanoparticles can be removed by the exposure of the films
to low-pressure (\textasciitilde500mTorr), low-power (7-30W) plasmas \cite{13, 23}. The removal yields
films that are essentially all-inorganic. While the detailed mechanism underlying the
etching of organics from within films that are hundreds of nanometers in thickness is
still unclear, the current evidence suggests that the mechanism is dependent on the
type of plasma geometry (capacitive vs inductive) employed, and the feed gas. This “cold” plasma processing is a solvent-free, low temperature process, and is routinely utilized in semiconductor processing, it is scalable to large surfaces, is compatible with heat sensitive substrates, is highly reproducible, and can be controlled to not harm or change significantly the functional inorganic fraction of the CNAs.

In general, etching of organics by plasmas proceeds by several simultaneous mechanisms: (i) crosslinking of the polymer backbones, (ii) bond scission and desorption of volatile fragments, (iii) polymerization in the gas phase, (iv) redeposition of polymerized fragments. The rates of these individual processes depend on the organic moiety as well as on the plasma processing parameters: while in certain conditions, the plasma will basically only crosslink a polymer substrate, in other conditions, it will rapidly etch it\cite{128}. We exploited this knowledge to use plasma as a way to transfer patterns into CNAs by what we called NPP lithography.

**Experimental Methods and Design**

**General process design**

Figure 1 shows the approach to obtain pattern transfer by the exposure of CNAs to plasmas, i.e., NPP lithography. At first, colloidal nanoparticles are obtained by colloidal synthesis and dispersed in organic solvents. They are then self-assembled into films on a substrate of choice. A hard mask (which prevent the plasma species to interact with CNAs) is placed on the film, defining areas that are protected from the plasma and areas that are not. The ligands in the exposed areas are then etched/polymerized and become insoluble in the original solvent. The unexposed areas can be developed by redispersion in a solvent, leaving behind the pattern defined by
the mask. For our process we made the following choices. (i) We used a highly cohesive oxide as the inorganic phase (e.g., ZrO$_2$) to minimize ablation (plasmas can cause ablation and sputtering that can complicate the diagnosis of the material). (ii) We used hard masks to enable the rapid optimization of the process and a facilitated understanding of the role of the interaction between plasma and mask on the pattern transfer. (iii) We chose a capacitive plasma setup to encourage vertical motion of the active species in the plasma and therefore an optimized resolution, assuming that charged species participate in the etching.

![Figure 1. Schematic of NPP-based lithography process](image)

**ZrO$_2$ nanocrystals synthesis**

The synthesis of ~3.7nm zirconia (tetragonal) nanocrystals was adapted from elsewhere[41]. Briefly, a mixture of zirconium precursors (zirconium isopropoxide propanal complex and zirconium chloride) were reacted at 340°C for 2hrs in trioctylphosphine oxide (TOPO - C$_{24}$H$_{51}$PO), which acts both as ligand and solvent for the reaction. The reaction was cooled to 80°C and the nanocrystals were separated
by destabilizing the colloid with a bad solvent (acetone). The product was then separated by centrifugation at 112g for 1min. The precipitate was washed two times with acetone to remove excess ligand and then redispersed in a non-polar solvent like hexane. A final centrifugation step at 1780g for 10mins ensured the removal of most colloidally unstable products. The supernatant was filtered through 0.2 μm nylon filter to obtain a dust-free product ready for spin coating.

**HfO₂ nanocrystals synthesis**

The synthesis of HfO₂ nanorods was a slight modification of a previously published procedure [53]. The reaction employs Hf isopropoxide and HfCl₄ as precursors and TOPO as a ligand and solvent. The reaction mixture was first heated to 300°C and held at that temperature for 30mins and thereafter raised the temperature to 320°C and held at that temperature for 20mins. Purification is performed similarly to that of ZrO₂ nanocrystals.

**Nanocrystal assemblies or resist coatings**

Crack-free and smooth films of resist are formed by spin coating nanoparticles dispersed in hexane. A list of other dispersants that can produce similar quality of resist films can be found elsewhere [84]. The substrate of interest (typically Si) was completely covered with the dispersion and then spin coated in two-steps. The substrate was accelerated at 330 rpm/sec to 1000 rpm, which uniformly spread the dispersion and left a thin film on the substrate. It was then held at 1000 rpm for 25 secs, for the liquid layer to dry. Depending on solvent and the concentration of the dispersion, these spinning parameters produce CNAs with a defined and reproducible thickness between 50 and 100 nm.
**Nanocrystal Plasma Polymerization**

NPP lithography was performed with a YES G1000 plasma etcher with plasma power and pressure of 250W and 150mTorr respectively for 5 or 10 min. Oxygen plasma (100% ultra-high pure quality gas) was used to change the solubility of exposed CNAs. Two kind of hard masks was employed. One of them was 200 mesh Cu TEM grid from Electron Microscopy System with catalogue# 0200-Cu and other one was solid sapphire wafer of dimension 5x5x0.5mm from MTI Corporation with product #ALC050505S1. Hard masks were pressed gently after putting in contact with the inorganic resist layer in a way similar to how photomask is applied in Contact lithography.

**Characterization techniques**

High resolution transmission electron microscopy (TEM) images were taken using a 2007 JEOL 2100 200kV STEM (operated in TEM mode at 200kV) at the Microscopy and NanoImaging facility at Iowa State University. To image the colloidal nanocrystals, a ~3μl drop of dilute nanocrystals dispersion was drop casted at room temperature, on a carbon-coated copper grid lying on top of a Kim wipe. TEM samples for plasma-treated CNAs were prepared by first scrapping layers/flakes from the substrate using a sharp knife, which was then made to adhere on the carbon-coated copper grid.

Powder X-ray diffraction was performed with a Siemens D500 X-ray diffractometer at the Materials Analysis and Research Laboratory (MARL) at Iowa State University. XRD patterns were collected in the 2θ range 20-60° by using 0.15DS, 0.05° steps, and 3s per step. For nanoparticle size analysis, diffraction pattern was
collected in slow scan mode (0.03° steps and 10s integration) to improve peak-to-noise ratio. Averaged measurement of nanoparticle size using the Scherrer equation was done following a previously reported protocol \cite{7}.

The effect of plasmas on the ZrO$_2$ CNA films was assessed by measuring the composition of the films at different stages of processing in an inductive plasma etcher (Harrick Plasma Cleaner, 7-30W power, 100mTorr pressure, O$_2$ feed) until full removal of the organic fraction. The elemental analysis of the samples throughout the film’s depth was determined by combining non-Rutherford elastic backscattering spectrometry (EBS) and elastic recoil detection (ERD) ion beam analysis techniques at the Surrey Ion Beam Centre\cite{57}. Three particle detectors were used, two out of those at a backscattering angle of 172.4°(DetA) and 147.7°(DetB), whereas a third one at a scattering angle of 30.8°(DetC) with a foil of 31µm of Kapton. The solid angles of detection were 2.6 ± 0.1 msr, 3.1 ± 0.3 msr and 0.8 ± 0.1 msr for DetA, DetB and DetC, respectively. Spectra were collected using a 4He beam at 3.05 MeV and 4.3 MeV for sensitivity to oxygen and carbon respectively. The incident beam was close to normal at the sample at 3 MeV, while the sample was tilted by 70° towards DetC during measurements at 4.3 MeV. The beam spot size was about $1.5 \times 1.5$ mm$^2$ and the beam intensity was between 10 and 30 nA. Spectra was self-consistently analysed using DataFurnace\cite{60}. The elemental analysis presented in this work are the average of the three measurement points performed on each sample.

Scanning electron microscopy (SEM) imaging was performed at MARL, with FEI quanta 250 field-emission SEM. Imaging was done in secondary electrons mode at 10 keV with beam spot size of 3.
Results and Discussion

Chemical and Morphological Insights to Plasma Processing of Nanocrystal Assemblies

The particles employed for this study are shown in Figure 2. Panel a shows spherical nanoparticles of ZrO$_2$ (3.7 nm diameter), while panel b shows the rod-like particles of HfO$_2$ (2.5nm x 5 nm).

![Figure 2](image)

**Figure 2.** Colloidal nanocrystals used in this study. (a) spherical ZrO$_2$, and (b) HfO$_2$ nanorods.

After NPP, the nanoparticles preserve their individuality and their size as indicated in the TEM shown in Figure 3a and in the histogram in Figure 3b. Scherrer analysis of the XRD spectra allowed us to determine the average size of the crystallites before and after plasma. Since the plasma is at low-pressure and dilute, the temperature of the sample never increases above 60°C, thereby preventing grain growth in the phases described here: as shown in Figure 3b, the size of the crystallites does not change significantly. Figure 3c shows compositional depth profiles obtained
by processing the EBS/ERD data through DataFurnace. The plot indicates the atomic fraction of carbon as a function of depth. Apart from providing compositional depth profiles, EBS/ERD data provides some important insights into plasma processing of CNAs. (i) The film densifies during processing: the concentration of carbon drops to nearly zero. (ii) The amount of zirconium and oxygen per unit area of the film remains nearly constant (data not shown here), which indicates that the inorganic fraction of the film is not significantly ablated in these plasmas. (iii) The concentration of carbon remains constant throughout the thickness of the film in spite of its asymmetric exposure to the plasma. Finally, (iv) the organic fraction can be reduced to \( \sim 0.6 \) at\% after 48hrs in O\(_2\) plasma.
Figure 3. Morphological and chemical characterization of CNAs after NPP. (a) TEM image of ZrO$_2$ CNA after 24hrs of oxygen plasma treatment, (b) crystallite size measured from XRD data of ZrO$_2$ CNAs before and after plasma, (c) carbon depth profile extracted from RBS data from CNAs (initial thickness = 353 nm) exposed to different duration of plasma exposure.
NPP for Lithography

The change in solubility does not require the complete removal of the organic fraction. Shorter exposures to plasma result in crosslinking of the exposed CNAs, which makes the nanoparticles impervious to redispersion in solvents: the exposed films become insoluble in solvents after 1hr of processing in the inductively coupled plasmas, at which point the organic fraction is only partially removed. In order to substantially reduce exposure time (to 5-10 min) and, therefore, to reduce lateral diffusion of active plasma species under the mask, the plasma processing used to perform lithography is capacitive rather than inductive. The power is also increased from 30W to 250W.

Resist Development

Resist development is one of the critical steps in lithography. The interaction between the resist and the developer defines the final resist profile and thereby affect the line-edge & line-width roughness (LER & LWR) of the pattern. In NPP-based lithography, the knowledge of ligand solvation is key to the resist development process. Solvents that can fully solvate the ligand shell for e.g., toluene, p-xylene are excellent for nanoparticles dispersibility\cite{94} and ideally better developers. However, they are found to damage the patterns. Solvents with insignificant polarity (i.e., low value of the Hansen solubility parameter $\delta_P$) were used instead as developers (for e.g., hexane) to mitigate pattern damage. Our understanding of this observation is as follows. The exposed CNAs is essentially a crosslinked polymer composite whose polymer fraction is chemically similar to the original ligand. Therefore, a solvent in which the ligands will have high solubility (the solubility of TOPO in hexane is $\sim0.07\text{gm/ml}$ compare to $\sim0.3\text{gm/ml}$ in toluene) will swell the crosslinked polymer matrix causing strain in the
pattern that can result in cracking and delamination. Another important measure to reduce pattern damage in the development process was to allow the CNA to cool to room temperature after plasma treatment before development.

**Pattern Transfer**

Figure 4 indicates a proof-of-concept demonstration of pattern transfer by NPP lithography, whereby in panel a the mask was a Cu TEM grid used to pattern a ZrO$_2$ nanoparticle CNA. Panel b shows instead pattern transfer in a HfO$_2$ CNA using a sapphire mask. In spite of some evidence of underetching, the use of insulating masks was found to benefit the overall quality of the patterning and allowed us to improve LER from $\sim10^3$ nm in initial tests to $\sim10^2$ nm.

We believe that transitioning to soft masks will remove what appears to be the main limitation (i.e., underetching) and enable a better understanding of the fundamental capabilities of this approach to patterning inorganic matter.
Figure 4. Proof-of-concept showing NPP-based lithography can transfer patterns on CNAs blanket. Patterns formed on, (a) ZrO$_2$ CNA blanket using 200 mesh Cu TEM grid as a hard mask, (b) HfO$_2$ CNA blanket using 0.5cm x 0.5cm sapphire mask.

**CNAs: Potential Active Materials**

One of the most remarkable aspects of this technology is that the patterning and development is independent of the composition of the resist or active material. In a multimaterial environment all etching steps must usually consider the chemistry of the components because chemical dissolution is required. In this case the dissolution is a colloidal dissolution which is independent of composition and can be controlled by the ligands that cap the surface of the nanocrystals.
There is a serious demand of both high-κ and low-κ materials for the advanced integrated circuits. The need for high strength, porous low-κ materials stem from Cu being used as interconnect in ICs. Pattern formation on Cu through plasma etching is not feasible since it does not form volatile compounds with reactive gases\textsuperscript{[129]}. So, Cu is deposited as interlayer between patterned dielectric layers, with the excess removed through CMP. For this reason, the dielectric layer needs to be stiff enough to sustain the stress created by CMP. Once ligands are fully removed by plasmas, CNAs are \(\sim\) 40\% porous with superior mechanical properties (for e.g., \(E \sim 40\text{GPa}\) and \(H \sim 2\text{GPa}\) for ZrO\textsubscript{2} CNAs\textsuperscript{[42]}). The porosity can be easily tuned by heating CNAs to temperatures \(<500\text{C}\), simultaneously increasing their mechanical properties (up to \(\sim 100\text{ GPa}\textsuperscript{[130]}\)). This ability to tune porosity provides us a capability to tune the dielectric and mechanical properties of the material, without incurring in cracking and delamination that affect so many other bottom-up materials processing methods. The demand for high-κ materials arise from the gate leakage problem through “quantum mechanical tunneling” as the SiO\textsubscript{2} gate layer gets thinner to meet the continuous scaling of the IC. High-κ materials, such as HfO\textsubscript{2}, ZrO\textsubscript{2} and TiO\textsubscript{2} have \(\kappa\) values higher than SiO\textsubscript{2} (3.9) are better candidate for gate dielectrics. HfO\textsubscript{2} is being used as gate dielectric from 45nm transistors onwards with a new compatible metal electrode replacing polysilicon. Our capability to synthesize HfO\textsubscript{2}, ZrO\textsubscript{2} and TiO\textsubscript{2} (not shown here) inorganic resists with the particles size of \(\sim 3\text{nm}\) in diameter can be potentially used as gate dielectric materials in CMOS technology.

In traditional lithography set-up, usually inorganic materials are etched out to create pattern which is basically a top-down approach. However, certain inorganic
materials for e.g., Cu, Au (used as interconnect layer) are difficult to be etched or patterned as they form very limited volatile compounds at lower temperatures or required very high temperatures to desorb the etched products\textsuperscript{[131]}. This limits the use of organic photoresists as mask. With our technology, colloidal copper nanoparticles can be easily deposited and patterned, as our technology is not dependent on etching the inorganics but changing the solubility of the films by polymerizing or etching the ligands attached to the nanoparticles surface.

**Conclusions**

We have demonstrated a plasma-based approach to transfer patterns into colloidal nanocrystal assemblies. The plasma polymerizes and etches the organics surrounding the nanoparticles leading to a change in the solubility of the colloids. By shielding areas of the film with a hard mask we demonstrated basic pattern transfer. Importantly, the material leftover after development is purely inorganic, and its microstructure (and therefore its properties) is fully defined by the nanoparticle building blocks that were initially used to form the assembly.

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Creating materials with programmable microstructure/nanostructure will help us reliably understand the microstructure-property relationships of materials. Although material scientists have gained significant control on the microstructure of the materials, true control of nanoscale microstructure and of interfaces is still missing. We believe this bottleneck is preventing us from resolving long-standing debates about basic questions of structure/property relations such as the validity of the inverse Hall-Petch behavior. In this work, we developed a facile and scalable approach to create materials with predictable nanostructure from colloidal nanocrystals as precursors, bypassing the fundamental limitations of traditional manufacturing methods. With our approach, we can reliably control the following microstructural features, (i) grain size, (ii) grain shape, (iii) grain composition, (iv) grain size distribution, (v) grain boundary composition, (vi) porosity. Reliable control of the above features was made possible as we independently synthesize the “grain” i.e. colloidal nanocrystals before integrating them into the solid state.

While integrating colloidal nanocrystals assemblies (CNAs) into all-inorganic solids through plasma processing, we have solved a long-standing problem in nanochemistry, i.e. crack formation during consolidation of hybrid phases into fully inorganic phases. Simply by choosing appropriate solvent in which particles are dispersed we have made the film more resilient to cracking. These findings allowed for the fabrication of cm² crack-free, phase-pure polycrystalline films. Our crack-free, ligand-free semiconducting PbS CNAs conduct electrons in cm-scale and their
conductivity (1.370 S/cm) is comparable to bulk PbS crystal. By comparison most of the conductivity studies on similar systems were limited to micron scale electrode separations, most likely to avoid, reduce, or mask the effect of extended defects like cracks.

The highly porous state obtained after ligand removal result in high surface area materials with nearly 100% crystallinity, and exposed inorganic surfaces that could be very attractive for any application involving interface processes (e.g., energy storage, photovoltaics, thermoelectric and catalysis), but to extract the structure-property relationship for bulk nanostructured materials, the layer need to be densified. Future effort will be to densify the plasma processed CNAs by Spark Plasma Sintering to at least achieve densification of 95% and then characterized their physical properties.

We have then demonstrated a simple approach to control the grain boundary composition of colloidal nanoparticles through combination of chemical composition of ligands and plasma processing. With our unprecedented control on grain boundary composition, we can selectively alter the grain growth mechanism of same particles.

In the grain growth study of our ZrO$_2$ nanoparticles, we have observed that grain growth stops and nearly plateaued with sintering time. This behavior would be desirable for application of these layer as thermal barrier coatings in jet engines, micromechanical devices, electronic packaging, and maybe for hypersonic vehicles.

Plasma effectively processes ~350nm thick CNAs, but the etching process is limited by mass transfer, i.e., active species need to diffuse in and the byproducts of the etching need to be purged out of the CNAs. Although we have developed a
technique (i.e. oscillating pressure in the plasma chamber during plasma etching process similar to what was found to be effective in binder burnout) to accelerate the etching process, but there is a need of a solid approach to create a bulk nanostructured material. An effort in this direction could be to nebulize the colloidal nanocrystal solution into a plasma chamber, which then similar to Chemical vapor deposition (CVD) technique process the colloidal nanocrystals and can deposit materials of varying thicknesses on desired substrate/template. This approach could eliminate the problem of crack formation since most of the volume loss will happen in the vapor phase; it is highly unlikely that particle deposited will form ordered assemblies which then will remain crack-free during densification. This effort could also be modified to create bulk nanocrystalline powders with superior quality.

The above proposed approach could be integrated with additive manufacturing techniques to manufacture materials with predictable nanostructure. Additive manufacturing of ceramics is limited by extremely high melting point of ceramics as opposed to metals and polymers. Because our particles are so small with such high surface energy and low melting point depression could be compatible with additive manufacturing set-up. We have so far demonstrated our approach on thin films i.e. on a support only – although good that our approach could be integrated with additive manufacturing techniques to build materials with predictable nanostructure but it will be nice to have fully processed cm thick ceramic pellet with monodisperse nanoparticle size. Our future effort in infiltrating a paper with nanocrystals and then expose to plasma to etch simultaneously the ligands and the paper could build bulk nanostructured solids.
We have demonstrated the workability of our approach so far to oxides and chalcogenides, future efforts will be to utilize our understanding of plasma interaction with CNAs to process metal and other CNAs. Problems that might be associated with processing of metal CNAs is the sintering of nanoparticles after ligand removal due to the melting point depression expected through the Gibbs–Thompson equation.

Finally, we show the applicability of our approach in developing an optics-free lithography (in collaboration with Intel Corporation) in which CNAs are used as resist or as an active material. By selectively masking the interaction of plasma with CNAs, patterns can be transferred. Our patterning technology can easily pattern materials which are hard to pattern by traditional inorganic etching-based pattern transfer (example, copper, gold), because our lithographic approach is based on changing the solubility of the films by polymerizing or etching the ligands attached to the nanoparticles surface.
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