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Marino, E.

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## Summary

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*A journey is a person in itself; no two are alike. And all plans, safeguards, policing, and coercion are fruitless. We find that after years of struggle that we do not take a trip; a trip takes us.*

— John Steinbeck

### Assembling Nanocrystal Superstructures

At the nanoscale, electronic materials can develop size-dependent properties due to quantum-confinement effects. This is the case for semiconductor nanocrystals, also known as quantum dots (QDs). In these materials, the confinement of charge carriers leads to a size-dependent electronic bandgap; as a consequence, the light absorption and emission properties of QDs can be tuned over a wide spectral range by simply changing their size. Furthermore, QDs can be synthesized as a colloidal dispersion, making their use compatible with inexpensive and efficient roll-to-roll printing technologies (Chapter 1).

The unique photophysics of QDs, together with their ease of fabrication and processability, make them promising candidates as building blocks for novel optoelectronic devices, such as solar cells, photodetectors, light emitting diodes, and lasers.

However, to be used as active layer in a device, QDs must be assembled to form macroscopic solids. Since the macroscopic properties of the assembled solid, such as its electrical conductivity, crucially depend on microscopic aspects such as interdot distance and surface passivation, methods to control the assembly of QDs into close-packed and reproducible superstructures are universally desirable (Chapter 2).

In atomic systems, the rate of temperature quench controls the crystallinity of the resulting solid; in colloidal systems, this role is played by the rate of increase of particle volume fraction. To control this quantity, we prepare an oil-in-water emulsion where each droplet contains a dispersion of QDs in a volatile hydrophobic solvent. The low solubility of the hydrophobic solvent in water limits the droplets' rate of evaporation, allowing for an assembly time scale slow enough to study the kinetics of QD condensation into a solid. We measure this process directly by synchrotron-based small-angle X-ray scattering, and extract crucial structural and thermodynamic parameters revealing the driving forces of QD assembly into crystalline solids, or supercrystals (Chapter 3).

The emulsion-templated approach drives the assembly of QDs into spherical supercrystals with diameters comparable to the wavelength of light in the visible range. The spherical supercrystals can therefore support confined optical modes known as Mie modes, with the potential of enhancing the otherwise relatively low absorption cross section of QDs. By comparing the experimentally measured absorption and scattering spectra to the simulated absorption and scattering cross sections of single supercrystals, we demonstrate that spherical QD supercrystals support Mie resonant modes; these modes allow for an enhanced optical performance, yielding to an estimated absorption efficiency of supercrystals up to 125% in a wide range of diameters and in the visible range. Furthermore, by decreasing the interdot spacing, we show that excitons can readily delocalize in QD supercrystals marking the transition from bound to free biexciton system, together with an increased probability of energy transfer (Chapter 4).

Ligand exchange is crucial to enhance charge transport in QD superstructures. As synthesized, the surface of QDs is typically decorated with long, organic ligands making QD solids largely insulating. The conductivity of QD solids can be increased by replacing these ligands with short molecular complexes, establishing conductive bonds between neighboring QDs that allow charge transport. To improve our understanding of this ligand exchange process, we use the model system of flat CdSe nanoplatelets (NPs) with atomically defined thickness. Importantly, we find that this ligand exchange process can induce the growth of defects in NPs, clearly visible as punctures in the crystalline lattice. Importantly, we find that the extent of structural damage can be reduced by choosing specific experimental conditions for the ligand exchange. Furthermore, we demonstrate that damaged NPs can be repaired by inducing surface reconstruction through chemical or thermal routes (Chapter 5).

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The insight gained on the ligand exchange of NPs also benefited our efforts in their assembly. Charge carriers can freely travel in the plane of NPs; for this reason, the assembly of NPs holds great promise in the development of solution-processed 2D macroscopic electronic materials. We drive the assembly of NPs at the air/liquid interface into 2D solids featuring smectic order, and we show that this phase is energetically favored as it minimizes the interfacial energy. Furthermore, we exploit the attractive depletion interaction resulting from excess ligands present in solution to drive the formation of micrometer-long nanowires constituted by stacked NPs (Chapter 6).

More generally, the phase behavior of colloidal particles can be controlled by exploiting the interplay of repulsive and attractive interactions. Recently, a novel solvent-based attractive interaction has attracted the interest of the scientific community due to its universal nature and exclusively temperature-dependent properties. This interaction, known as the critical Casimir interaction, relies on the confinement of temperature-dependent solvent-density fluctuations between particle surfaces to drive the assembly. In this thesis, we report the first attempt to control the assembly of QDs by using critical Casimir forces. By investigating their assembly kinetics, we determine that hydrophilic QDs preferentially assemble in the presence of water-rich fluctuations, while the assembly can be suppressed by using water-poor fluctuations. Critical Casimir forces can drive the growth of micrometer-sized QD superstructures, that sediment to form QD solids (Chapter 7).

The morphology of these QD solids can be controlled by tuning the strength of the Casimir interactions, strongly dependent on the distance in temperature from the critical point of the dispersing solvent. We exploit this effect to tailor the space-spanning properties of Casimir-grown QD solids, yielding a clear dependence of conductivity on the strength of the attractive interaction used (Chapter 8).

The confinement of solvent-density fluctuations between a flat surface and a colloidal particle is also predicted to yield a net attractive force. We exploit this effect to drive the growth of a crystalline layer of QDs on a unfunctionalized and unpatterned silicon substrate: QD epitaxy. By tuning the strength and length scale of attractive Casimir and repulsive electrostatic interactions, we drive the growth of QD monolayer superstructures. These superstructures show reproducible morphologies, that can be varied from crystalline, amorphous, to spinoidal, by controlling the balance of attractive and repulsive interactions. (Chapter 9).

In the next chapter, we conclude this thesis with a brief personal outlook on the matters of nanoscience discussed (Chapter 11).