Self-assembly of flexible and rigid structures: from colloidal molecules to lattices

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Chapter 1

Introduction

Abstract

In this chapter, we present a brief introduction to colloidal particles, their types and self assembly. We also provide the brief literature review on the diverse synthesis methods designed for the synthesis of colloidal molecules through heteroaggregation is provided. We also discuss the types of molecules formed and the yield achieved. Furthermore, we explore studies on the assembly of DNA-coated colloids, elaborating on their assembly into both colloidal lattices and flexible colloidal molecules. We highlight the existing gaps in the current research. Finally, we outline both its scope and the broader objectives of this thesis.

Colloidal particles are present in various everyday products such as coffee, paint, ink and creams. These particles have size ranging from hundreds of nanometers to a few microns. Due to their Brownian motion in water, which is a result of collisions with the surrounding fluid, colloids exhibit similar behavior to atoms and molecules. Additionally, their size allows to us see, observe and study them using conventional optical microscopy. Colloidal particles can be made from a variety of materials including metals, glass, and polymers. These particles have various properties such as kinetic, electrical, magnetic and optical properties. These properties of the particles can also be tuned depending on the nature of the particles and the suspending medium and can be measured using techniques such as light scattering, electron microscopy, and dynamic light scattering. The unique properties of colloidal suspensions make them suitable for the fabrication of photonic crystals,[1, 2] as model systems for atoms[3] and drug delivery systems.[4, 5]

Isotropic spherical colloidal particles are an excellent model for investigating the phase behavior of atoms. They accurately mimic the fluid, crystal and glass phases of real atoms at low, intermediate, and high particles concentrations, respectively. It was found that these particles self-assemble into thermodynamically favorable face-centered cubic (FCC) and hexagonal close-packed lattices (HCP).[3, 6] Using a variety of shape, size, material, and surface properties, other crystals of this type could be also produced.[7]

1.0.1 Self-Assembly of Colloids

Colloidal self-assembly is the process of spontaneous organization of colloidal particles into ordered structures without external force. It is an effective method for constructing complex colloidal structures and materials, for example colloidal molecules,[8, 9] colloidal polymer chains,[10] and crystals.[3, 7] The assembly of colloidal particles into these structures is achieved by manipulating the interactions between the particles like electrostatic interactions, van der Waals interactions, and hydrogen bonding which also can be tuned by changing the size, shape and charge of the particles.[7, 11] An example of various types and sizes of colloidal particles is shown in the Figure 1.1. An interesting colloidal shape are colloidal clusters, as they closely resemble shape filling models of real molecules and hence were referred to by van Blaaderen as "colloidal molecules".[12] Such colloidal molecules were first realized as colloidal clusters composed of isotropic spherical particles, and were first prepared by Pine and his colleagues by aggregation of a small number of particles in emulsion droplets.[13] Concepts such as colloidal molecules are particularly of interest as they allow

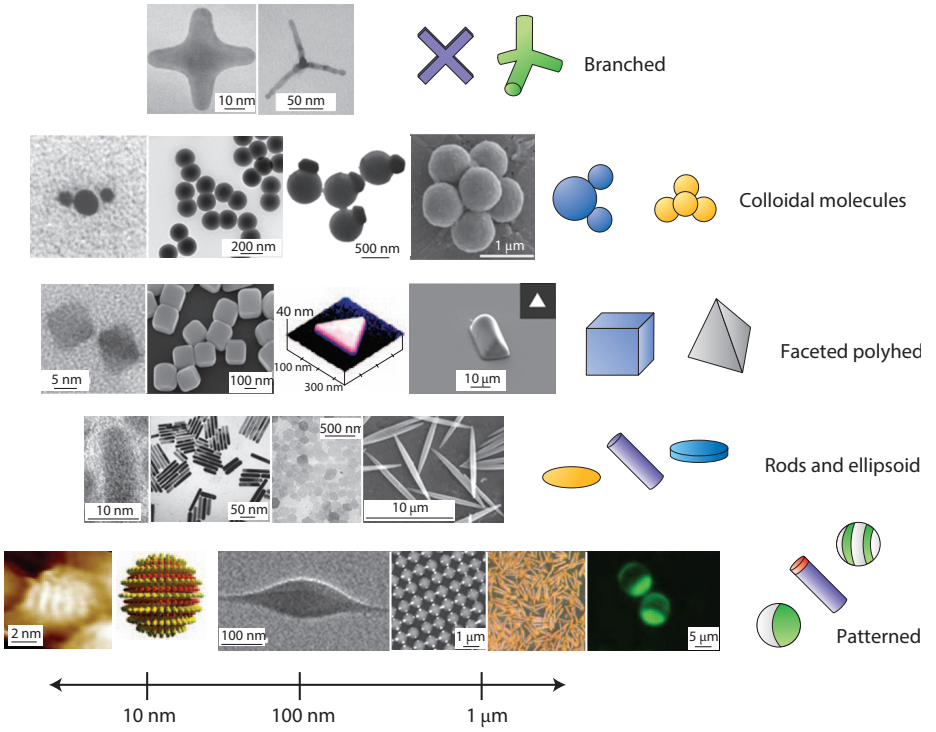

Figure 1.1: Length scale of various types of colloidal particles. Particles arranged by anisotropy (top to bottom) and size (left to right), showcasing varieties from branched tetrapods to patterned Janus spheres. *Adapted from Ref[11] with permission from Nature Springer.*

for limited and directional interactions between particles. Further, with the goal of expanding the range of colloidal architectures, researchers have focused on the utilization of anisotropic colloidal particles. Such colloidal molecules can be used to create new assemblies of higher dimensions with more complexity as shown in Figure 1.2.[8, 9, 11, 14, 15]

Various techniques have been developed to create colloidal molecules with different shapes, sizes, and properties. These include synthetic methods such as nucleation and growth,[14] seeded emulsion polymerization,[14] and physical vapor deposition,[16] as well as self-assembly approaches like emulsion-based clustering.[17] While synthetic methods can produce large quantities of uniform colloidal molecules, they often have limitations in terms of the complexity of the shapes and interactions that can be achieved. Self-assembly, on the other hand, can lead to more complex shapes and interactions. This can be achieved through various mechanisms such as hybridization of surface-bound or surface-mobile DNA linkers,[18] hydropho-

bic interactions,[19] depletion interactions,[20] and opposite charges.[21, 22] However, self-assembly also requires strategies to limit the assembly to finite-sized clusters, to achieve uniform arrangements of the constituent particles within the clusters, and to separate the resulting colloidal molecules by size or type.

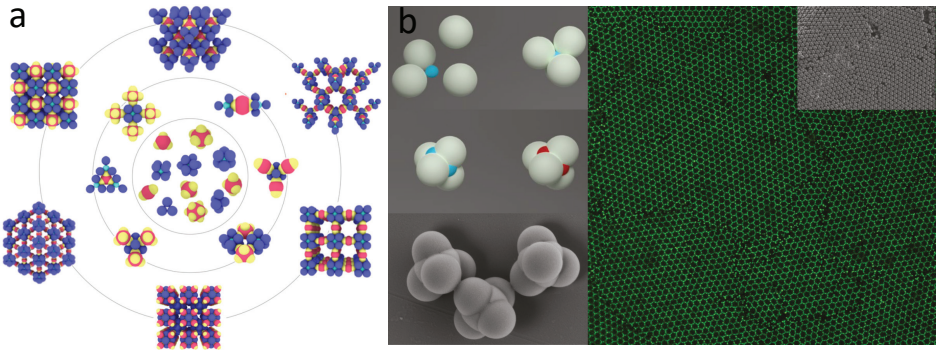

Figure 1.2: (a) Colloidal particles as a potential building blocks for self-assembly: from colloidal molecules to crystals.[14] (b) Experimental example of diamond crystal structures self-assembled from colloidal molecules. *a) Adapted from Ref[14] with permission from Wiley and b) Adapted from Ref[15] with permission from Nature Springer.*

Hetero-aggregation is a promising method of producing colloidal molecules from binary mixtures of colloidal particles. This process involves the controlled clustering of colloidal particles through various interactions such as electrostatic interaction, clustering in emulsion droplets, polymerization-induced clustering, hydrophobic interaction, and depletion force.[8, 14] From this method, the electrostatic assembly of colloidal particles is the most prevalent approach for making colloidal molecules. The strength of the electrostatic interactions can be adjusted by changing the surface charge density of the particles and the ionic concentration of the solution.[22] Experimental and simulation results have shown that hetero-aggregation can produce colloidal molecules with a potential yield of 100 % for tetramer and dimer.[23] However, except for these two shapes, hetero-aggregation typically results in a broad cluster size distribution and a low yield of colloidal molecules of a given shape. To obtain highly pure colloidal molecules from excess residual particles, density gradient centrifugation is employed.[13] In this process, a density gradient is created by using a polymer solution. The colloidal molecules are then placed in the gradient and centrifuged, allowing the molecules to separate based on their density. However, the polymer used to create the density gradient may react with the colloidal molecules, altering their surface properties.

1.0.2 DNA Coated Colloids

DNA-coated colloidal particles are colloidal particles with DNA grafted onto their surface. The DNA molecule consists of four main nucleotides: adenine (A), thymine (T), cytosine (C) and guanine (G) (see Figure 1.3a). The nucleotide A forms two hydrogen bonds with T, and C forms three with G. When single-stranded DNA is mixed with complementary single-stranded DNA, it binds specifically to complementary nucleotides in a highly precise manner and forms double-stranded DNA. These characteristics of DNA strands has applications in drug preparation,[24] to stabilize the drug for prolonged storage,[24] as a model to investigate virus-cell interaction,[25] to stabilise colloidal particles[26] and as a scaffolds for cell attachment and growth.[27] Additionally, DNA's sequence specific interactions also has been utilized to organize colloidal particles into highly order complex structures.[28, 29] For example, colloidal molecules were created by combining DNA-coated spherical particles of varying sizes.[23, 30] Moreover, by employing DNA patches on the surface of particles which replicate directional atomic or molecular interactions often called "DNA patchy particles", it is possible to create structures with greater complexity.[31] Depending on the number and size of patches, the particles form aggregates, chains and clusters.[32] This method can be expanded by multistep hierar-

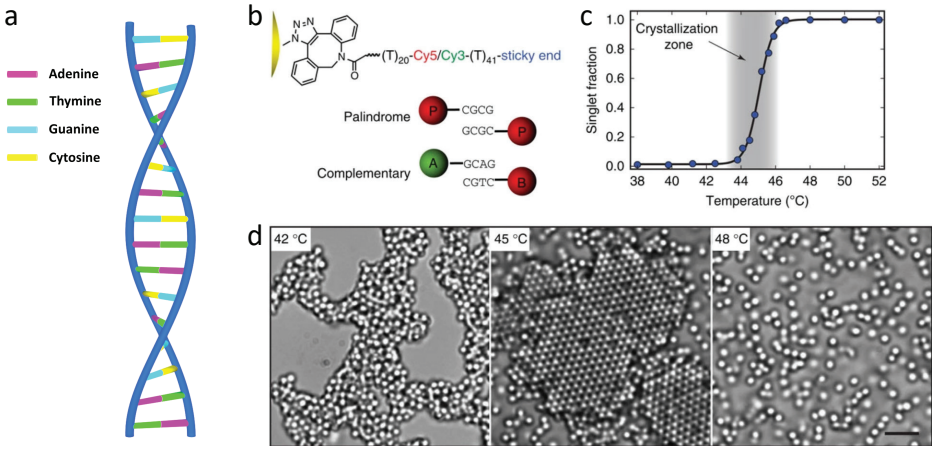

Figure 1.3: Crystallization of DNA coated colloids. (a) Schematic representation of the DNA Structure. (b) Colloids grafted with complementary DNA. (c) their melting temperature graph. (d) Self-assembly of these particles at different temperatures. At 42 °C form random aggregates. At 45 °C (melting temperature) particles DNA bonds melts, and particles reorganize and form crystal structures, and above meting temperature at 48 °C at particles melt and disassemble into single particles. *b-d) Adapted from Wang et al.[29]* (CC By 4.0).

chical assembly, which can be utilized to produce bigger colloidal clusters, hence enabling the fabrication of even more intricate structures.[33]

DNA-coated particles are also an interesting candidate for creating various crystal structures, such as face-centered cubic, hexagonal close-packed, simple cubic and diamond.[29, 34] However, initially, during crystallization process they form kinetically arrested random aggregates (see Figure 1.3b). The strength of DNA interactions is sensitive to temperature and length, making them useful tools for regulating the interactions and ultimately controlling the self-assembly of the colloids. Studies have shown that by heating and quenching the sample above the melting temperature, the random aggregates can reconfigure into the crystal structures. This means that by manipulating the temperature, it is possible to create different crystals from the same size particles. The ability to tune the DNA interactions through temperature allows full control over the assembly and disassembly of the DNA-coated colloids.

1.0.3 Flexible Colloidal Structures

The bond flexibility of flexible colloidal structures has a direct influence on their properties such as hardness, strength and durability. Only a few experiments have been shown to prepare flexible colloidal structures. Phillips et al.,[35] for example, developed reconfigurable tetramer colloidal molecules by mixing complementary shapes held together by optical tweezers via depletion interactions. In response to thermal fluctuations, these clusters can rearrange, changing shape from one form to another. The process of constructing these flexible colloidal clusters one at a time is time-consuming and unscalable, limiting their potential uses. Self-assembly is a more efficient means for generating large quantities of colloidal structures. Besides depletion interaction based self-assembly, there are currently two experimental approaches available for realizing flexible structures: one is base on solid colloids being decorated with a lipid bilayer that is functionalized with surface-mobile DNA linkers [26, 36] and the other on droplets equipped with DNA linkers as shown in Figure 1.4.[37] Using self-assembly, different flexible structures could be prepared, such as flexible colloidal molecules and chains.

The recent experimental realization of flexible joints of surface mobile DNA linkers on solid colloids enables the creation of new types of colloidal molecules with flexible bonds, in which the satellite colloids can freely move around the central one.[18, 26, 36] Silica particles were coated by a lipid bilayer, where the lipid bilayer is in the fluid state . DNA-based linkers which consist at one end of either hydrophobic cholesterol or stearyl groups that can insert into the lipid bilayer and at the other end of a DNA-sequence

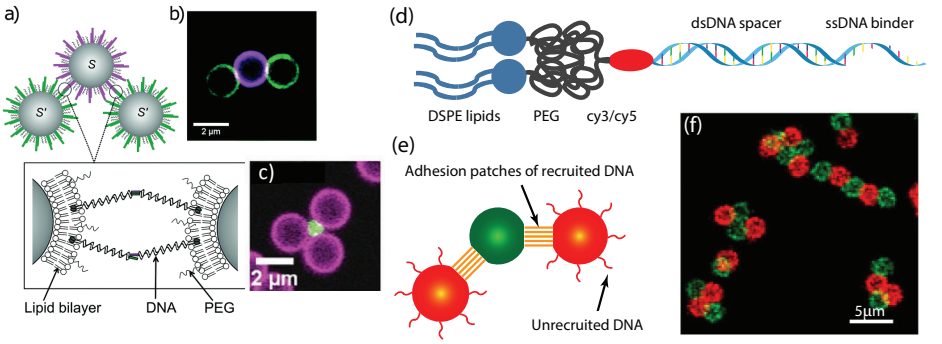

Figure 1.4: Functionalization and self-assembly of flexible colloidal molecules. (a)-(c) Solid colloidal particles functionalize with lipid bilayers and surface mobile linker DNA and self assembly into flexible trimer and colloidal molecule.[18, 26] (d)-(f) Liquid droplets functionalize with lipid bilayers and surface mobile linker DNA and assembly into flexible chains.[37] *a)-c) Adapted from chakraborty et al.[26] and [18] (CC BY-NC 3.0 and CC By 4.0). d) and e) Adapted from Mcmullen et al.[37] with permission from American Physical Society.*

that points outward in solution. Once two types of particles that are functionalized with two complementary DNA sequence are mixed, they form a flexible bond and results in flexible colloidal molecules. These DNA strands are free to move around the particles as long as the lipid bilayers remains fluid, and hence the attached colloids are able to move freely relative to one another in the resulting flexible colloidal structures. However, they lack directionality of their bonds and control over their degree of flexibility, for example through a limited angular range.

1.0.4 Scope and Outline of this Thesis

Chapter 2 presents particle shape and size effects on the cluster formation during electrostatic self-assembly of polystyrene or silica spheres onto hematite cubes. Using experiments and simulations, we find that the cubic particle shape is key for producing distinct colloidal molecules, and that electrostatic repulsion is important for assembling spheres on facets rather than edges and corners. Our protocol is material-independent and utilizes the cubes magnetic dipole moment to separate colloidal molecules from satellite particles. This simple and effective strategy could be applied to other templating particle shapes, expanding the library of high-yield, pure colloidal molecules.

In chapter 3, we demonstrate the self-assembly of flexible colloidal molecules with controlled motion range and bond directionality by assembling spherical particles onto cubes functionalized with surface-mobile DNA

linkers. We assemble colloidal molecules with different number of spheres by varying the size ratio and find a constrained range of motion above a critical size ratio. A change in temperature allows us to switch between full and constrained flexibility of these colloidal molecules *in-situ*.

In chapter 4, we employ colloids functionalized with complementary surface-mobile DNA to establish flexible connections between particles and assemble flexible lattices. We observe the development of flexible colloidal crystals in situ and investigate the effect of the particle shape and size on the reconfiguration process and final structure of the flexible colloidal crystals. These flexible colloidal structures may be useful in making flexible electronic materials and photonic crystals with tunable photonic properties.

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