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MANIPULATING MATTER WITH A SNAP OF YOUR FINGERS: A TOUCH OF THANOS IN COLLOID SCIENCE

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ABSTRACT

Being able to manipulate matter has been a long-standing goal in material science. Would it not be amazing if we could control matter on the grand scale that Thanos does when in possession of the Infinity Stones in *Avengers: Infinity War*? In this paper, we evaluate how far mankind has come in the pursuit of Thanos-like matter manipulation powers. As the properties of everyday objects are directly linked to the spatial organization of the elementary building blocks on the micro- or even nano-scale, control on these length scales is crucial. In this respect, the use of colloids is a promising strategy. Colloids are characterized by dimensions in between those of atoms and macroscopic objects such as a chemistry textbook and your smartphone. Although colloidal particles are small enough to display behaviour reminiscent of that of atoms and molecules, they are big enough for scientists to manipulate them on the single-particle level. By playing with the shape and chemistry of these colloids, materials that are sensitive to external triggers, such as light or temperature, can be created. By controlling the trigger, the colloidal matter can be manipulated, formed, or destroyed. Clearly, at the microscale, we can compete with Thanos, even without the Infinity Stones.

PROLOGUE

The universe is silent and dark. Thanos sits on his throne, contemplating his destroyed home planet Titan from a distant meteorite. A Chitauri general approaches him to give some unexpected news. The humans managed to stop Earth's invasion: they are not made to be ruled. Without taking his eyes off Titan, Thanos smiles. He finally found a worthy opponent.

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INTRODUCTION

Thanos (derived from the Greek personification of Death Thanatos) was born as a member of the Titans [1, 2]. He grew up loving his home planet Titan unconditionally. When his beloved home was threatened by catastrophic destruction due to overpopulation, he proposed a horrific solution: the elimination of half the population, at random and without prejudice. Thanos' idea was dismissed out of hand. He was condemned as a madman and exiled from Titan. Nevertheless, his insights were proven right. Eventually, Titan could no longer support its ever-growing population. Consequently, the Titans almost went extinct, leaving Thanos one of the few survivors of his race. As a result of Titan's demise, he understood that the whole universe would suffer the same fate. Driven by the belief that he could restore the balance, he depopulated and annihilated entire races and planets. To accelerate the process, Thanos set out to collect the six Infinity Stones. Once the stones were united in his Infinity Gauntlet, he instantaneously became the most powerful creature in the universe. With a snap of his fingers, he could destroy half of all life, finally restoring the balance he desperately sought for many years [3].

Thanos is one of the most infamous villains in the Marvel Cinematic Universe (MCU) and has unprecedented physical and mental capabilities [1, 2]. He combines brute force with an exceptional geniality in science, allowing him to create technology far exceeding our technological endeavours. By wielding the Infinity Gauntlet, his capabilities were extended to true matter manipulation. Examples include the transformation of Star Lord's pistol into soap bubbles, temporarily disintegrating Drax and Mantis into arbitrary shapes, partially destroying a complete moon and instantly sending fragments to the surface of Titan, and transforming a crashing spaceship into a swarm of bat-like creatures [4]. The absolute forces and energies that Thanos uses to manipulate matter on these enormous scales are beyond human capability. It could even be argued that it violates the laws of physics as we know them. However, the ability to manipulate matter is certainly not entirely science fiction. In this paper, we will highlight key scientific advances in mimicking Thanos' matter manipulation skills on the microscale, where the required energies, forces, and levels of complexity are manageable. Working on these small length scales allows chemists and physicists to create, transform, and control matter, making us become slightly more Thanos-like.

COLLOIDS: EXCUSE ME?

In general, all matter is composed of atoms, which are the smallest elementary building blocks (as far as chemists are concerned). Materials such as rocks or salt grains are highly ordered macroscopic materials directly composed of atoms. Alternatively, atoms can first group together and form molecules. These molecular building blocks can then assemble into objects we can interact with, such as apples, books, trees, cars, and of course, all living beings, including humans and Thanos. In terms of sizes, between atoms and the objects we can observe with the naked eye lies the world of colloids [5, 6].

Colloidal materials consist of a large number of small particles (solid particles, gas bubbles, or liquid droplets) that are mixed through a medium (such as a liquid, gas or solid). Despite their non-homogenous, multi-component nature, these materials appear uniform and homogeneous to the eye. This is due to the characteristic dimensions of the dispersed components, which ranges from 10 to 1000 nanometre (nm) [7]. Figure 1 shows the position of this colloidal length scale with respect to the dimensions of familiar objects from daily life in our world and the MCU. Molecules are typically no larger than 1 nm and are at least an order of magnitude smaller than a typical colloid. On the other end, an average hair on your, or Thor's head for that matter, is 100 to 1000 times as thick as a typical colloid, and 50,000 times smaller than Ant-man when he rides on the back of one of his mind-controlled ants [8,9].

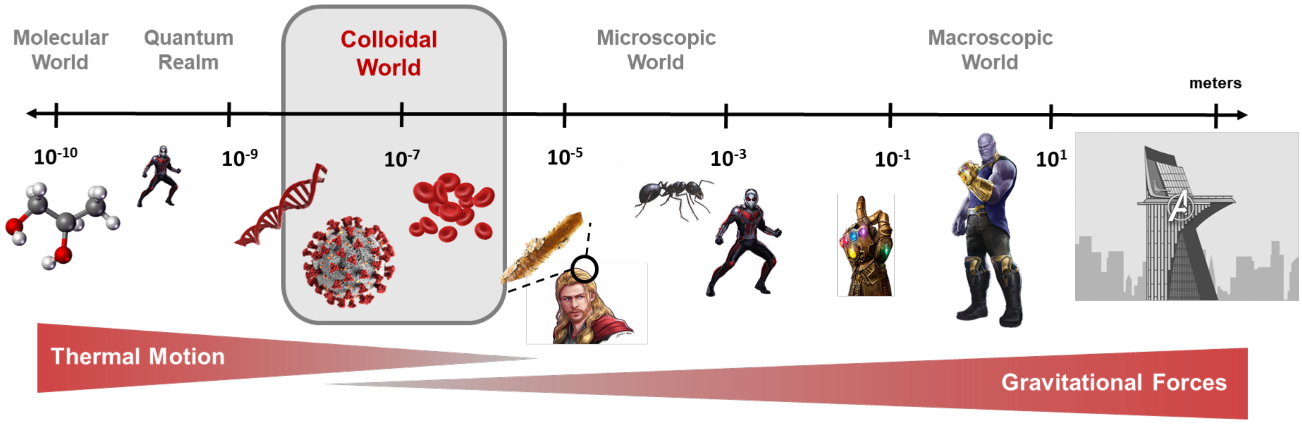

Figure 1. Schematic representation of the dimensions of objects ranging from the molecular/atomistic world to the macroscopic world. Representative examples of objects from life (real world and the MCU) are depicted to illustrate the specific length scales. The red triangular arrows depict the contribution of thermal motion and gravitational forces for objects with different characteristic dimensions. The colloidal domain ranges from roughly 10^{-8} to 10^{-6} m and is highlighted on the diagram.

Due to these small dimensions, the earth's gravity has little to no effect on these particles [6]. This means that colloids dispersed in a medium do not (or barely) sink to the bottom of the container in which you keep them. However, this does not imply that colloids are immobile. Colloids are continuously moving, a phenomenon that scientists refer to as Brownian motion [10]. These movements are the result of constant collisions between molecules of the dispersing medium (such as water molecules) and the colloids.

During Brownian motion, the particles do not follow a predetermined trajectory, simply because the probability that a dispersing molecule will hit a particle of interest is the same in all directions. To get an impression of the movement of colloidal particles, one could imagine a balloon moving over a crowd of people. Every time the balloon lands on a person, it takes a hit and moves via an unspecified path to the next person. This process continues indefinitely, and the balloon can pass over the whole crowd [11]. The speed at which the colloids perform these movements depends mainly on the temperature. Higher temperatures cause the molecules of the dispersing medium to move faster. If they bounce into a colloid, the particle will feel a larger kick, leading to faster movement of the particle. Hence, the relevant forces acting on the particles originate the input of thermal energy and are therefore called thermal forces.

As the colloids are continuously moving, they repeatedly encounter each other. If the particles are mutually attractive, similar to, for example, two magnets, they will accumulate into larger structures (Figure 2(b)). Since the movements of the particles are autonomous, assembly occurs without any human intervention. This process is known as self-assembly [12]. This is in sharp contrast to conventional assembly, for example, when Tony Stark builds the Mark III Iron Man suit from nuts, bolts, and gears (Figure 2(a)) [13, 14]. In this assembly process, all components have to be placed in the right position at the right time by someone or something that builds the suit, simply because the parts themselves do not move autonomously.

Clearly, self-assembly offers a versatile and effortless method to build large structures. Once all the individual building blocks are programmed correctly, the system can build itself. Imagine how much money and time you would save if it were possible to program colloids to self-assembly into anything you can think of!

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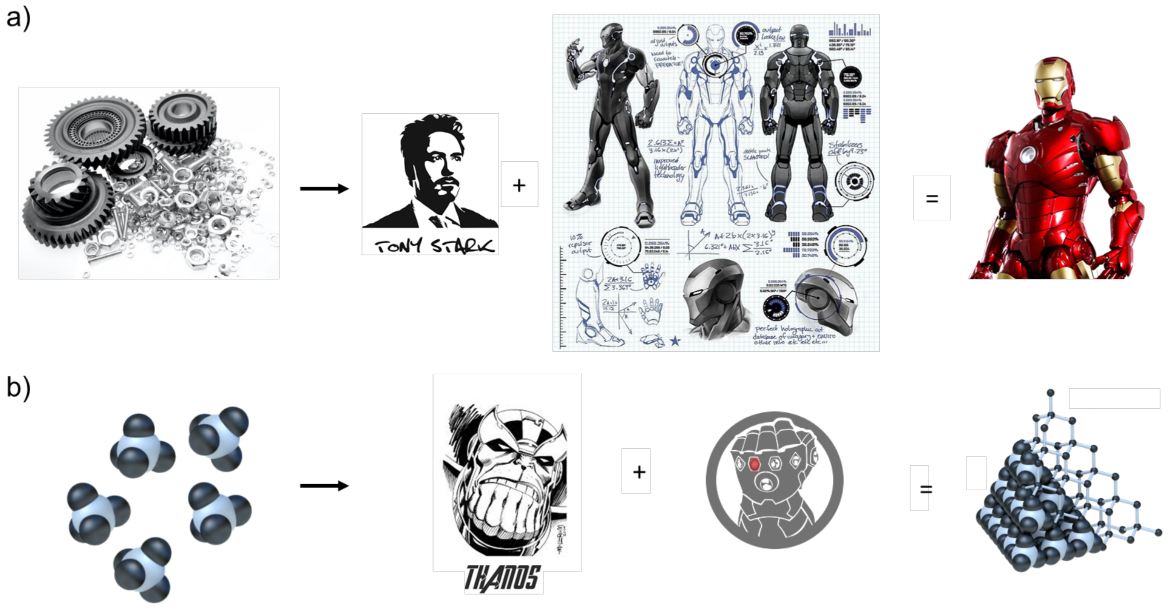

Figure 2. Schematic representation of the differences between (a) assembly and (b) self-assembly. Assembly requires active placement of passive building blocks following detailed manufacturing instructions to come to a successful final structure, for example when Tony Stark builds the Mark III Iron Man suit out of bolts, nuts, and gears. Self-assembly is a spontaneous process. Mobile particles can explore space autonomously and, when designed correctly, form a predetermined structure. Self-assembly is as easy as activating an Infinity Stone.

THE COLLODIAL EVOLUTION

Thanos gained his matter manipulation skills after collecting the Infinity Stones over the course of the film *Avengers: Infinity War*. The path leading to the collection of the Stones was tough and painstaking for the Mad Titan. Similarly, scientists over several generations have gathered knowledge and information on colloids that can be applied in the development of new ways for manipulating the building blocks of matter.

The first systematic scientific endeavours into colloid science were reported by Michael Faraday back in 1856. He managed to make a dispersion of small gold particles and proved that the gold atoms could be grouped together in colloidal entities [15]. Interestingly, the colloidal gold particles had different properties than the gold atoms you find in a gold ring. For example, the dispersions were red in colour instead of the typical yellow. Although, in retrospect, these experiments defined the start of the field that we now know as colloid science, the scientific and technological implications were not appreciated at the time. It wasn't until the titans of colloid science such as Derjaguin, Landau, Verwey, Overbeek, Onsager, Perrin, and Einstein (yes the same Einstein behind the theory of General Relativity) in the first part of the 20th century developed a theoretical framework that the potential hidden in the colloidal world was brought to light [16-20]. Once this cornerstone was laid and the fundamental physics behind colloid particles were outlined, it was time to explore how colloids could be used for real-world applications.

Early efforts to make colloids in the lab focused on spherical particles with uniform sizes. By studying these spherical particles, it was found that they could spontaneously arrange themselves or self-assemble into crystalline structures [21-23]. Crystals

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are highly ordered assemblies in which the individual particles are located at fixed positions with respect to each other. This order is periodic and extends in all three dimensions. The physics behind this ordering has plenty in common with the crystallization of atoms into solids, and it turned out that colloids are very useful model systems for atoms. The benefit of using colloidal particles is that they are much easier to work with than with atoms. Although colloids are small enough to behave just like atoms, they are big enough for scientists to manipulate (see the next section). In addition, colloids can be easily visualized with fairly simple microscopy techniques; [24-28] something that is not possible for atoms and molecules. Naturally, the possibility of literally seeing your building blocks provides a wealth of information on the system's behaviour.

Interestingly, the assemblies of spherical colloids studied in the early days of colloid science displayed vibrant colours, even though the individual particles were not coloured at all. These colours are caused by the spatial arrangement of the colloids, which affects the wavelength of light reflected by the assembly. These optical properties are unique to materials composed of colloidal building blocks. Examples of colloidal colours (known as 'structural colours') can be found in the wings of butterflies [29-33]. Additionally, if the Infinity Stones that Thanos collected in *Avengers: Infinity War* are made from colloidal particles, their range of colours might be linked to the differing colloidal building blocks and underlying colloidal arrangements, as it's safe to assume that the Infinity Stones are no ordinary stones.

Motivated by the success of spherical particles, scientists developed methods to prepare colloids with different shapes, such as rods [34, 35], platelets [36, 37], and cubes [38, 39]. By changing the shape of the particles, crystals with different (degrees of) internal structuring could be made [18, 40]. For example, rod-shaped particles form so-called liquid crystals that are not ordered in three, but only in one or two dimensions. The underlying physics was later used on a molecular scale to fabricate the LCD screen that you may be using right now to read this paper [41, 42].

Based on the properties of these first colloidal crystals, scientists wondered what material properties would be accessible if they could control the relative orientation of the particles in space even further. This idea is inspired by the atomic scale, where the orientation of atoms in periodic arrangements is very important. A striking example is the vastly different properties of graphite (which can be found in pencils) in comparison to diamonds, even though they are both made from carbon atoms [43]. In graphite, the flat carbon layers can slide past each other with ease, meaning that the material is brittle and ideal for writing on paper. On the other hand, in diamond, each carbon atom is connected to four neighbouring atoms, and it is because of this structure that diamond is one of the hardest materials known to mankind. Recently, researchers even extended this by coining the possibility that the Tesseract could be composed of carbon [44]. By optimizing the positions of the atoms in space, structures even stronger than diamonds were identified. The Tesseract might well be a form of carbon not known to humans (yet).

As changing structural order provides a way to control the properties of colloidal assemblies, matter manipulation is within reach and relies on simply changing the arrangement of building blocks on demand. As a result, this became one of the focus points of modern colloid science.

BEYOND SPHERES: THE ROAD TO MATTER MANIPULATION

TRIGGERING COLLODIAL SELF-ASSEMBLY

Similar to Thanos' ability to modify matter with by activating or triggering the appropriate Infinity Stone in the Infinity Gauntlet, colloid scientists started to study colloidal systems that can switch between the assembled and disassembled states, or even between assemblies with different internal structures. A popular and successful route for scientists towards these responsive particles is to decorate the surface of the colloids with molecules that can

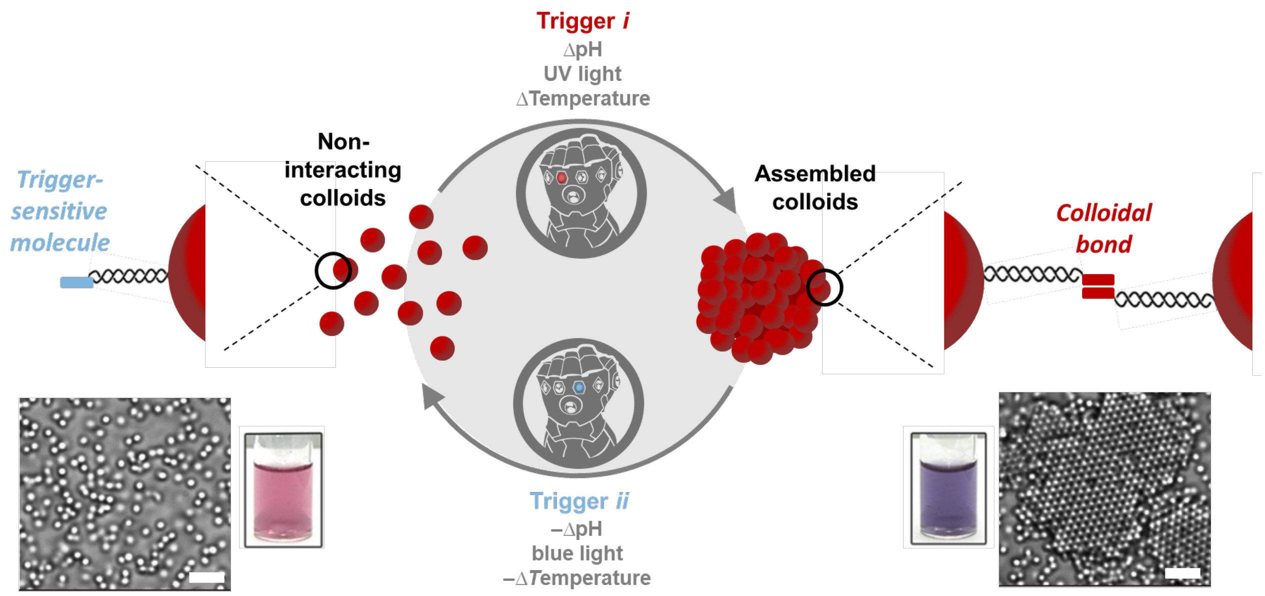

Figure 3. Illustration of responsive colloidal systems. Upon applying Trigger i, e.g., a change (Δ) in pH, temperature, or illumination with UV light, the particles are switched from a non-interacting (left) to an activated state (right). In the active state assembly takes place. The assembly can be disintegrated by applying Trigger ii. Controlling these triggers is analogous to Thanos activating an Infinity Stone to manipulate matter. Switching between the disassembled and assembled state can be followed by microscopy or even macroscopic color changes. Scale bars: 5 µm. Microscopy images were adapted from ref. 50. 2015, Nature Publishing Group.

feel and respond to external changes or triggers in the environment, such as changes in pH, temperature, or the level of illumination with particular types of light (Figure 3) [45-47].

Initially, the particles are not drawn to each other (they are in a non-interactive state). Applying a trigger creates an attractive force between the particles that eventually leads to the creation of hierarchical structures. Applying a second trigger (or stopping the first one), removes the attraction between the particles and the assembly gradually falls apart again. This is a genuine “activation of the appropriate Infinity Stone” moment to manipulate colloids. In contrast to the instantaneous changes Thanos can make with his gauntlet, the assembly and disassembly of colloidal particles generally takes some time. A little patience is required to allow the colloids to find or move away from each other via Brownian motion. The time required for (dis)assembly can vary from seconds to hours and depends on the particle concentration and the strength of the attractive or repulsive forces generated by the applied triggers.

The possibilities of this strategy are virtually endless. New surface modifications and even procedures that simultaneously incorporate sensitivity to multiple triggers are frequently reported [45-49]. A flavour of the different triggers available to colloid scientists nowadays is depicted in Figure 3. In these examples, attractions between colloidal particles can be switched on and off by using light, changes in pH, or changes in temperature. The (dis)assembly can be followed using microscopy imaging [50] or even with a colour change (Figure 3) [51].

In our laboratory at the Eindhoven University of Technology, we develop colloidal systems that are

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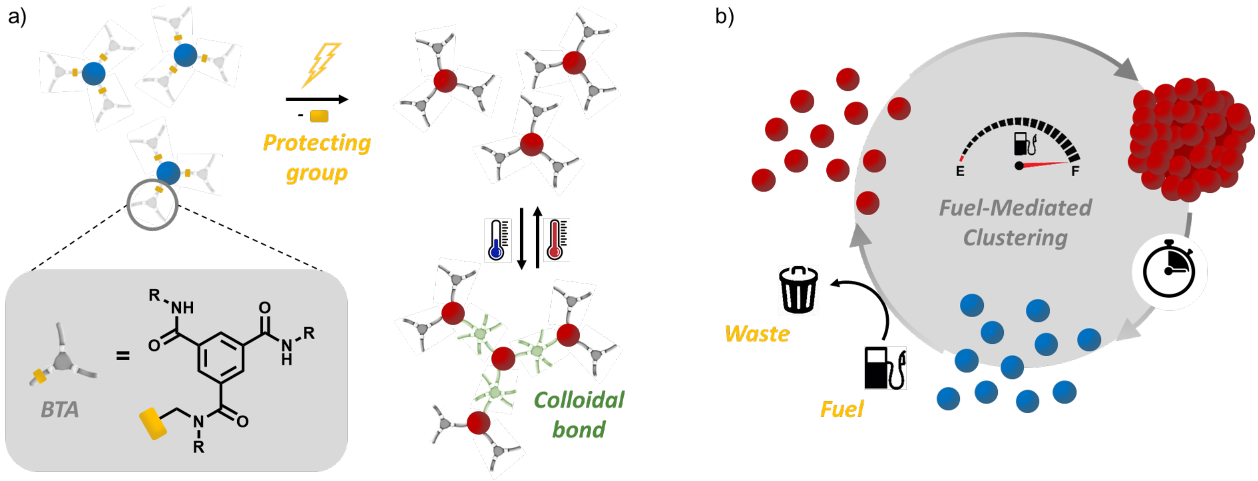

Figure 4. a) Illustration of the triggered assembly of benzene-tricaboxamide (BTA) functionalized colloids. In the non-active state (blue), the BTA molecules are protected, thereby preventing assembly. By shining light on the particles, the protecting group is removed. Once activated (red), the particles assemble at low temperature through the formation of bonds between the BTAs. These bonds are reversible and can be broken upon heating. b) Schematic representation of fuel-driven colloidal assembly. Providing a fuel to repulsive particles (blue) transforms them into attractive colloids (red) which can undergo assembly. The resulting clusters can only be maintained in the presence of fuel. Upon fuel depletion, the driving force to assemble vanishes and the clusters spontaneously fall apart.

capable of responding to different external triggers. For example, colloids can be functionalised with molecules known as BTAs (which is short for benzene-1,3,5-tricarboxamides) (Figure 4(a)) [52-54]. These are flat molecules that are attracted to each other at low temperatures, leading to the formation of molecular fibres. Heating a solution of BTAs reduces this attraction resulting in disassembly. When attached to the surface of colloids, the BTAs transfer their temperature-dependent aggregation properties to the colloids. We can then control the attraction of the resulting BTA-modified colloids simply by tuning the temperature. At low temperature, the particles are assembled. However, upon heating, these clusters fall apart. This process is completely reversible and can be repeated many times over. Furthermore, we can chemically modify the BTA molecules with a bulky substituent that hinders aggregation (Figure 4(a), yellow rectangle). Only after the application of an initial trigger in the form of UV light does the protecting group leave the BTA, which paves the way for the start of the assembly process. This system, therefore, neatly shows the use of multiple triggers (light and temperature) to not only tune the aggregation state of the particles, but also to control when the process is allowed to start.

The assembly of colloids may also be programmed to be temporary. This is not a strange phenomenon in the MCU. Thanos, for example, converts Drax and Mantis into arbitrary shapes but only for a limited time during a confrontation between the Guardians of the Galaxy and Thanos at Knowhere in *Avengers: Infinity War* [4]. In collaboration with researchers from Delft University of Technology, we can also cluster colloids that initially are repulsive towards each other (Figure 4(b), blue) [55]. This repulsion can be induced, for example, by negatively charged molecules attached to the surface of the particles. Remember equal charges repel each other. Therefore, when all particles carry a negative charge, they will not assemble. Upon the addition of a chemical fuel, the particles are activated. In this activation step, the fuel (dimethyl sulphate) is used to convert the negatively charged surface groups to non-charged ones (Figure 4(b), red). Since no charge is left in the activated state, the particles become attractive and cluster. However, clustering is not permanent. When the fuel has been consumed, the particles can no longer be kept in the activated state. The negative charges will spontaneously reappear on their surfaces, which eventually leads to disassembly. The addition of new fuel can return the system to a clustering state, and this process can then be repeated on demand.

PATCHY CONTROL OF PARTICLES

By using triggered interactions, we are already able to manipulate matter at the colloidal length scale. However, most spherical colloids lead to undefined structures. The poor control over the colloidal structure is caused by the fact that functional groups that induce attractions between the particles are equally distributed over the whole particle surface. Hence, there is no preference for a certain number of colloidal bonds per particle. The particles simply get stuck in the position that they meet each other via Brownian motion. Additionally, as the entire particle becomes attractive, there is no control over the number of colloids that cluster together. Assembly will just continue to until all particles are bound together. Similar to atoms, the internal arrangement of colloids in the assembled state influences the properties of the assembled structure. Tuning the properties of colloidal materials thus requires control of the internal structure beyond random clusters.

A promising way to do this is using patchy particles [56-59]. As indicated by their name, these particles have specific regions (patches) on their surface. The particles will exclusively interact with each other via these attractive spots. A plethora of materials can be produced by controlling the number of patches and their location on the particle. In fact, this strategy is very similar to the way carbon atoms can assemble into either graphite or diamonds. The position and direction of the bonds between these carbon atoms are determined by non-homogeneous distributions of electrons surrounding the atomic nucleus [60].

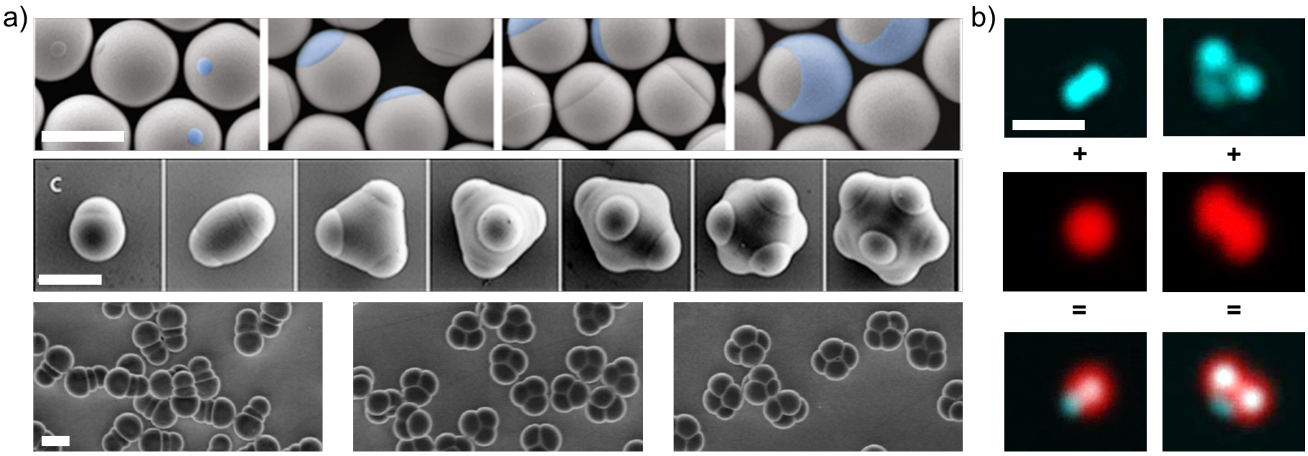

Figure 5. a) Images of patchy particles. Besides having control over the patch size (top row, blue), we can also tune the shape and number of patches. Middle row shows particles with 1–7 patches (left to right). In the bottom row, patchy particles with different patch orientations are depicted. These particles are typically no larger than a few micrometers. b) Demonstrating that particles contains chemically different patches. This is done by adding fluorescent molecules to the particles. If the particles are patchy, these molecules will only attach to the reactive patches. Combining the image of the shape (blue) and the fluorescent labels (red) gives an indication of the patchiness. Scale bars in all panels: 1 µm. Adapted with permission from ref. 61 – 64. 2019, Nature Publishing Group; Copyright: 2007, John Wiley and Sons; 2013 and 2014, American Chemical Society.

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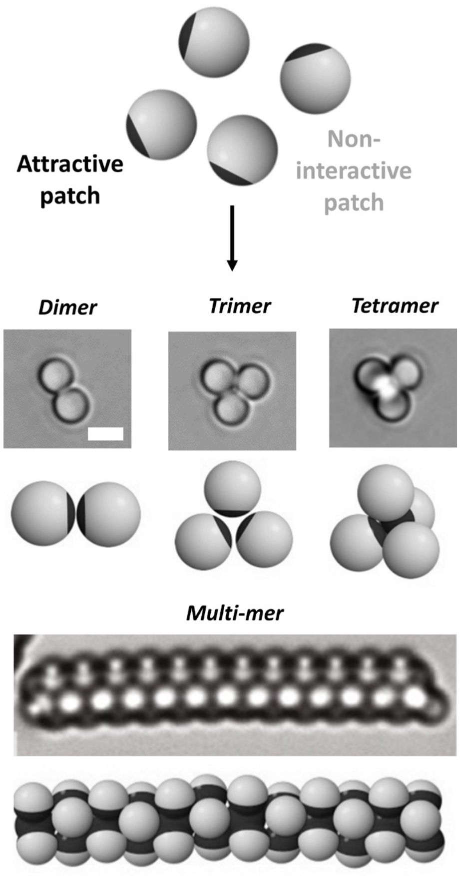

Figure 6. Self-assembly of 1-patch particles into dimers, trimers, tetramers, and larger colloidal chains. The attractive patches (black) form bonds between the particles, while the non-interacting lobes do not. The size of the patches determines how many particles can fit in one cluster. The predicted structures based on the shape of the particles (bottom row) is in excellent agreement with experimental microscopy analysis. Adapted from ref. 62. Scale bar: 5 µm.

Because of their high potential in creating well-defined assemblies, tremendous efforts have been devoted to making and designing patchy particles. In fact, so many procedures are reported that it is impossible to discuss them all here. For the interested reader, we refer to a recent specialized review article on this topic [57]. Figure 5(a) provides a small selection of the advanced patchy particle systems available today [61-64]. Clearly, the number, size, orientation, and even shape of the patches can be tuned over a broad range.

Typically, the particles are synthesized in such a way that the patches are chemically functionalised. These functionalities can then be used to selectively couple specific molecules to these patches that introduce responsive/triggered properties to the particles (see "Triggering Colloidal Self-Assembly"). To prove that these chemical functionalities are located on the patches only, the particles are typically reacted with fluorescent light-emitting tags (Figure 5(b), red). By using specialized microscopy techniques, the location of the fluorescent spots, and hence the reactive patches, can be imaged and detected. This process is shown for 1- and 2-patch particles that were synthesized in our lab and at Utrecht University (Figure 5b) [63, 65].

With the patchy particles in hand, the road to predictable colloidal matter manipulation is open. Motivated by the exciting thought of making materials with unnatural (responsive) properties, and frankly also to see how far we can push our matter manipulation skills, scientists are now exploring the range of exotic structures that can be made at the microscale using patchy particles as the building blocks.

Colloid scientists can apply the strategies presented in Figure 3 to functionalise the patches to control the types of structures that result after particle interactions. For example, the assembly of a non-interacting colloid (grey) containing an attractive patch (black) can result in a range of different clusters such as dimers, trimers, tetramers, and even long colloidal chains (Figure 6(a)) [62]. In all these clusters, the attractive black patches are facing each other to maximize the number of contacts between the patches. The preferred cluster or structure depends mostly on the size of the patch. Larger patches result in clusters that contain a larger number of colloids. The predicted structures (based on simple geometry) match with the experimental structures observed under the microscope. Applying the concept of selective patch functionalisations opens a world of virtually endless colloidal structures, especially when particles with different number of patches are programmed to interact with each other in highly specific ways [66]. These examples combine temperature-induced triggered interactions with precise control over the size and shape of the assemblies. In a sense, this is true matter manipulation at the colloidal length scale.

CONCLUSIONS

In this paper, we have shown that controlling matter, regardless of the length scale, requires control over the forces between objects. To control large (macroscopic) objects, a large amount of energy is needed. One way to control such objects is to acquire the Infinity Gauntlet complete with the six Infinity Stones, just like Thanos in *Avengers: Infinity War*.

Scientists can now mimic part of Thanos' control over matter at the microscopic scale thanks in part to advancements in our knowledge and understanding of how forces operate at the colloidal level. This understanding has been applied to colloidal particles and allowed scientists to build complicated and intricate structures using colloidal building blocks that have been produced using sophisticated synthetic procedures. We can now make a wide range of colloidal particles with tunable responsiveness, patchiness, shapes, and sizes. By controlling the interparticle forces, we can manipulate billions (yes billions!) of colloids at the same time by varying triggers such as temperature, pH, and light.

Thanks to these patchy and responsive colloidal systems, the colloidal community is aiming to build macroscopic materials that could be used for future sensors, shock absorbers, and even optical materials. To manipulate matter, the Infinity Stones are not strictly necessary. There is no need to roam the universe for the stones just like Thanos did in *Avengers: Infinity War*. The answer may very well be right in front of us, and at the microscopic scale. The answer is colloids.

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