

Recent advances in the preparation of nanocrystal solids

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Abstract. Colloidal chemistry offers several tools to synthesize and manipulate nanoscopic objects. Despite the existence of a plethora of tools to design building blocks, methods for assembling these components into functional macroscopic materials are still in their infancy. This review discusses the recent progress made towards assembling rudimentary nanoscale building blocks into functional macroscopic materials.

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Colloidal nanocrystals (NCs) are well known because of their emission tunability [1]. Additionally, these materials exhibit exceptionally high quantum yields and photostability in colloidal solution [2,3]. Luminescence is however only one among several intriguing properties exhibited by these materials. In fairly general terms, the unique properties of colloidal NCs arise from two different sources. Quantum confinement [4,5] acts differently and to a varied extent on the several excitations within a NC. Quantum confinement manifests itself through a change of the density of states. The magnitude of this effect is different for various excitations, as each excitation samples distinct characteristic volumes of a material [6]. NCs therefore end up with vastly different physical properties compared to bulk materials. The other key influence on NC properties comes from the flexibility afforded by colloidal chemistry. Colloidal techniques enable the synthesis and manipulation of materials with a host of functionalities: Semiconductors [1], metals [7–11], semimetals [12], superconductors [13,14], thermoelectrics [15], etc. For example, figure 1 shows a host of metallic as well as semiconductor NCs synthesized using colloidal techniques [16]. Structures as diverse as platelets, nanorods, bipyramids, core/shell architectures, etc. may be prepared by varying the reaction conditions, surfactants or both [11,17–19]. While nanostructuring modifies the physical properties of individual materials [20], colloidal chemistry opens up the additional possibility of combining rudimentary building blocks into materials with counterintuitive dual functionalities. For example,

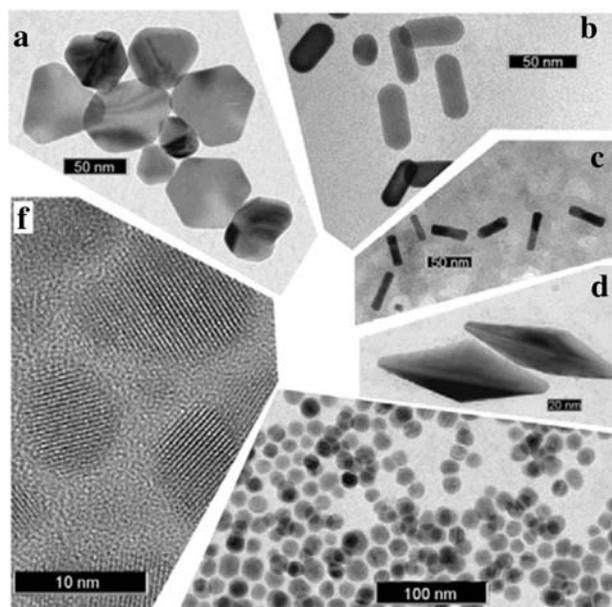


Figure 1. TEM micrographs of various particles synthesized using colloidal techniques. (a) Silver platelets, (b, c) gold nanorods of various aspect ratios, (d) gold bipyramids, (e) ZnSe/CdS core/shell nanocrystals and (f) HRTEM images of ZnTe/CdS particles. Scale bars: (a–c) 50 nm, (d) 20 nm, (e) 100 nm, (f) 10 nm.

composite excitations such as plexcitons [21] (a contraction for plasmon-exciton) are observed when excitonic materials and metallic nanoparticles are brought into close proximity.

Continued exploration of the nanoscale therefore requires increased emphasis on the development of techniques to couple different kinds of nanostructures. Early successes towards this end were achieved by the use of bifunctional molecular linkers. Derivatives of polyethylene glycol can bind to both semiconducting and metallic surfaces. Jin *et al* employed this technique to add a gold shell to CdSe NCs [22]. Silica templates provide a more controlled route towards achieving the same end. Khanal *et al* [23] were able to demonstrate significant increases in the two-photon cross-sections of NCs that were tethered to functionalized gold-coated silica templates. Cross-sections as high as 4×10^5 Goepfert–Meyer that were observed in this work [23] are among the highest observed in colloidal NCs. The enhanced cross-sections correlate with the field enhancements expected in the near-field of metallic nanoparticles. The study of extended assemblies of such materials is therefore clearly of significant interest.

Given that colloidal NCs are usually handled as solvent dispersions, the simplest technique to prepare NC solids is to remove the solvent. Murray *et al* reported the formation of NC superlattices formed from CdSe NCs [24]. Micron-sized crystals observed in this work correspond to an ordered packing of millions of NCs. While this number is still smaller than the number of ordered molecules present e.g. in a typical grain of sugar, it is nonetheless an impressive display of long-range structural ordering by a somewhat polydisperse motif.

The demonstration of ordering in binary nanocrystal mixtures represents further advancements. Through controlled drying of NC dispersions, Shevchenko *et al* prepared large area films of binary NC superlattices [25]. While careful regulation of the preparation conditions does enable the achievement of long-range order in NC superlattices, there is no straightforward correlation between the starting NCs and the preferred final structure. The absence of a definite crystal structure of choice in these materials is a consequence of the poor selectivity of the forces that is responsible for the formation of such solids. Thus, such solids are often prone to defects as well as secondary phases. Increased selectivity and preferential lattice structure are observed in situations where NCs are decorated with DNA ligands or otherwise associated with surface charges. Park *et al* [26] and Auyeung *et al* [27] have successfully enumerated energetic criteria that are responsible to drive the formation of NC solids with specific superlattice structures [26,27]. The attainment of a particular superlattice structure still requires careful control of the conditions of preparation as well as stoichiometry.

Most of the literature on NC thus puts great emphasis on the preparation of ordered solids. There is however no physical reason to anticipate ordered nanocrystalline solids to have any advantages at all over their structurally disordered counterparts. Both semiconductor as well as metal particles typically show hopping transport when cast into films, though studies have indicated band-like transport in some systems [28–30]. The transport characteristics of superconducting particles are found to depend on their resistance characteristics prior to the onset of transition [31]. Films exhibiting resistance lower than a particular value exhibit superconductivity at low temperatures, while more resistive films continue to exhibit dissipative transport despite the onset of superconductivity in individual NCs. While the overwhelming influence of disorder on charge transport does at first suggest putting emphasis on ordered solids, it is imperative to first tend to the mechanisms of transport in nanocrystal solids.

The problem of transport in disordered materials has been dealt with by several researchers; here we focus exclusively on the picture proposed by Efros and Shklovskii (ES–VRH). Within the ES–VRH picture, disorder in a solid causes the density-of-states at the Fermi level to approach zero quadratically with energy [32,33]. This is highlighted in figure 2. This is a reflection of the existence of a Coulomb energy between the configuration before and after an electron hop. Transport thus requires the excitation of an electron across this Coulomb ‘gap’. Within the ES–VRH picture, the gap appears not only because of disorder but also because of the inability of multiple electrons to move simultaneously.

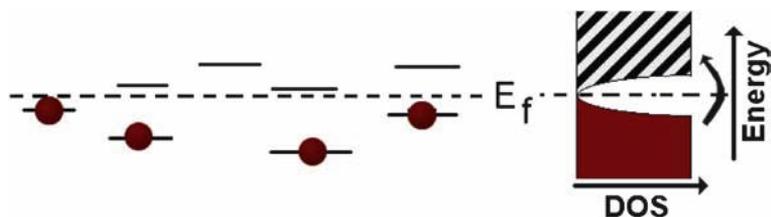


Figure 2. Schematic of the Efros–Shklovskii variable range hopping model in semiconductor nanocrystals.

The width of this gap in the density-of-states is the guiding parameter that determines mobility in the disordered substance. Structural disorder is only one among several factors that influence the width of this gap, with parameters such as density-of-states available in individual NCs, as well as the carrier density in the system also playing significant roles [28,29]. In a colloidal NC film, the abrupt termination of the lattice between NCs ensures hopping-type transport regardless of structural ordering. In this situation, the presence of two NC neighbours with similar but vacant energy levels in proximity of each NC is a sufficient guarantee for successful charge transport. This clearly does not place any constraints on the organization of the coordination sphere of each NC. The simple requirement for successful transport thus is the presence of NCs with correct energy levels in the vicinity.

Our current understanding of transport properties of colloidal NC solids therefore suggests an overwhelming importance of the density-of-states of the participating NCs as well as the number of carriers in NC films. In contrast, precise structural order appears to be of little or no consequence. With this background, we focus exclusively on exploring methods to prepare disordered solids in the remaining sections of this review.

Given that regulation of the number of carriers in NC solids is a primary concern, we begin by considering ways in which their population may be controlled. Several transition metal (TM) ions exhibit variable valence, and are capable of oxidizing or reducing other redox active species located in close proximity. Based on this observation, an elementary way to dope NCs is to bring NCs containing TM impurities into close proximity of redox active NCs. In the examples that follow, we shall exclusively consider the problem of charge transfer from copper containing II–VI NCs.

Copper is a well-known impurity in II–VI semiconductor NCs [34–37]. Within II–VI hosts, copper ions typically exist in a +2 oxidation state and act as cation substituents. Copper is most generally associated with a blue–green emission band in ZnSe and ZnS hosts; this band is usually generally associated with substitutional Cu^{2+} impurities, with interstitial copper being nonluminescent in general. Semiconductors such as ZnSe, ZnS, CdS etc. are redox inert with respect to the copper ion, and therefore the +2 state may be readily introduced into these materials [38,39]. Other semiconductors such as ZnTe [16] and PbSe have significantly higher valence band offsets that can reduce the copper ion into its +1 oxidation state [40]. This redox process therefore also causes the injection of a hole into the semiconductor valence band.

This charge transfer process is highlighted schematically in figure 3a [41]. The effects of charge transfer are most apparent on the positively charged NC. Here, the valence band hole manifests itself through photoluminescence quenching, band edge bleach as well as the appearance of a valence band intraband transition. Figure 3b shows the valence intraband transition associated with mixtures of magic-sized clusters of PbSe and Cu:CdS NCs. Magic-sized PbSe NCs are small (~ 2 nm), very strongly confined particles with the first valence band intraband transition energy as high as 0.7 eV [42]. Despite the strongly confined nature of magic-sized NCs, Cu:CdS is nevertheless able to inject charges into this material. This causes the appearance of a positive charge on magic-sized NCs of PbSe as well as a negative charge on Cu:CdS. Among the many spectroscopic features observed in the case of charged NCs, the appearance of an intraband transition perhaps has the greatest significance.

NC–NC solid formation therefore occurs as a consequence of charge transfer, rather than solvent removal. This feature of the solid formation process has several advantages

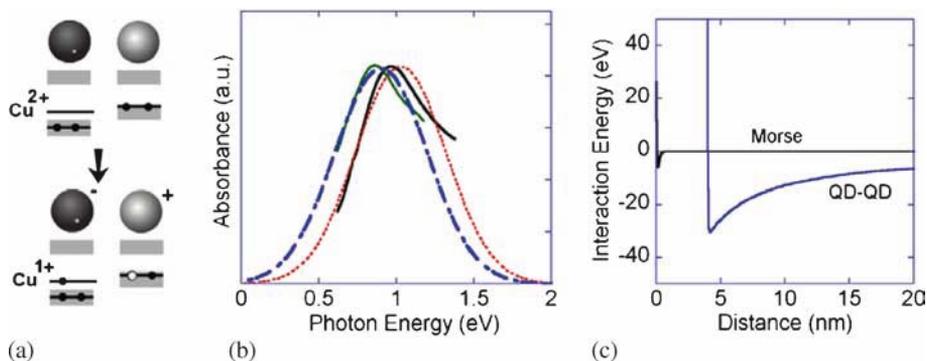


Figure 3. (a) Schematic of the charge transfer process in binary NC mixtures. (b) Infrared features observed in mixtures of PbSe and CdS:Cu NCs. The dashed lines correspond to Gaussian fits. (c) Interaction energies of a pair of charged spheres in a medium of dielectric 10. The interaction corresponds to 30 charges per sphere. The Morse potential corresponding to a typical chemical bond (black) is much smaller in comparison.

that are unavailable in other schemes. The optimization of transport characteristics requires limiting the segregation of the two individual NCs into spatially distinct regions of the NC solid. In the case of NC solids that are prepared by solvent removal or by the use of lock-and-key ligands, segregation remains a concern. In the case of solids prepared by solvent removal, there is a lack of recognition between the two participating NCs, and therefore the structure of the material is guided primarily by configurational as well as vibrational entropic concerns. Due to similarities between the entropic content of various ordered phases, segregation of similar NCs is extremely likely in these materials. While the use of lock-and-key ligands does significantly improve selectivity, attractive interactions between similar NCs are still feasible. In contrast, in the case of NC solids held together by ionic interactions, similar NCs bear the same charge and consequently repel each other thereby eliminating the possibility of segregation of similar NCs.

The formation of NC solids bound by Coulomb interactions also represents a significant step in our understanding of chemical bonding. Chemical bonds are typically not longer than a fraction of a nanometre. Covalent, metallic and dative bonds are limited to this length scale because of the necessity of electron distribution over multiple centres. Ionic bonds, in principle, can be much longer because the localization of charge is necessary on only one of the fragments. In practice, the length scales of ionic interactions are much shorter due to screening by counterions. The effective range of ionic bonds in condensed media is thus related in good measure to the size of the participating moieties. For NC solids, the large sizes of NCs cause these interactions to extend over length scales exceeding several nanometres. The contrast between the typical NC–NC interactions and a chemical bond is highlighted in figure 3c. NC–NC interactions therefore represent the longest chemical bonds observed in any known system. Besides their unique interaction range, these interactions are also extremely strong, with estimated pair interaction energies in excess of 10 eV in condensed medium.

The peculiar interaction strength of these materials also has a profound impact on their structure. While these materials are formed purely due to Coulomb interactions, the large

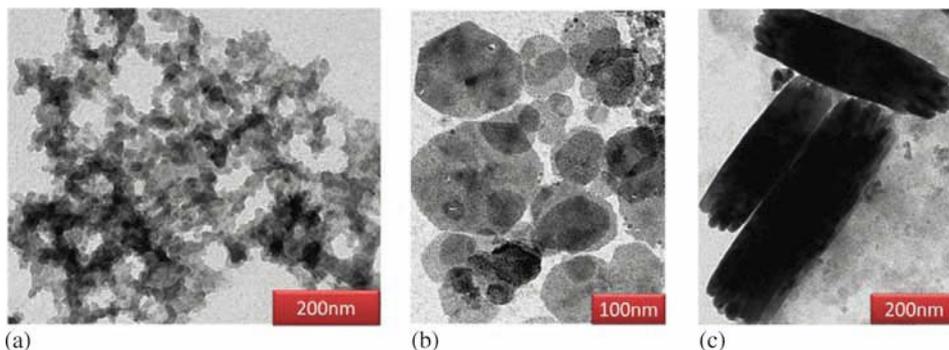


Figure 4. (a) Coulomb bound dendritic aggregates, (b) diskettes observed in the case of quick drying and (c) rods observed in the case of slow drying. All three solids are formed from various PbSe-based NCs and Cu:CdS.

magnitude of the interaction energy leads to kinetic freezing of the solid. The final morphology of these materials is thus still dependent upon parameters such as the solvent removal rate. In particular, as shown in figure 4, faster rates of solvent removal lead to the formation of structures of higher surface area such as dendrites and sheets (figures 4a and 4b). In contrast, slower rates of drying lead to more compact structures such as nanorods (figure 4c).

NC solids held together by charge transfer-induced Coulomb interactions thus offer several advantages over NC materials prepared by other means. Besides achieving the rudimentary tasks of doping as well as elimination of phase segregation, these materials are also unique in terms of bond lengths as well as interaction energies. The continued progress in assembling nanocrystalline building blocks into functional materials will ultimately benefit devices and lead to the emergence of novel applications.

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