# Colloidal Processing: Enabling Complex Shaped Ceramics with Unique Multiscale Structures

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## Abstract

Colloidal processing of fine ceramic powders enables the production of complex shaped ceramics with unique micro and macro structures which are not possible to produce via conventional dry processing routes. Because of this enhanced structural control and shaping capabilities, colloidal processing has been exploited to produce ceramic components with ever increasing complexity and functionalities. In this review, we revisit some of the research efforts on this topic to highlight its relevance and growing importance for the advanced manufacturing of functional ceramics. Selected examples of colloidal systems with increasing level of complexity are discussed to showcase the wide range of structures that can be generated through wet processing approaches. The historical development and background knowledge pertaining to colloids and surface interactions is first briefly reviewed. The major colloidal shape forming and additive manufacturing processes that utilize colloidal pastes and inks are then reviewed, highlighting the control of suspension rheology needed in these techniques. Next, methodologies that combine suspended particles with a pore-forming phase are discussed as a means to produce porous ceramic materials. Further control over the interactions between anisotropic particles and their alignment in suspensions can be gained via externally applied fields (such as magnetic) to produce texturally aligned green bodies. This leads to bioinspired ceramics that can programmably morph into complex shaped objects upon sintering. Hierarchical porous structures with high mechanical efficiency are also shown as an example of the multiscale designs that can be generated through advanced colloidal processing. As drying of ceramic bodies is an inevitable consequence of wet colloidal processing, the current understanding of this critical processing step is reviewed. Finally, the gaps in knowledge in these fields are discussed to provide our perspective on where the field may support advances in ceramics in the future.

## 1 Introduction

Ceramics in the form of clays have been used by mankind for thousands of years, with some of the oldest fired ceramic figurine artefacts having been dated at 26,000 before present (BP)[1]. Ceramics used for utilitarian purposes such as cooking and food storage were discovered in East Asia that was dated at 20,000 BP[2]. The clay particles of such ceramics were of such small size that they are classified as colloids. Colloids are materials (particles and molecules) with such small size (typically between about 10 nm and a few microns) that Brownian motion and surface interactions dominate their behavior relative to body forces (due to mass) such as gravity. These clays used in ancient pottery are the earliest examples of colloidal materials that exhibit forming ability and consistency that allows for the production of complex ceramic shapes. Despite these very early examples, the colloidal phenomena underlying such remarkable plasticity and shaping ability were only elucidated much later. The foundations of colloidal chemistry can be traced back to the work Robert Brown[3] (Brownian motion) and Francesco Selmi[4] in the early 19th century. During the mid-19th century Graham[5] during the mid-19th century, whereby the author classed solutions of high molecular weight substances such as gelatins as 'colloids'. The term was later expanded to include all finely divided substances in a dispersed state[6–10] and 'colloids' have since become the widely accepted description of materials that remain dispersed in suspension via Brownian motion and surface interactions[11].

The field of ceramics began to display notable interest in colloid science when it was reported that the plasticity, and hence the wet strength of green body clays, was a function of the amount of colloidal matter present in the clay mixture[12, 13]. Ashley[14] presented a detailed study in 1909 where the author applied the knowledge of colloid theory at the time to describing and measuring the properties of clays. The author also detailed methods of measuring the plasticity of the clays by the amount of dye absorbed by the colloidal matter. The increasing use of ceramics and ceramic based materials around the beginning of the 20th century in both building and engineering applications led to further studies on understanding certain material processing-property relationships of clay bodies. Increasing the wet strength of clays was of particular interest since it would allow for better formability and hence final dimensional control of ceramic components. Acheson[15, 16] showed that adding a certain amount of tannin to the clay not only increased the yield strength of the plastic mass, but also increased the plasticity and reduced the drying shrinkage by approximately 40%. Bleininger and Fulton[17], and Kerr and Fulton[18] studied the effect of acids and alkalis on the drying shrinkage of plastic clays. The two aforementioned studies highlight the sensitivity of clay to additions of reagents, and in addition, both showed a tendency for the acids to reduce the drying shrinkage. Although these ceramists did not know it at the time, they were controlling the surface interactions between the particles in the suspension.

These initial studies then led to more detailed work by Schurecht[19] published 100 years ago in the first volume of the Journal of the American Ceramic Society, which quantified the strength of wet clays by performing three-point bend tests and determining the resulting modulus of rupture. The clay suspensions were modified with varying amounts of electrolytes including sodium hydroxide, sodium silicate, sodium carbonate, calcium hydroxide, tannic acid, and sulphuric acid. Schurecht[19] reported that alkalis, such as the sodium hydroxide that produced the strongest air-dried clay, appeared to have dispersed the clay particles resulting in a fine grain structure when examined with a microscope. In addition, the strength imparted by the addition of sodium hydroxide was translated to the fired clay that was also reported as having the greatest strength of all the modified clays. Apart from the difficulty of molding clays dispersed with NaOH, Schurecht's[19] work revealed these clays also exhibited the highest densities and lowest percent porosity of all the acids and alkalis tested. A patent filed some years later by Bleininger[20] laid claim to the use of alkalis and acids to control the plasticity and formability of clays, yet the true understanding of the surface charge imparted onto the particles by such additions was some years off.

With clays being the catalyst of how colloids and colloidal processing can aid in the formability and properties of ceramic materials, investigation into how to make non-clay ceramics plastic began. As early as 1910 alumina ($Al_2O_3$) was rendered plastic by acid treatment followed by zirconia ($ZrO_2$) and other ceramics by the mid 1920's[21]. Around this time, colloidal processing found use in the fabrication of dense composite bricks made from thoria ($ThO_2$) and $ZrO_2$ used primarily as refractory wall liners[22, 23]. Work carried out by Cox[24] using simple potter's methods such as stoneware turning showed that the addition of colloidal bentonite to traditionally non-plastic clays was able to alter their formability and produce crack-free hollow forms, enabling the use of a wider range of clays on brick and tile machines. Chemical resistance and mechanical strength of ceramic materials was improved by producing ceramics in the colloidal state from alkali-free silicates with an addition of alkali earths[25], or by applying a colloidal zirconia based coating to components before firing[26]. Furthermore, the addition of aluminium silicate fibers to clay colloids was also used as a mechanism to greatly increase the strength of ceramic bodies while decreasing shrinkage during firing[27, 28]. The colloidal nature of the clay allowed for an even dispersion of the aluminium silicate fibers so that during the firing process, as organics were oxidized, the fibers were able to grow longitudinally and fill the voids occupied by the organic matter.

During the 1930's research on the processing side of casting and forming ceramics for more advanced applications was carried out. Slip casting was seen as a viable method in producing ceramic crucibles for use in casting refractories[29]. The surface finish associated with the traditional forming methods such as pressing or tamping produced a degree of roughness that would lead to premature fractures. For this reason, Thompson and Mallett[29] applied the slip casting process to produce thin walled crucibles along with thick cross section bricks of $Al_2O_3$, beryllia (BeO), zircon ($ZrSiO_4$), $ZrO_2$, and electrically fused $ThO_2$ – all of which were cast from aqueous colloidal suspensions. The authors drew on Hall's[30] review of slip casting clays that highlighted aspects such as controlling suspension impurities, found in both the solid materials and in the solution. In addition, the authors applied work by Ruff *et al.*[31–34] that showed suspensions of finely ground oxide could be produced to yield the desired amount of plasticity for forming operations with only additions of acids or alkalis without the additional solids that were traditionally added to provide plasticity. However, as encountered in many technological breakthroughs both in the past and in the present day, the empirical knowledge was still not understood from a fundamental scientific point of view.

Another significant advancement in the mid-1940s was the development of tape casting by Howatt *et al.*[35, 36]. Thin titanium dioxide ($TiO_2$) sheets were produced for use as capacitors, with the process depending strongly on the suspension properties and, as to be expected, on the apparatus settings. Work carried out by Hauth[21] in 1949 on the slip casting of $Al_2O_3$ studied the effect of pH on casting properties such as density, porosity, green strength and others, with suspensions ranging between acidic (3.0) and basic (12.5) pH levels. Most noticeably, the author applied the diffuse double layer theory[6, 37] to describe the charge on the colloidal particles used in the $Al_2O_3$ suspensions that was earlier adopted by Johnson and Norton[38] in describing the dispersion of clay slips. Higher green densities with low porosities were achieved with the less viscous and dispersed suspensions. Although the use of ceramics in various industries was increasing, ceramic colloidal processing received little attention in terms of technological applications onwards of the 1940s, with techniques such as hot pressing being the preferred method for shaping and processing oxide and non-oxide ceramic materials and colloidal processing being primarily applied to clays[39].

Simultaneously but independent of the ceramic processing work on clay and other ceramic based products was the development of understanding of surface forces and their role in colloidal stability. Summary of the modern understanding of how to manipulate surface forces to control suspension behavior in ceramic powder processing is presented in Section 2. However, in the late 1930's Hamaker[40] built on the concepts of van der Waals attractive intermolecular forces by summing the interactions between all atoms in a macroscopic body (such as a sphere or particle) to develop the concept of a Hamaker constant (A) to characterize the attractive interactions between particles now referred to as van der Waals forces[41]. Lifshitz[42] and others[43] advanced Hamaker's concepts over the coming decades.

During the 1940s the development of understanding of surface charging behaviour and colloid stability based on electrical double layer forces between like charged surfaces was developed independently by Boris Derjaguin and Lev Landau[44] and Evert Verwey and Theodoor Overbeek[44, 45] commonly referred to as the DLVO theory. Further refinement to understand interactions between dissimilarly charged surfaces resulting in heterocoagulation was developed by Hogg, Healy and Fuerstenau in 1966[46]. During this period the zeta potential (ζ-potential) of a surface began to be recognized as an important parameter in controlling suspension stability[47]. A fundamental study was carried out by Parks[48] to understand what properties, such as the counterion type, hydration rate and purity of the solid, effect the isoelectric point (IEP) of various oxides in aqueous suspensions. Anderson and Murray's[49] work related the zeta potential (ζ-potential) to the pH and rheological properties of oxide dispersions. The authors were able to show both theoretically and experimentally that a maximum ζ-potential was related to the low viscosity required for adequate pouring and degassing of slips, along with achieving a high particle packing density in resulting green bodies. Similarly, Robinson *et al.*[50] showed that the IEP of $Al_2O_3$ in an aqueous suspension increased when maintained in water at room temperature over a period of weeks.

The understanding of the conformation of polymers in solution, and at interfaces and how polymers at interfaces influence particle interactions was developed based on the foundation in polymer physics laid down by Flory[51] and de Gennes[52] in the 1960s and 1970s. The Bristol group[53] studied polymers at interfaces and Napper[54] explained how polymer solvency, and conformation at the surface influence the repulsive or attractive steric interactions. Such information about influence of polymer molecular weight, solvency and adsorbed amount provided the understanding necessary to use polymers to produce either flocculated or dispersed suspensions.

Ceramists began to incorporate knowledge of colloidal particle interactions into their thinking about processing advanced ceramics in the 1960s and 1970s with focus on oxides (including dielectrics) and silicon carbide (SiC)[49, 55]. By the end of the 1970s ceramists began to realize that in order to produce higher quality ceramics with fine grains and minimal porosity, they needed to use finer powders and pack them to higher and more uniform density[56, 57]which could be accomplished using colloidal processing but generally not with dry pressing. The modern age of colloidal ceramic powder processing really took off during the 1980s when pioneers like Lange and Aksay[58] began to translate concepts from surface chemistry (such as surface forces) and suspension rheology into ceramic powder processing of advanced ceramics. The relationship between processing flaws and low strength was firmly established by this time[59, 60]. The idea that repulsive (dispersed) suspensions were useful to reduce agglomerates and flaws as well as to produce high density and uniform green bodies became common knowledge by the end of the decade[61, 62]. Using the knowledge developed in understanding electrical double layer and steric interactions of polymers adsorbed to particles surfaces (mentioned above), wide spread use and understanding of polymeric dispersants ensued[63, 64].

During the 1980s and 1990s a range of near net shape forming techniques such as injection moulding[65–68], gel casting[69, 70], direct coagulation casting (DCC)[71] and freeze casting[72, 73] began to be developed in addition to the traditional colloidal shaping processes of ram pressing, jiggering, extrusion, slip casting and tape casting. The details of the most significant of these processes are illustrated in Figure 1. Although only widely investigated from the 1990s, several of these techniques have roots in much older investigations[74–77]. One of the significant challenges in near-net shape forming is ensuring sufficient wet green strength to enable removal from the mold without damaging the part. This is particularly challenging when there is syneresis (shrinkage) of the object during gelation and the shaped object has concave profiles. The new century ushered in development of colloidal processing approaches to develop complex microstructures particularly cellular materials[78]. Concepts such as freeze casting for ice templating[79] and particle stabilized foams[80] began to proliferate in addition to sacrificial templating[81]. Many different types of near net shaping processes have now been applied to a wide variety of different ceramic materials[82–86].

Figure 1 Location

The widespread interest in nanoparticles began in the 1990s. It became clear that such small particles could not be handled dry but there were also significant challenges in dealing with them in suspension[87–89]. This sparked effort to improve understanding of stabilization strategies and the development of tailored dispersants to enable nano-particles to enjoy the advantages offered by colloidal processing. Special care needs to be taken to properly disperse fine nano-sized particles[90, 88, 89, 87]. Furthermore, when densifying nano-powders, one needs to carefully control the sintering conditions to avoid grain growth[91–93]. Preparing ceramics with nano-particles or reinforcements, such as carbon nanotubes (CNTs) and graphene, is very difficult to do by conventional dry processing. The nano-scale objects tend to agglomerate and do not pack to high green densities by dry pressing. Colloidal processing is useful to aid in deagglomeration and mixing of reinforcements and enables complex shape forming of high density green bodies. Significant progress has been made in incorporating carbon nano-materials into ceramic matrices using colloidal processing techniques[94–99].

The objective of this review is to highlight the types of unique multiscale structures that can be created in complex shaped components using wet colloidal techniques that cannot be produced *via* traditional dry processes. These include porous or cellular ceramics produced by a variety of techniques including replica, particle stabilized foams and ice templating. Many of the additive manufacturing (AM) processes for ceramics rely on the production of colloidal suspensions as the pastes or inks required for 3D printing applications. The key concepts required to produce ceramics with unique microstructures span over several length scales, including knowledge of how to control interparticle forces, particle orientation, suspension rheology and particle packing as well as knowledge of how to control the drying of the green bodies to avoid cracking.

## 2 Controlling Interactions between Particles

The van der Waals interaction produces an attractive force between particles of the same material[100–103]. In dry systems, there is no effective means to counteract the van der Waals attraction. For instance, while static charge produced by friction may initially lead to electrostatic repulsion in air, this dissipates with time and is significantly reduced by humidity. In wet systems there are a variety of mechanisms that can be used to produce repulsion, which overwhelms the van der Waals attraction[41, 104–106, 47] as shown in Figure 2.

Figure 2 Location

In aqueous solutions, surfaces become charged by reaction of sites such as surface hydroxyl groups with acid and base as shown in Figure 2b. At low pH the surface becomes positively charged while at high pH the surface is negatively charged. The pH at which the surface is neutral is called the isoelectric point (IEP) and depends on the particular material[48, 107, 108, 106]. When highly charged surfaces of similar sign interact in aqueous solution, the surfaces are repelled from each other. The counterions in solution which keep the entire system electrically neutral, become concentrated in the gap between particles. The high concentration of ions in solution results in an osmotic pressure that produces repulsion between the particles known as electrical double layer (EDL) repulsion[41, 44, 45, 47].

Molecules such as polymers or surfactants can be adsorbed from solution onto the particles surfaces. Small charged molecules such as citric acid[109, 110] can specifically adsorb on to particles surface, shifting their IEP and increasing the zeta potential to increase EDL repulsion. If the molecules are highly soluble in the solution, they extend out from the particles surface producing steric repulsion[54, 105]. Adsorption of charged polymers results in combination of EDL and steric repulsion known as electrosteric repulsion[63]. If the molecules are too short, the repulsion will not overwhelm the van der Waals attraction. Likewise, if the molecules are not well solubilized by the solution, there can be attraction between particles due to the entropic association of poorly soluble polymer chains adsorbed on particles' surfaces. In the case of the molecules being surfactants with a hydrophobic component, the contact angle of the surface can be increased such that the water will not easily wet the particles surface (see particle stabilized foams in section 4.2). Such conditions result in the much debated "hydrophobic" attraction between particles which may be able to be explained by nano-bubbles, van der Waals attraction, steric attraction or other phenomena[54, 111, 112]. Very high molecular weight polymers are known to produce bridging attraction between particles which is related to how binders provide improved strength to green bodies. Finally, depletion interactions, most commonly depletion attraction result from polymers in solution that are not adsorbed to the particles surface[105].

The interaction forces between particles are important because they control the suspension behaviour such as viscosity and yield stress, particle packing (green density) under applied pressure, (see Figure 2) and interaction of particles with interfaces such as air-water and oil-water interfaces. Suspension rheology and the structure of gelled colloids have been studied extensively but will not be covered in detail here as there are other good sources of information on these topics[47, 113, 105]. Strong attraction produces high viscosity, paste-like suspensions with yield stresses[47], low green density due to inefficient particle packing under applied pressures[114] and aggregated rapidly settling suspensions[47]. Repulsion between particles produces dispersed suspensions that have low viscosity, pack to high and uniform green density under applied pressures and remain stable against sedimentation if colloidal in size[113]. Weakly attractive particle networks may be useful in ceramic processing in situations where clay-like or paste-like rheology[115] is useful, such as in additive manufacturing by direct ink writing (DIW). Controlling interparticle interactions is a useful approach to design colloidal pastes with rheological behavior tuned for extrusion-based additive manufacturing. The growing interest in such digital manufacturing processes has made such tuneable colloidal systems highly relevant for the fabrication of advanced ceramics with complex geometries through 3D printing and other additive manufacturing techniques, as discussed in the next section. The long term stability of slips, however, is still a challenge.

## 3 Development of Pastes and Inks for Additive Manufacturing (AM)

Over the past two decades, what was referred to as rapid prototyping (RP) or solid freeform fabrication (SFF) is now commonly called additive manufacturing or 3D printing. These approaches are moving from prototyping techniques into the manufacturing industry. This is due to their ability to rapidly fabricate net or near-net shaped three-dimensional components with the required geometry, reduced fabrication times, smaller floor space requirement, lower tooling costs and reduced post-machining resulting in overall lower production costs for customized parts. The additive manufacturing technologies have been used to fabricate objects from polymers, resins, metallic materials and even ceramics. Using additive manufacturing technologies, green ceramic objects with tailored microstructures (dense or specifically designed porosity) can be generated based on the CAD (computer aided design) files. The AM-processed green ceramic parts are then sintered in a furnace to obtain the final products.

Some early additive manufacturing of ceramics was developed to accommodate dry powder feedstocks. The consecutive layers of powder are bonded using a binder solution deposited in-between the powder layers. This method is known as powder-based 3D printing (P-3DP). Powder-based selective laser sintering (P-SLS) uses a laser to partially sinter the powder or melt the binder phase in a binder-coated powder. In most cases, it is difficult to achieve ceramic objects with relative density above 95% without adding dopants or liquid forming phases[116, 117], post-processing (cold or warm isostatic pressing)[118–122], and post-infiltration[123–128].

To overcome such difficulties in obtaining dense products, different additive manufacturing techniques requiring suspension (slurry or paste) feedstocks were developed. These are the focus of the present review. Understanding surface interactions plays an important role in determining the suspension stability and rheological properties. The use of well-dispersed slurries enables the formation of green bodies with higher densities (> 55 %TD (theoretical density)) compared to the random packing of dry powders[129, 130]. In addition, fine ceramic powders can be used to prepare the slurry feedstock for AM without compromising the material flowability and the slurry bed stability[130]. Both the high packing density and smaller particle size within the green bodies are beneficial for manufacturing dense ceramic objects.

As shown in Figure 3 the suspension-based additive manufacturing techniques can be categorized into direct ink writing (DIW) using pastes (including Robocasting (RC)[131–133], fused deposition of ceramics (FDC) [134–136] and similar filament based DIW techniques), direct inkjet printing (DIP)[137–139], stereolithography (SL)[140–143], slurry-based 3D printing (S-3DP)[130, 144–146] and slurry-based selective laser sintering (S-SLS)[146]. These AM techniques start with well-dispersed slurries with typical solid loading of 30-50 vol% with the exception of DIP which can be as low as a few volume percent solids. The slurries must also possess a shear thinning behavior and be within a viscosity range that vary broadly between 0.001 and 100 Pa.s at between 100 and 1000 $s^{-1}$ depending on the AM technique. The suspensions for DIW should have a yield stress as discussed in more detail in the next section. The S-3DP and S-SLS processes are similar to the powder-based versions, except for the slurry feedstock. Aqueous slurries stabilised with polymeric dispersants such as polyacrylic acid and polymethacrylic acid are usually employed for the S-3DP and S-SLS processes[130, 144–146]. We describe each of these in detail in the following sections including a discussion on the rheological properties required for successful additive manufacturing.

Figure 3 Location

### 3.1. Direct Ink Writing (DIW)

In the current paper, we use the term direct ink writing (DIW) to classify a range of additive manufacturing techniques which rely on extruding a line of suspension through a small diameter nozzle to write a shaped object on a stage. These techniques encompass what has been referred to before as filament DIW[129, 147] and extrusion freeform fabrication[148, 149] and includes Robocasting[131, 132, 150–152], fused deposition of ceramics[136, 153, 154], and freeze extrusion [155–158].

#### 3.1.1. Robocasting (RC)

Robocasting (RC) is a trade name used to describe an additive manufacturing technique developed at Sandia national labs[133], although here we use it to describe the entire class of 3D printing based on paste extrusion. These techniques involve the extrusion of a highly loaded colloidal slurry close to dilatancy, typically containing 50-65 vol% ceramic powder, <1 vol%

organic additives and 35-50 vol% solvent (usually water)[131] To maintain the structural integrity while building an object, RC relies on the rheology of the deposited slurry and on partial drying of the individual layers. The slurry must be extremely shear thinning to enable flow during deposition through a nozzle and solidify in place once shear stresses are removed. Slurry that is too fluid will spread uncontrollably, while slurry that has too high yield stress lays down like ropes and maintains rounded tops. The extruded slurry then undergoes a transformation from a pseudoplastic to dilatant behavior triggered by a minimum amount of drying[131, 132]. The transition to a dilatant behavior allows the slurry to maintain its shape and resist deformation when a new layer is deposited on top of the first ones.

Many authors refer to suspensions with the type of rheological behavior suitable for DIW as gels. Such suspensions are composed of particles which interact via attractive interactions or have a continuous phase gelled with a polymer. They typically have viscoelastic behavior, where the storage modulus is greater than the viscous modulus to resist flow. A quick calculation based on the height of a typical filament (50 to 500 μm) and the density of the suspension indicate that a yield stress on the order of 1 to 10 Pa is required to prevent the filament from slumping under its own weight[159]. This value is generally about 2 to 3 orders of magnitude lower than the actual yield stress typically required (100 Pa to 1000 Pa)[129, 160, 159]. The reasons for the discrepancy are that the filaments need to bridge the span across empty space above lower levels and need to support the weight of all the layers above them without deforming. Moreover, a high yield stress is not only important to create spanning filaments, but also to prevent local distortion of overhangs due to the action of capillary forces. Estimates of typical capillary pressures developed across the curved surface of 0.4 mm filaments lead to stresses on the order of 100 Pa[161], which better explains the empirical yield stresses required for successful DIW.

Another important factor in considering the paste formulation is the volume fraction of solids. As the concentration of solids increases, the rheological properties such as yield stress increase according to a power law relationship with exponent about 4 or 5. As such, a slight amount of drying will increase the yield strength of the suspension dramatically[113]. The preferred paste formulation has solids content close to the maximum packing concentration so that when the deposited filament dries a bit during the time between deposition of subsequent layers, the material increases in strength due to particle jamming or dilatancy. The paste must also be formulated to avoid drying shrinkage which may cause cracking as discussed in section 7.

Manipulating the particle interaction forces using the surface chemistry concepts presented in section 2, enable one to control the flow behavior of the suspension. Tuning of the attractive interaction between the particles such that a weak attraction is produced is preferred[115] so that the viscosity does not become too high during extrusion of the high solids content paste nor does the yield stress become too low after deposition.

More recently, concentrated colloidal gels have been extruded into a non-wetting oil bath that prevents drying and allows finer features to be printed without clogging the nozzle[162–165]. To be used for RC, the colloidal pastes must satisfy two important criteria: (1) they must exhibit a well-controlled viscoelastic response (i.e. they flow through the dispensing nozzle and set immediately to retain the shape of the deposited features even if they span gaps in the underlying layer(s)), and (2) they must contain a high solid content to minimize drying shrinkage after green forming. To fulfil such requirements, Smay and colleagues[162, 163, 166] employed the strategy of first preparing a highly concentrated, stable dispersion followed by a controlled flocculation of the slurry to promote the fluid-to-gel transition. Controlled flocculation can be achieved by changing pH, addition of salt or incorporation of oppositely charged polyelectrolyte species. The colloidal paste flows through the deposition nozzle as the gel structure breaks under high shear conditions during extrusion and it rapidly recovers its stiffness to prevent deformation. It is possible to build unsupported spanning structures by controlling the magnitude of the yield stress and the time required for the ink to return to its fully gelled state[163].

Due to its ability to generate fine features (i.e. print fine strands of filament), the RC technique is mainly used to fabricate lattice truss structures. Cai *et al.*[150] produced cylindrical and cuboid lattice objects by robocasting of a composite SiC, $Al_2O_3$ and yttria ($Y_2O_3$) (weight ratio of 80.0:8.6:11.4) ink. After spark plasma sintering (SPS) at 1700°C in argon, the objects achieved final densities above 97 %TD. Using a similar forming process but with different sintering conditions, various lattice structures with dense (> 92 %TD) struts have also been generated from $Al_2O_3$ [132, 167, 168], lead zirconate titanate (PZT)[163, 165], silica ($SiO_2$)[162], mullite[169], hydroxyapatite (HA)[170, 171], tricalcium phosphate (TCP)[151, 152], barium titanate ($BaTiO_3$)[164, 172], boron carbide ($B_4C$)[173] and silicon nitride ($Si_3N_4$)[174–176].

### 3.1.2. Fused Deposition of Ceramics (FDC)

Fused deposition of ceramics (FDC) is based on the extrusion of either a colloid-filled polymer filament[177–180, 134] or ceramic/binder blend[181–183] at a constant rate through a heated liquefier, where the material melts to form a shear-thinning, particle-filled organic fluid. The extruded material then solidifies upon cooling to prevent deformation. The FDC method usually employs filamentary feedstock[177–180, 134], but the use of powder/binder paste (similar to an injection molding feedstock) has also been reported[181–183]. The filled-polymer filament has an advantage of long shelf-life. To be used in FDC, the filament must possess sufficiently low viscosity when heated to be extruded through a fine nozzle and a high solid loading (50-55 vol%) to minimize component shrinkage during binder removal and sintering. The filament fabrication process can be divided into 3 steps as follow[177–180]:

(1) The powder coating step: the ceramic particles are coated with a dispersant (usually stearic acid), in order to form a uniform powder-binder mix.

(2) The mixing step: the coated powder is mixed with a thermoplastic binder in a heated mixing chamber to accomplish a thorough mixing and to break up any agglomerates. The powder-binder mix is then granulated at the end of this stage.

(3) The screw extrusion step: The granules are fed into a screw extruder which heats and mixes the powder-binder mix before extruding it through a die with diameter in the millimeter

range. The extruded filaments are picked up by a conveyor belt and spooled for use in the FDC process.

Various structures have been successfully generated using the FDC technique. Griffin and McMillin[135] fabricated FDC-processed $Al_2O_3$ from a filament containing 55 vol% $Al_2O_3$ and 45 vol% polymers (binder, elastomer, tackifier, wax, surfactant and plasticizer). After a slow binder removal at 600°C and sintering in air at 1550°C for 2 hours, final parts with densities above 96 %TD were obtained. A similar binder system was employed by Agarawala *et al.*[184] to generate a filament for FDC of $Si_3N_4$. The FDC-processed and sintered $Si_3N_4$ parts exhibited final densities above 98 %TD and strengths comparable to specimens produced by conventional ceramic processing (isopressing and extrusion). Other objects fabricated by FDC from polycaptrolactone/hydroxyapatite (PCL/HA with a weight ratio of 60:40)[185], polypropylene-tricalcium phosphate (PP-TCP)[186], PZT[136], fused $SiO_2$[187] and tungsten carbide-cobalt (WC-Co)[188] have also been reported.

### 3.1.3. Freeze-form Extrusion Fabrication (FEF)

FEF is an extrusion-based additive manufacturing technique that involves a controlled deposition of aqueous-based colloidal pastes in an environment below the freezing point of water to solidify the pastes after deposition. The feedstock for FEF usually contains high solid content up to 50 vol%, 2-4 vol% binder and 1 vol% dispersant and debinder[157, 158]. In addition, glycerol (~1 vol%) is often added as a cryoprotectant to prevent large ice crystal formation during the freezing of the ceramic paste. Huang *et al.*[156] reported the use of the FEF technique to fabricate $Al_2O_3$ parts with a final density of 90 %TD. The same group of authors have also reported the FEF of zirconium diboride ($ZrB_2$), functionally graded ZrC/W, $Al_2O_3/ZrO_2$ composites[189] and bioactive scaffolds[157, 158]. However, the surface quality of parts produced by FEF is generally not as good as in objects generated by FDC and RC, due to the use of relatively large nozzle sizes.

### 3.2. Direct Inkjet Printing (DIP)

The DIP technique involves the formation and deposition of droplets of slurry that spread on impact to produce a layer thickness of less than 1 mm[190]. After deposition, the material (usually referred to as ink) is allowed to solidify, either through evaporation of the solvent or through cooling, before proceeding to deposit the next layer[191]. The DIP method does not require binder to be deposited in between slurry layers and thus, pyrolysis may not be required depending on the organic content of the slurry. Several works have reported the preparation of ink for DIP using aqueous[139, 192, 193] and non-aqueous (such as paraffin wax)[137, 138, 194] media, with the ceramic particles stabilized using polymeric dispersants. When wax-based inks are employed, the slurries are deposited in a hot melted state and solidify when in contact with the cold substrate.

Özkol *et al.*[193] reported the DIP of aqueous inks containing 27 vol% yttria-stabilized zirconia (YSZ). The DIP processed and sintered parts possessed a high density (96 %TD) and a superior flexural strength (~843 MPa) compared to objects slip cast from similar suspension (~684 MPa). Ainsley *et al.*[138] employed the DIP technique to process wax-based $Al_2O_3$ suspensions (40 vol% solid in paraffin/kerosene media) into green parts that can be sintered to yield final objects of 80 %TD. Other dense structures produced from different materials, such as $Si_3N_4$[139], functionally graded $Al_2O_3/ZrO_2$ composite[190] and PZT[195], have also been reported with the DIP method.

The suspensions used in DIP are typically much lower on solids content (typically less than about 30 to 35 vol% solids) in order to maintain a low viscosity (typically on order of 10 mPa.s @1000 $s^{-1}$)[129, 196], so the suspension can flow through the nozzle at high speed. The inks for DIP require additional attributes compared to those for DIW since they need to break up into droplets, spread on the substrate and avoid forming coffee stain rings[129, 197–199]. The window of operability that enables all these attributes depends on a complex way on the suspension viscosity, density, surface tension, fluid velocity and characteristic length scale as described by Derby[199].

### 3.3. Stereolithography (SL)

Stereolithography (SL) is a technique based on photopolymerization of slurries containing a photosensitized monomer in a layer-by-layer fashion. During the SL process, certain areas of the freshly deposited slurry are solidified through exposure to UV radiation for a few seconds at certain wavelengths. The SL process consisting of repeating steps of slurry spreading and UV polymerization is illustrated in Figure 3. The typical slurry for SL contains ceramic powder (40-60 vol%), dispersant, monomer solution, and photoinitiator[140, 200–204]. The monomer solutions are either monomer resins (such as derivatives of vinyl ether, acrylate, epoxy and oxytane), or monomers (such as acrylamide derivatives) dissolved in aqueous or organic solvents [140–142, 203, 205–208]. A wide range of photoinitiators are also available for the SL process, including but not limited to thioxanthone, 2,4,6-trimethylbenzoyldiphenylphospine oxide[140] and 2,2-dimethoxy-2-phenylacetophenone[143]. The influence of the optical properties of the monomer, ceramic, and photo-active components on the cure depth, cure width, and cure profile have been investigated[209–211].

Wang *et al.* [141] employed solvent (methanol)-based slurries containing 50 wt% $Al_2O_3$ powder and commercial photopolymer resin and photoinitiator to yield SL-processed parts with a green density of 65.5 %TD. Parts sintered for 2 hours at 1600°C were free from delamination or cracks and reached a final density of 98 %TD, with average tensile and flexural strength of 327 and 476 MPa, respectively. It has also been shown that careful control of the residual monomers is required to minimize cracking[212]. Ceramic SL parts were also fabricated using 40 vol% nanosilica suspensions, which yielded 99% dense structures after sintering at $1250^0$C for 2 hours. In addition, porous materials have also been produced by the SL technique using terpene–acrylate vehicles[213]. Other promising SL-processed objects made from YSZ[214], HA[215], Bi($V_xNb_{1-x}$)$O_4$ (BVN)[216], and β-tricalcium phosphate (β-TCP)[217] have also been found in the literature.

### 3.4. Slurry-based 3D Printing (S-3DP)

The S-3DP process consists of spreading (or spraying) a thin layer of slurry, heating the slurry to dry excess solvent and selective printing of the binder material. These three steps are continuously repeated until the object is completed. The part can be retrieved by dispersing the unprinted regions in an ultrasonic bath. The binder must provide sufficient strength to hold the part together during the retrieval process. Using the S-3DP technique, Grau *et al.*[144] and Cima *et al.*[145] processed $Al_2O_3$ slurries into complex-shaped objects with green and sintered density of 67 and 99 %TD, respectively.

### 3.5. Slurry-based Selective Laser Sintering (S-SLS)

The use of S-SLS technique to generate green $Al_2O_3$ parts was reported by Tang *et al.*[146]. The authors prepared $Al_2O_3$ slurries (~50 vol% solid) by first coating the $Al_2O_3$ powder with fully hydrolyzed polyvinyl alcohol (water insoluble PVA) and dispersing the coated powder in a solution containing water, dispersant and sub-partially hydrolyzed PVA (water soluble). As shown in Figure 3, SLS was performed on the slurry deposited layer by layer using a doctor blade. Laser irradiation melted and caused the two kinds of PVA to mix with each other, forming a water-insoluble phase that connected the $Al_2O_3$ particles. Meanwhile, the PVA in regions unscanned with laser remained water soluble and can be dissolved in water to retrieve the green parts that are insoluble in water. After debinding (30 minutes at 600°C) and sintering (2 hours at 1600°C), the green parts of 57 %TD yielded final products of 98 %TD with a flexural strength of 363.5 MPa. Recently, laser sintering has been combined with direct ink printing to produce complex shaped 3D metal structures[218]. The technique could be readily adapted to producing ceramic materials.

# 4 Macroporous Ceramic Structures Enabled by Colloidal Processing

One of the most significant benefits of colloidal processing versus other shaping technologies is the possibility of creating and designing very controlled porous ceramic structures, while maintaining near-net shaping capabilities for that porous component. The term porous ceramics is generally used to refer to ceramic components that contain pores, voids, windows or holes created "intentionally" into the material. Ceramic components can have pores and voids related to powder agglomeration, flaws and defects during processing or incomplete densification, but they are not regarded as porous ceramics. The solid material surrounding the pores or voids is often times called either the "strut" (when the volume of the solid material is significantly lower than that of the pore around which they are assembled) or "pore wall" (when the volume of the solid material is in the same range than that of the pore around which they are arranged). Porous ceramics are normally characterized by the overall percentage of porosity, the pore size, the pore shape and other key features related to the pore size distribution and porosity morphology across the component. The terminology used in describing the various attributes of porous ceramics is shown in Figure *4*

Figure 4 Location

The range of applications for porous ceramics span across several fields based on the porosity features mentioned above. In addition to filters and membranes for separation processes and engineered thermal and acoustic insulation[219–221], porous ceramics are gaining attention in the medical field to encapsulate and release substances in the human body[222, 223], grow cells and tissues in tailored scaffolds[224–226] or act as microfiltration membranes for viruses[227].

The other growing applications are in catalysis, chemical sensors and electrodes for fuel cells and lithium air batteries and other dielectrical and optical applications[219, 228, 229, 78, 230].

The porous ceramic structures that are necessary for these applications can best be achieved by colloidal processing for several reasons. First, colloidal processing is the only processing approach able to accommodate the integrated use of ceramics, salts, droplets, air bubbles, polymers, macromolecules, solvents and other compounds necessary to create porous structures through an intimate and homogenous mixture of all these building blocks. Second, colloidal processing is particularly suited for tailoring of the interaction forces (see section 2) between all those components to design the desired porous architecture while minimizing aggregation, agglomeration and the presence of other flaws that can compromise the reliability and other properties of the component. Finally, the utilization of colloidal processing provides the ability to consolidate and lock-in the designed porous structure and form it into any complex desired shape using the processes described in Figure 1.

When selecting a processing technique and a type of porosity to achieve, it is necessary to consider the starting particle size of the ceramic and the solid concentration in the suspension. Macroporous structures can be formed with any particle sizes in the colloidal range or even some particles larger than this range (up to 10 μm) The solid concentration of the slurry or suspension is generally lower than for making their dense counterparts to allow "room" for porosity. Traditionally, the solid concentration of slurries used for porous materials is below 40 vol%. The substance that will create the porosity in the ceramic (bubble, droplet, polymer beads or induced solid phase) is often called a "porogen", and it is removed from the ceramic component once the porous structure has been consolidated, as we will describe in the following sections.

There are a plethora of techniques to produce ceramic porous structures with different types of porosities, depending mostly on the type of porogen used and the pore generating mechanism. Several ways of processing porous ceramics have been proposed. In Figure 5, we classify them based on the main mechanism used to create the porous structures. The objective of this review is not to enumerate all of them in detail, but to describe some of the most commonly used techniques for the preparation of macroporous structures, highlighting the underlying mechanisms. For more detailed description of porous ceramics routes and techniques, please refer to Colombo *et al.*[231], Studart *et al.*[80], Deville *et al.*[79], Sakka *et al.*[232] or Ohji *et al.*[78].

Figure 5 Location

## 4.1. Replica and Sacrificial Fillers.

The terms "replica" and "sacrificial fillers" refer to techniques in which hard-templating agents are used to recreate a porous structure in a ceramic.

The term replica normally is used to refer to a processing technique in which a porous polymeric structure is coated by a ceramic suspension to generate pores through the mechanism schematically shown in Figure 5a and b[78, 80]. After drying, the polymeric-ceramic structure is calcined to remove the polymeric phase, and then it is sintered to strengthen the struts. Typical polymeric structures, such as polyurethane and polystyrene, show large pore sizes to ensure the required suspension flow and coverage of the polymeric network. Processing of these type of macroporous cellular materials has gone beyond sponges of more classical ceramic materials, such as $Al_2O_3$[233, 234], to explore other materials including lightweight $ZrB_2$ for aerospace applications[221]. The shaping of the replica components is determined by the shape of the polymeric network used.

Sacrificial fillers consist of a "secondary" solid phase that is mixed into a ceramic suspension to act as pore former. Pore formers include for example polymeric-based beads or other ceramic particles synthesized separately via sol-gel chemistry. The pore size is determined by the size of the sacrificial filler and the overall porosity is determined by the volume fraction of the sacrificial filler in the suspension. Once the green component has been shaped by one of the techniques mentioned in Figure 1, the sacrificial filler is then removed commonly by a calcination stage, before proceeding to densification. The porous structure will have the pore shape and pore distribution that the sacrificial filler had in the green body[232, 234–237]. The removal of the replica or the sacrificial filler can also be done via chemical etching or chemical dissolution (i.e., if the sacrificial fillers are $SiO_2$ spheres).

## 4.2. Particle-Stabilized Foams

By adjusting the surface chemistry of the ceramic particles in the suspension using surfactants one can tune the hydrophobicity and the contact angle of the particles at oil-water and air-water interfaces. Such particles can stabilize air (or gas) bubbles introduced in the suspension by irreversibly adsorbing at the air-water interface and/or forming a strong particle network that prevents foam destabilization through coalescence and Ostwald ripening[238]. This mechanism is schematically explained in Figure 5c and d. The amount of air (or gas) introduced in the system depends on the viscosity of the suspension. The surface chemistry (surfactant type and concentration), viscosity and solid content determine the amount and size of pores in the foam[239–241]. Once the foam has been created, various shaping and consolidation techniques can be utilized to convert the wet foam into a green body. In one possible route, a “quick” setting approach such as gelcasting is used[223, 242, 81]. This technology allows a versatile shaping technique suitable to many types of geometry. Traditionally, the ceramic foams present a “bubble-like” porosity, closed or open, and allow the creation of very high porosity up to 90% and pore sizes between 50 and 300 μm. This technique has been well studied and established using common materials such as $Al_2O_3$. The robust mechanism of this approach (see section 5.2 for more details) has also enabled the development of foams of “less common” materials, for instance; $ZrB_2$[221], MAX phases[81, 243], SiC[244, 245], $Si_3N_4$[246], geopolymers[247] and HA[223].

### 4.3. Ice Templating

This is one of the most versatile techniques to create macroporous structures. Pore formation occurs through a phase separation mechanism (Figure 5e and f) induced by freezing of the ceramic suspension. During the freezing process it is possible to control the growth of the ice (if water) or the frozen crystals (if another solvent) by the temperature, freezing device or by control of the cooling rate[79]. During the ice (or frozen crystal) growth, particles are pushed ahead of the advancing freezing front (induced phase separation), typically producing an interconnected type of porosity. The morphology of the frozen crystals can be modified by the addition of cryoprotectants or binders, salts and other molecules to create different porous structures such as; lamellae, hexagonal crystals or dendritic patterns[79, 248–250]. Once the sample is completely frozen, it is subjected to sublimation (freeze drying), in order to remove the frozen solvent and leave a porous structure behind, which corresponds to the volume previously occupied by the frozen solvent. In effect the ice crystals are used as porogens. The green sample is then sintered to strengthen the component. Different sublimable vehicles have also been explored and optimized for processing of porous materials, like camphene mixtures, as originally reported by Halloran *et al.*[251, 252], and most recently reported by Choi *et al.*[253] to produce 3D-extrusion multilayered ceramics.

Ice templating can produce porosities between 20 and 80%, with pore sizes ranging between 5 to 100 μm. The pores generated by the ice template are normally interconnected and can be aligned in a particular direction. Due to its versatility, the architectures generated and its ease of processing, ice templating is very relevant in other fields and for other materials. Recently porous borides and carbides for extreme environments[254], silicon oxycarbide (SiOC)[255] and zeolite mixtures[256] have been produced. There is plenty of scope to fully exploit its potential and interaction with other techniques. For example, recent work combine directional freezing of $ZrO_2$ and iron oxide particles with magnetic fields to produce controlled patterns and architectures with well-defined thickness of the porous lamellae walls[257]. Ice templating is also sometimes called freeze casting. The term freeze casting is normally used to refer to the shaping of a suspension into a component by freezing the suspension inside a mold with the desired geometry. Therefore, this technique is extremely versatile since it allows one to shape and create porous structures in the same step.

### 4.4. Emulsion Templating

In this technique, the ceramic suspension forms the continuous phase of an emulsion, while the disperse phase is typically an immiscible liquid used as the template for pore formation. The preparation of such templating emulsions requires two solvents and surfactant in the right ratio to create the two phase material. The surface chemistry of the particles is usually tailored to enable their dispersion in the solvent that forms the continuous phase of the emulsion. The droplets comprising the dispersed phase of the emulsion typically do not contain ceramic particles, thus acting as the porogen (or soft templating agent) for the porous structures. The method is similar to particle stabilized foams, but in this case the weakly hydrophobic ceramic particles stabilize the emulsion by adsorption to the oil-water liquid interface as in Figure 5c.

Emulsion templating is suitable for many types of ceramic materials, since the formulation of the emulsion can be tailored for organic/aqueous mixtures using a range of surfactants and solvent types. Thus, this technique has been applied to produce porous structures with a variety of chemical compositions from $Al_2O_3$ (using for example decane-water mixtures stabilized with surfactants or $SiO_2$ particles)[258] to $Si_3N_4$ (using for instance surfactants and aqueous mixtures of octane or decane)[259, 260]. Porosities between 40-80% and pore sizes between 30 and 100 μm are typically produced by this technique. The emulsion can be shaped into a component by solvent drying or in combination with a quick setting technique such as gelcasting or freeze casting. Typically, emulsion templating is combined with sol-gel routes to create a dual template process that results in porous structures of $Al_2O_3$[261], $ZrO_2$[262] and $SiO_2$[229], with narrow pore size distributions in the lower ranges of the macroporosity spectrum, between 2 and 5 μm. This approach has also been used with mixtures of polysiloxanes and polycarboxylosanes to generate a porous scaffold that after calcination leads to SiOC[263] or SiC ceramics. These precursors can be used in combination with ceramic particles and with any of the techniques to produce porous structures mentioned above to create a foam[264], ice template[255], emulsion[263] or replica[264] of the precursor mixtures before calcining and forming SiOC or SiC materials, in a range of porosities and pore sizes.

## 4.5. Additive Manufacturing

This technology enables the production of open lattice structures, with cells of varying sizes, normally in the 500-1000 μm range, by mixing the ceramic powders with binders, resins and solvents to create suspensions and pastes with the right viscosity as described in section 2. In this approach, porosity is not generated through one the assembly mechanisms outlined in Figure 5. Instead, pores in the form of open cells arise from the suspension deposition path defined by the controlling software and hardware. Once the green body has been created, the organic components are burnt out and the component sintered to final density. The biggest use of additive manufacturing is to create porous structures[265] often referred to as controlled architecture cellular materials[266] or metamaterials[267], mostly for lightweight applications. However, additive manufacturing is also being used in combination with other techniques like ice templating or foaming[268], to produce porous materials.

As described in this section, the creation of porous structures is one of the key and distinctive features that colloidal processing techniques bring to ceramics manufacture. The possibilities of combining the different techniques to create more unique and novel microstructures to tailor the properties for the needs of new industries and applications are virtually endless. In addition, these routes are totally compatible with and benefit from the near-net shaping approach and the increased reliability obtained through colloidal processing.

# 5 Directed Assembly of Particles

Fundamentals of soft matter science have impacted the colloidal processing of ceramics not only through the understanding of the conformation of polymer chains on the surface of solid particles (section 2), but also in exploiting new mechanisms to control the assembly of suspended particles using for example external fields or using soft templates.

## 5.1. Directed Assembly using External Fields

Soft matter scientists have long been interested in understanding the effect of external fields on the phase behavior and assembly dynamics of colloidal ensembles as a model for atomic systems[269]. Following on these earlier studies, attempts have been made to utilize external fields as a means to control the assembly of colloidal particles into tailored microstructures of potential relevance for ceramic materials[270–272]. Recent work[273–276, 257] on the magnetic-directed assembly of anisotropic ceramic particles has allowed for the fabrication of ceramic microstructures with unprecedented local texture control as shown in Figure 6. The response of anisotropic particles like platelets and rods to an external magnetic field is found to be strongest for particle sizes in the range of 5 – 20 μm (Figure 6a)[273, 274]. Such particles are large enough to be only weakly influenced by thermal (Brownian) motion and at the same time are sufficiently small to prevent prompt sedimentation due to gravitational forces. As a result, minimum magnetic fields on the order of a few milliTesla are enough to enable magnetic control. To achieve such alignment control with particles that are not ferromagnetic in the first place, a surface coating with superparamagnetic iron oxide nanoparticles (SPIONs) have been proposed[274]. SPION concentrations as low as 0.01 vol% are sufficient to make optimum-sized platelets magnetically responsive.

SPION-coated platelets can be aligned biaxially by applying a rotating magnetic field to the particle suspension (Figure 6b). Interestingly, the angular speed of the rotating field has to be sufficiently high to overcome the drag forces exerted by the surrounding liquid on the magnetized platelets. Below a critical rotational speed, such viscous drag prevents the particle from aligning its long axis parallel to the direction of the imposed field, leading to a characteristic rolling motion. Instead, speeds higher than a give threshold result in the alignment of platelets with their faces parallel to the plane of the rotating field. A balance between magnetic and viscous forces exerted at the edge of platelets can be made to predict the threshold frequency needed for biaxial alignment as a function of the liquid viscosity, applied field and particle magnetic susceptibility (Figure 6c)[273, 277]. Using a similar force balance, it is also possible to estimate the timescales required for particle alignment. This typically varies between tens of seconds to 1 minute, depending on the particle, fluid and intensity of the applied field (Figure 6d)[161].

The use of external fields to control the microstructure of ceramic parts enables unique alignment configurations beyond what can been typically achieved using the shear forces often applied in ceramic manufacturing processes like tape-casting and extrusion. In the example depicted in Figure 6d, $Al_2O_3$ platelets were magnetically aligned within a suspension of $Al_2O_3$ nanoparticles, which was eventually consolidated into a green body through direct coagulation casting[278]. Using the aligned platelets as seeds for templated grain growth[279], dense ceramic microstructures with distinct programmable local texture can be achieved. As an illustrative example, Figure 6e shows a ceramic bilayer with different specific orientations of elongated grains in each individual layer. As will be discussed in the next section, such a microstructure captures the functional design of natural plant seedpods and thus can generate unique self-shaping effects during the sintering process.

Figure 6 Location

## 5.2. Directed Assembly using Soft Templates

In addition to external fields, another effective approach to guide the assembly of colloidal particles into defined architectures is the use of soft templates such as bubbles and droplets in foams and emulsions[239, 238, 240–242, 280, 281]. As discussed in section 4.2, this approach has been successfully applied for the preparation of macroporous ceramics with tailored pore sizes and porosities[80]. In this processing route, soft templates are combined with ceramic particles of interest in a complex colloidal system, which is consolidated into defined geometries and dried for removal of the liquid phase to generate ceramics with controlled macroporous architectures. Because templating gas bubbles and liquid droplets are thermodynamically unstable, it is crucial for the process to implement mechanisms that prevent the natural tendency of foams and emulsions to coalesce and coarsen. An effective mechanism to stabilize bubbles and droplets is to adsorb colloidal particles at the air-water and oil-water interfaces to result in Pickering emulsions and foams, as demonstrated experimentally more than a century ago by Ramsden and Pickering[282, 283].

The underlying physics that explains the outstanding stability of Pickering emulsions and foams is the reduction of the thermodynamic free energy that is achieved through partial replacement of a high-energy gas-liquid or liquid-liquid interfaces by two lower-energy solid-liquid interfaces created upon particle adsorption on bubbles and droplets (Figure 7a)[284–286]. This energy reduction is often compared with the thermal energy on the order of $kT$ to evaluate the thermodynamic driving force for the interfacial adsorption process ($k$ is the Boltzmann constant and $T$ is the temperature). As opposed to the few $kT$s gained through the interfacial adsorption of surfactants, particles attached to the interface can reduce the free energy of the system by several hundreds to thousands of $kT$s, depending on the particle size and the contact angle of the particle at the interface (Figure 7b). With such a major decrease in free energy, particles with an appropriate contact angle are effectively irreversibly adsorbed at the interface, thus providing a viscoelastic armour and steric layer that prevents droplet/bubble coalescence and coarsening.

The resulting Pickering emulsions and foams are sufficiently stable to be used as colloidal inks for 3D printing of porous ceramics through the DIW technique (Figure 7c-e)[287]. Besides resisting coalescence during the extrusion process, emulsion- and foam-based inks should exhibit rheological properties that ensure flow under the shear stresses developed at the printing nozzle and that also provide enough viscoelasticity shortly after extrusion to prevent the distortion of deposited filaments. These rheological features can be achieved by preparing jammed emulsions (foams) with sufficiently high concentrations of particles and droplets (bubbles). Figure 7c confirms the viscoelastic nature of a jammed Pickering emulsion stabilized by surface-active $Al_2O_3$ particles. For applied stresses below the yield stress $\tau_y$, the storage modulus (G') is significantly higher than the loss modulus (G''), indicating the predominantly elastic response of the emulsion at low stresses. Stresses above $\tau_y$ lead to flow of the emulsion, making G'' values surpass the storage modulus G' (Figure 7c). Such viscoelasticity behavior may arise from the mechanical properties of the particle-laden interfaces and/or of the network of particles typically formed throughout the continuous phase. Higher concentrations of $Al_2O_3$ particles lead to an increase in the storage modulus and the yield stress of the emulsion (Figure 7d). These two parameters are essential to enable printing of free spanning filaments[163] and distortion-free highly-curved shapes (Figure 7e)[161]. As a result, cellular structures with well-defined periodicity can be printed and sintered into macroporous ceramics with controlled hierarchical porosity, as will be discussed in the next section.

Figure 7 Location

## 6 Unique Nature Inspired Ceramics

The remarkable potential of colloidal processing tools in generating materials with multiscale structural control that cannot be achieved using dry processing techniques is well illustrated by the complex shaped dense and macroporous ceramics presented in previous sections. Recently, such structural control has also been harnessed to create synthetic ceramics that mimic some of the design principles underlying the unique properties and functionalities of biological materials.

In the past decade or so, very tough composites have been produced by mimicking the structure of the mollusc shells known as nacre[288–294]. In this review, we will focus on more recent examples of biologically-inspired materials that demonstrate how natural design principles and colloidal processing can be combined to obtain ceramics with unprecedented mechanical efficiency and self-shaping effects. The selected case studies shown below were inspired by plant systems, more specifically the mechanically-efficient hierarchical structure of wood and the morphing bilayer architectures of seed dispersal units.

## 6.1. Mimicking Shape Changes that Plants use to Disperse Seeds.

Dispersal seed units of plants are able to undergo remarkable morphing effects that result from simple design of the local texture of these small organs at the microstructural level. One beautiful example is that of seedpods that open to release their seeds into the soil when triggered by humidity changes in the environment[295–298]. Interestingly, such shape change is entirely programmed within the microstructure of the seedpod and is not dictated by the action of living cells. In the seedpods of the orchid and pine trees, the microstructure is programmed in a bilayer consisting primarily of a water-swellable hemicellulose matrix reinforced with cellulose microfibrils oriented in specific directions. The microfibrils in each layer are oriented orthogonal to one another and at a specific angle relative to the long axis of the seed host structure. The fibrils within a pinecone are oriented parallel and perpendicular to the surface of the pod's scale, whereas an angle of 45° relative to the long axis of the pod is observed in the seedpods of the orchid tree[299]. The basic mechanism leading to the morphing effect is in both cases the differential shrinkage of each one of the layers upon dehydration of the hemicellulose matrix. Shrinkage is restricted in the direction of the fibril orientation, but remains unconstrained perpendicular to it. For the scales of the pinecone, this differential shrinkage results in a dehydration-induced bending motion that resembles the shape change of bilayer metal thermostats induced by temperature variations. Because of their angled fibril orientation, seedpods of the orchid tree find a twisted structure to be the minimum energy configuration upon dehydration.

Inspired by the programmable fibril design of such plant systems, the ability to control the orientation of anisotropic particles through colloidal processing has allowed for the creation of ceramic objects that can self-shape into programmed geometries during the sintering process as shown in Figure 8[278]. In these bioinspired ceramics, differential shrinkage is programmed within the structure by aligning $Al_2O_3$ microplatelets in specific orientations in seedpod-like bilayers. The aligned microplatelets are embedded in a matrix of $Al_2O_3$ nanoparticles that provide the high surface area needed for sintering-induced shrinkage. Similarly, to the biological material, shrinkage is constrained in the direction of platelet alignment. As a result, bending and twisting shaping effects akin to those of seedpods can be realized during sintering.

Several colloidal processing concepts are key to generate microstructures with the tailored local texture needed to program the self-shaping effect. First, the interactions between microplatelets and nanoparticles have to be controlled to prevent their agglomeration in the liquid phase in the first place. In this example shown in Figure 8, this was achieved by implementing an electrical double layer stabilization mechanism that results in repulsive forces between the $Al_2O_3$ nanoparticles (see section 2). Second, as already mentioned in the previous section, coating of the surface of the microplatelets with iron oxide nanoparticles (SPIONs) is necessary to enable their alignment in deliberate orientations using an external magnetic field. This is can be accomplished by tuning the pH of the suspension such that the surface of the SPIONs and of the microplatelets are oppositely charged, thus leading to the heterocoagulation of the magnetic nanoparticles on the surface of the platelets. Third, the rheological behavior of the suspension should allow for casting into molds of pre-defined shapes. This was possible by preparing suspensions with a concentration of particles of 50 vol%, which is sufficiently low to keep the suspension fluid for casting and high enough to obtain green compacts that can be fully densified during sintering. Finally, a gelation step is required to fix in place the SPION-coated microplatelets after the magnetic alignment process. For the $Al_2O_3$ bilayers shown in Figure 8, the suspension containing aligned platelets were gelled through direct coagulation casting using the urea-catalyzed hydrolysis of urea to cause an *in situ* pH change towards the isoelectric point of the particles. Eventually, this broad set of colloidal processing tools enables the fabrication of ceramic objects with the remarkable ability to self-shape into complex geometries that go beyond those found for the plant systems used as inspiration as seen in Figure 8.

Figure 8 Location

### 6.2. Mimicking the Hierarchical Organization of Biological Materials

In this example, the source of inspiration is the hierarchical organization of biological materials across multiple length scales from nano- through meso- to macroscopic levels. The concept of hierarchy is a hallmark of many biological systems[302] and is widely exploited in nature to construct load-bearing structures with remarkable stiffness-to-weight ratio. This design principle can be found in natural lightweight structures such as bamboo, wood and bone[303–306]. Figure 9 shows the structure of a bamboo culm at different length scales as an example of a hierarchical biological material[307, 289]. At the cellular level, the structure comprises hollow prismatic cells with thick, multilayered walls. Together with vascular bundles, such hollow cells give rise to bamboo's porosity at the microscale. At the macroscopic scale, the bamboo culm is shaped in the form of a tube, whose walls contain the microscale porosity arising from hollow cells and vasculature. This results in a hierarchical porosity that maximizes the stiffness-to-weight ratio of the overall structure. Such effect is further amplified in bamboo through the presence of a gradient in concentration of fiber and vascular bundles in the radial direction[307].

Following the mechanically efficient design principle of natural structures like bamboo, particle-stabilized emulsions have been 3D printed into hierarchical cellular ceramics with unprecedented strength-to-weight ratio (Figure 9b)[287]. In this example, pores at three different length scales are generated from the millimeter-sized openings within the printed grid structure, the 5-10 μm macrovoids arising from the templating droplets and the 0.5-2 μm windows resulting from particle-free patches formed on the surface of the droplets. While the grid openings and the macrovoids are set by the printing path and the size of the droplets, the windows originated from particle-free patches are presumably formed due to the adsorption of poly(vinyl alcohol) macromolecules at the oil-water interface. These polymeric patches likely prevent full coating of the droplet surface with particles, leading to well-defined pore windows after drying of the printed structure.

Compression tests on such hierarchical porous ceramics confirm the higher mechanical efficiency of structures containing pores at multiple length scales. The enhanced mechanical efficiency is evidenced by the significantly higher compressive strength of hierarchical structures around the very low relative densities at which a percolation threshold is expected. Around such threshold the quantity of load-bearing solid phase is just enough to provide measurable mechanical strength (Figure 9c). Remarkably, the strength of structures containing pores at 3 hierarchical levels is about one order of magnitude higher than that of state-of-the-art porous ceramics at such low relative densities. This clearly illustrates the potential of colloidal processing approaches in generating hierarchical porous architectures with improved performance compared to counterparts structured at a single length scale. Besides load-bearing situations, other applications that require the higher surface area provided by small pores and the higher permeability given by the large pores should also benefit from the hierarchical porous structures discussed here.

Figure 9 Location

## 7 Drying and Cracking

The potential for drying cracks is always going to be an issue for any ceramic components produced with the colloidal approach. Although it has been studied by many investigators, this topic has been and remains an issue that requires further fundamental understanding. The drying process generally occurs in three stages[309–314]. The first stage is a constant rate drying stage. The evaporation of liquid is the rate determining step at low particle concentration and the pore channels between the particles are open enough to allow liquid to be transported to the air liquid interface at a rate at least as fast as the evaporation rate. Increase in particle volume fraction uniformly in the suspension is not hindered by the transport of the liquid in the pores and no significant stress occurs in this stage. The duration of this stage is proportional to the initial volume fraction of liquid in the suspension[311]. The particle concentration increases as liquid evaporates and the particle concentration is uniform throughout the drying body. Eventually the particle volume fraction is increased to the gel point ($\Phi_g$) such that a three-dimensional touching particle network forms[314, 315] signaling the start of the second stage of drying. The touching particle network develops a finite compressive yield stress that increases as drying continues because the volume fraction of the suspension increases. The particle network is only able to resist compaction (increasing solids concentration) if the applied pressure is less than the compressive yield stress. The global stresses arising from removal of liquid from the particle network acts in combination with local capillary forces due to the formation of a curved liquid-air interface (meniscus). It is this meniscus that forms between neighboring particles and creates a compressive pressure on the particle network due to the surface tension. It also produces a pressure gradient from the surface of the liquid to the liquid inside the drying body. In the case of slow drying (see below), the liquid rises to the surface as a result of the pressure gradient and continues to evaporate at a constant rate. The air–water interface remains attached to the surface layer of particles and shrinks at the same rate as the particle network. This occurs because the compressive pressure on the particle network induced by the capillary forces exceeds the compressive yield strength and the body compacts uniformly. The increase in volume fraction of the particle network that occurs with compaction results in an increase in compressive yield stress of the particle network. Eventually as the volume fraction and compressive yield strength increase, the particle network will have sufficient strength to withstand the capillary pressure and further compaction stops. At this point the third and final stage of drying begins. The liquid/vapor interface begins to penetrate the powder compact and the drying rate decreases as the liquid/vapor interface recedes into the pores between the particles reducing the area available for evaporation. The shrinkage of the solid particle network stops at this point in the drying process.

Cracking, if it is going to occur, usually happens at the start of the third stage[309, 311, 312, 316, 317]. Several studies have investigated the causes of stresses in drying powder compacts and how those stresses can lead to cracking[309, 311, 318, 316, 319–322]. Tensile stresses can develop at the surface of a drying body due to the constraint of drying shrinkage by the interior of the body. The development of such stresses depend on the drying speed[314, 323]. Fast drying occurs when the rate of evaporation exceeds the rate of transfer of the liquid from the interior of the body to the surface. Slow drying occurs when the rate of evaporation is slower than the rate of transfer of liquid to the surface. The rate of evaporation is determined by the temperature, vapor pressure of the liquid, the ambient pressure and convection. Flow of the liquid to the surface (through the porous packed bed) is determined by Darcy's law, which is dictated by the pressure gradient, the viscosity of the fluid, the length of the path through the powder bed, the particle size and the voidage as described by the Carman–Kozeny relationship[324].

If the drying is slow, the shrinkage of a drying body occurs uniformly (volume fraction of solids is uniform throughout the body). If the drying is fast, pressure and moisture gradients will exist within the drying body. The gradients will produce non-uniform shrinkage; the low moisture surface (higher volume fraction solids) will try to shrink more than the wetter (low volume fraction solids) interior of the body which constrains the exterior dryer layer. Constraint of the shrinking surface by the interior results in tensile stresses at the surface. A peak in measured stress typically occurs at the end of the second constant rate drying period and leads to cracking if fracture of the particle compact is energetically favorable[309, 311, 312, 316]. Reducing the surface tension of the liquid, adding binder to strengthen the particle bonds, opening up the pore channel (increase particle size or reduce particle concentration) and drying slower will tend to minimize the cracking[325].

Although there is a large body of knowledge about flow and structure of colloidal gels[47, 105] (ref 45) there is less understanding of the fracture mechanics of wet particulate systems. The recent developments, are mainly in the area of improving fundamental understanding of the fracture of both wet and dry particulate materials. Uniaxial and diametral compression tests are frequently used to evaluate the mechanical properties of both wet and dry particulate materials, the latter being a unique test that allows for an indirect tensile test of brittle solids due to the biaxial stress state. These methods were being increasingly utilized to study the tensile[326, 327] or compressive[114, 328, 329] strength, fracture behaviour[330] and deformation behaviour[331] of wet or dry particulate materials under particular conditions. Moreover, as applications demand finer control of microstructures and porosity structures, determining mechanical and thermo-mechanical properties along with elastic constants for colloidal materials produced *via* the methods listed in this review are becoming increasingly important[244, 332].

The experimental study of fracture toughness and toughening mechanisms in wet particulate materials has been very limited[333], although some progress is being made in modeling[334–336]. Recently, Goehring *et al.*[336] have suggested that decreasing the yield stress of a suspension, could increase its fracture toughness by increasing the plastic dissipation around the crack tip. Sengupta and Tirumkudulu[337] also have suggested that viscous dissipation in front of the crack tip influences crack dynamics, while Mattern *et al.*[338] proposed the increased strength exhibited in wet bodies was due to the rearrangement of capillary bridges. It has been observed that when the crack forms, the tip extends from the surface into the saturated area[339], but it is not known how the cracks initiate. Also, the mechanisms that control the resistance to fracture of the wet particulate body are not known. The study of the spacing between cracks has also been a recent interest[340–343].

## 8 Conclusions and Perspectives

Colloidal processing has played a major role in the development of ceramic components with enhanced properties, functionalities and reliability. This stems from the fact that colloidal approaches offer improved control over the structure of particle compacts as compared to dry processing techniques. By combining colloidal suspensions with templating building blocks and structures, exploiting phase separation phenomena, tuning the rheology of suspensions to enable additive manufacturing and controlling particle assemblies using external fields, ceramic components with increasing levels of complexities have been demonstrated. This historical development is expected to gain further momentum with the deeper understanding of soft matter sciences and its translation to ceramics colloidal processing. To further advance the field, research at multiple fronts is required. From the point of view of the authors, these multiple fronts are outlined below along with expected future challenges and developments.

a) Additional knowledge is needed such as more information about surface functional groups on complex ceramics such as transition metal borides, carbides and nitrides. Such knowledge including zeta potentials and Hamaker constants will enable more controlled processing of these materials via colloidal methods. Thanks to the extensive research carried out on the processing of non-oxide materials, soon we will see the application of ceramic matrix composites containing carbon and other nano-structures in micro-electronics and structural applications.

b) Long terms stability and storage of slips could be improved by developing formulations based on colloidal processing principles similar to those applied in the paint industry. The challenge in such complex formulations is to identify the individual and synergetic roles that each molecular and/or particulate constituent plays on the suspension long-term stability.

c) Additive manufacturing will move from a research and prototyping endeavor into full scale design and manufacturing of personalized ceramic components and composites. Knowledge of colloidal processing will need to be used to enable this transition particularly in formulation of pastes and inks. Better understanding of structure-property relationships of printable ink systems and of the underlying physical processes that determine macroscopic rheology of inks will be crucial challenges to be addressed to advance this topic.

d) Many types of porous ceramics will begin to move into production enabled by fundamental understanding of colloidal processing. Multi-scale porous materials will enable enhanced performance in terms of structural mechanical efficiency (strength to weight ratio), high temperature insulation and electronic applications such as in metal-air battery electrodes. Expanding the limits of current processing technologies to be able to better control the achievable pore size and distribution in an economically scalable process is one of the main challenges in this area.

e) Freeze casting will be increasingly applied to producing dense shaped components[72, 73] in addition to being used to produce porous materials via ice templating. Better understanding of the complex freezing process itself and devising cost-effective approaches for up-scaling is essential to help develop this method further.

f) The directed assembly of particles will enable the production of textured and graded ceramics whose properties are more strongly dictated by the material's microstructure. Guiding the assembly of particles using for example external magnetic and electrical fields opens the possibility to gain further control over the multiscale structure of ceramics because the assembly process can be deliberately manipulated externally rather than follow pathways dictated only by random thermal energy. Further investigations on the effect of directed assembly approaches on the dynamics and structure of concentrated suspensions should help us extend texture and composition control to highly packed colloidal systems.

g) Multi-scale and hierarchical structures will produce materials and composites with unprecedented properties such as ultra-lightweight, toughening at multiple length scales, optimized flow properties in combination with high surface area and enhanced impact and damping properties. Understanding structure-property relationships at multiple length scales and their possible synergetic effects on global properties is needed to aid the design of such hierarchical materials.

h) Although there have been many ceramic microstructures developed which mimic nature, such inspiration will continue due to the plethora of exquisite materials and structures found in the natural world. The synthetic analogues developed will enable new functionality in a wide range of applications. As illustrated by the first example of self-shaping ceramics described in section 6.1, the concepts of 4D printing[344] will quickly move into the ceramics realm enabled by colloidal processing. A major challenge in this topic is to devise processing routes that enable replication of the rich multiscale structure of biological systems.

i) Drying of wet ceramic compacts deserves further research efforts. Developing understanding of the complex relationship between the development of tensile stress as shrinkage occurs simultaneously to the increase in strength of the material as it compacts will be a challenge worth pursuing. Advance in understanding the mechanisms that are responsible for toughness in wet particulate materials will provide clues about how to improve the toughness of materials during drying, so as to prevent drying cracks.

In the 100 years since the first paper in the Journal of the American Ceramic Society related to colloidal processing science was published[19], advances in the field have already brought us to unexpected places, techniques, concepts and designs. We are confident that colloidal processing will continue to grow to include other material classes, to be instrumental in the development of smart technologies and to enable new functionalities and manufacturing approaches.

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# Figures

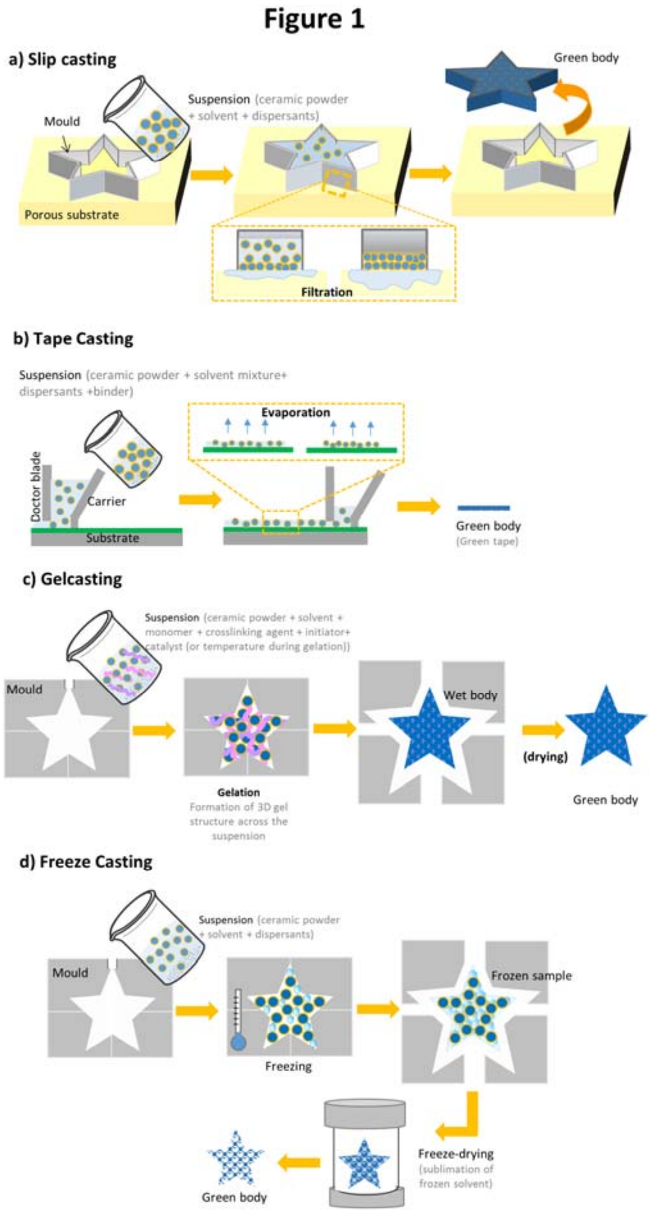


*Figure 1. Colloidal Shape Forming Processes. This group of processing techniques allows for the shaping of dense and porous ceramic components. Suspensions of ceramic powders with additives (dispersants, monomers, crosslinkers, binders, surfactants and cryoprotectants) are prepared in the appropriate solvent in order to control the interparticle forces. The resulting suspension in general must comply with the following requirements: i) stability, to avoid segregation and sedimentation of the ceramic particles during the consolidation stage; ii) low viscosity, to allow ease of flow and filling of the mold; iii) homogeneity, to ensure a uniform green body with high particle packing, that will lead to dense sintered material; iv) dispersed state, where the particles are present as "individual" particles, free of agglomerates and aggregates to minimize flaws in the green body. There are numerous shaping techniques based on the colloidal processing approach. Some of the most common routes are shown in this figure. The consolidation mechanisms are the following: a) Filtration- slip casting; b) Evaporation- tape casting; c) Gelation- gelcasting; d) Freezing- freeze casting. Other techniques such as electrophoretic deposition, spin coating, pressure casting, direct coagulation casting and additive manufacturing are also based on the principles of colloidal processing. Most of these techniques allow the near-net shaping of both dense and porous ceramic components.*

Figure 2

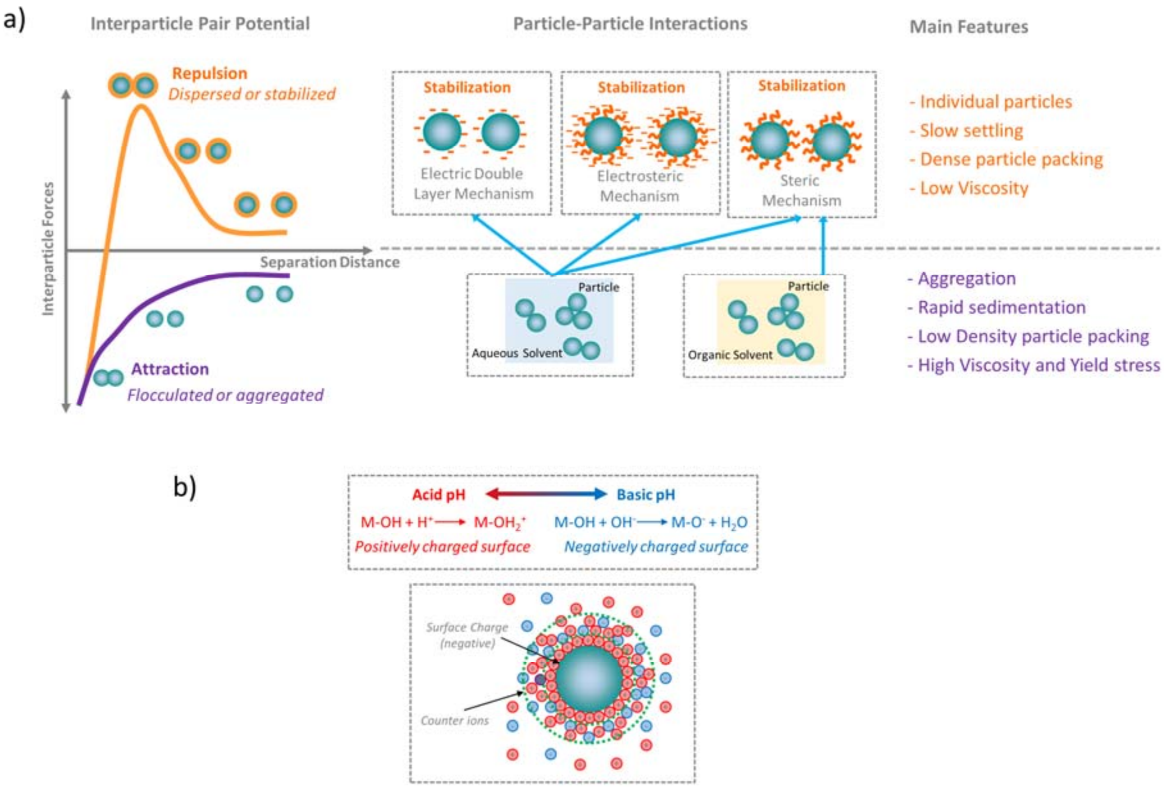


*Figure 2. (a) Schematic representation of the interparticle pair potential (force) between ceramic particles. In order to overcome the attraction forces (lower portion of part a) between particles, they are suspended in solvents (aqueous or organic). Repulsion forces (top section of part a) can be created by electric double layer, steric or electrosteric mechanisms in water. Ceramic particles in organic solvents normally rely on steric stabilization to create repulsion forces for dispersion. The change of interaction from attraction to repulsion alters the suspension behaviour as indicated on the right of the figure. (b) Ceramic particles in aqueous suspension will develop a surface charge by reacting with acid or base at the appropriate pH. The charged surface is neutralised by counterions of opposite charge in solution that surround the particle resulting in electrical double layer repulsion.*

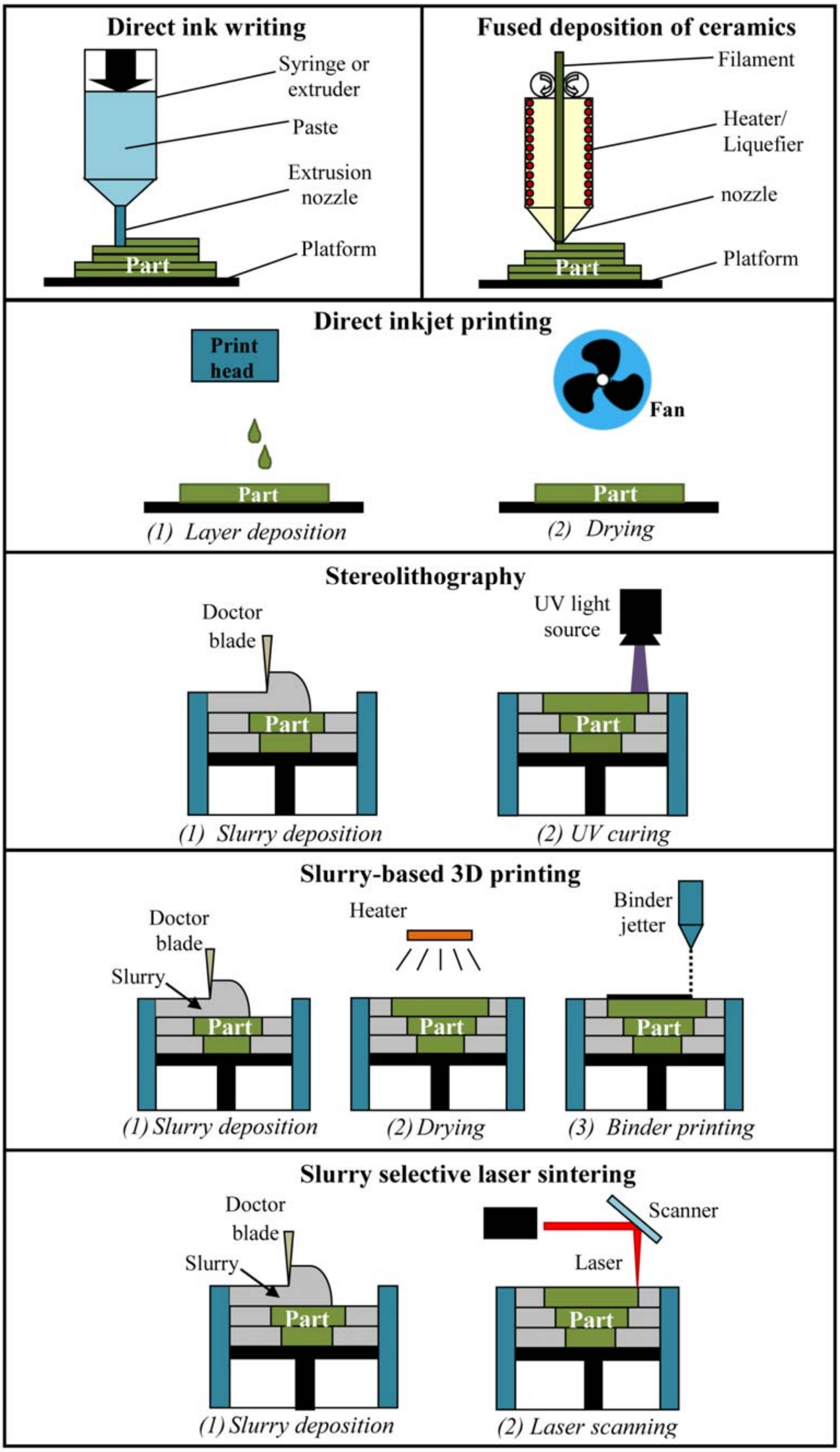
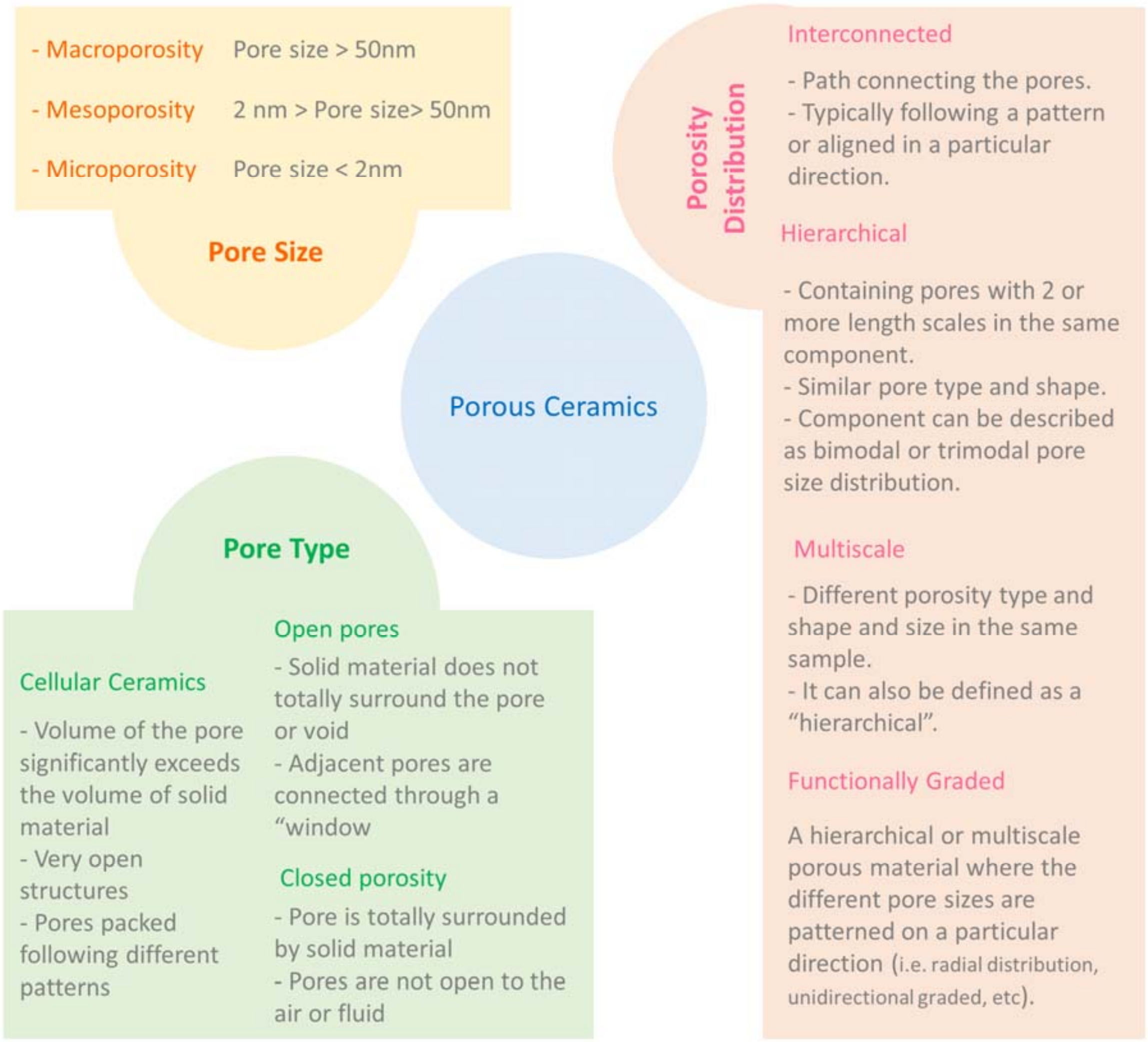


*Figure 3. Schematic illustration of the most significant ceramic additive manufacturing techniques utilizing suspensions, adapted from Zocca et al.*[129]*.*

Figure 4



- Macroporosity Pore size > 50nm
- Mesoporosity 2 nm > Pore size> 50nm
- Microporosity Pore size < 2nm

Pore Size

Pore Type

Cellular Ceramics

- Volume of the pore significantly exceeds the volume of solid material
- Very open structures
- Pores packed following different patterns

Open pores

- Solid material does not totally surround the pore or void
- Adjacent pores are connected through a “window

Closed porosity

- Pore is totally surrounded by solid material
- Pores are not open to the air or fluid

Porosity Distribution

Interconnected

- Path connecting the pores.
- Typically following a pattern or aligned in a particular direction.

Hierarchical

- Containing pores with 2 or more length scales in the same component.
- Similar pore type and shape.
- Component can be described as bimodal or trimodal pore size distribution.

Multiscale

- Different porosity type and shape and size in the same sample.
- It can also be defined as a “hierarchical”.

Functionally Graded

A hierarchical or multiscale porous material where the different pore sizes are patterned on a particular direction (i.e. radial distribution, unidirectional graded, etc).

*Figure* 4. *Terminology used to describe various attributes of porous ceramics.*

Figure 5

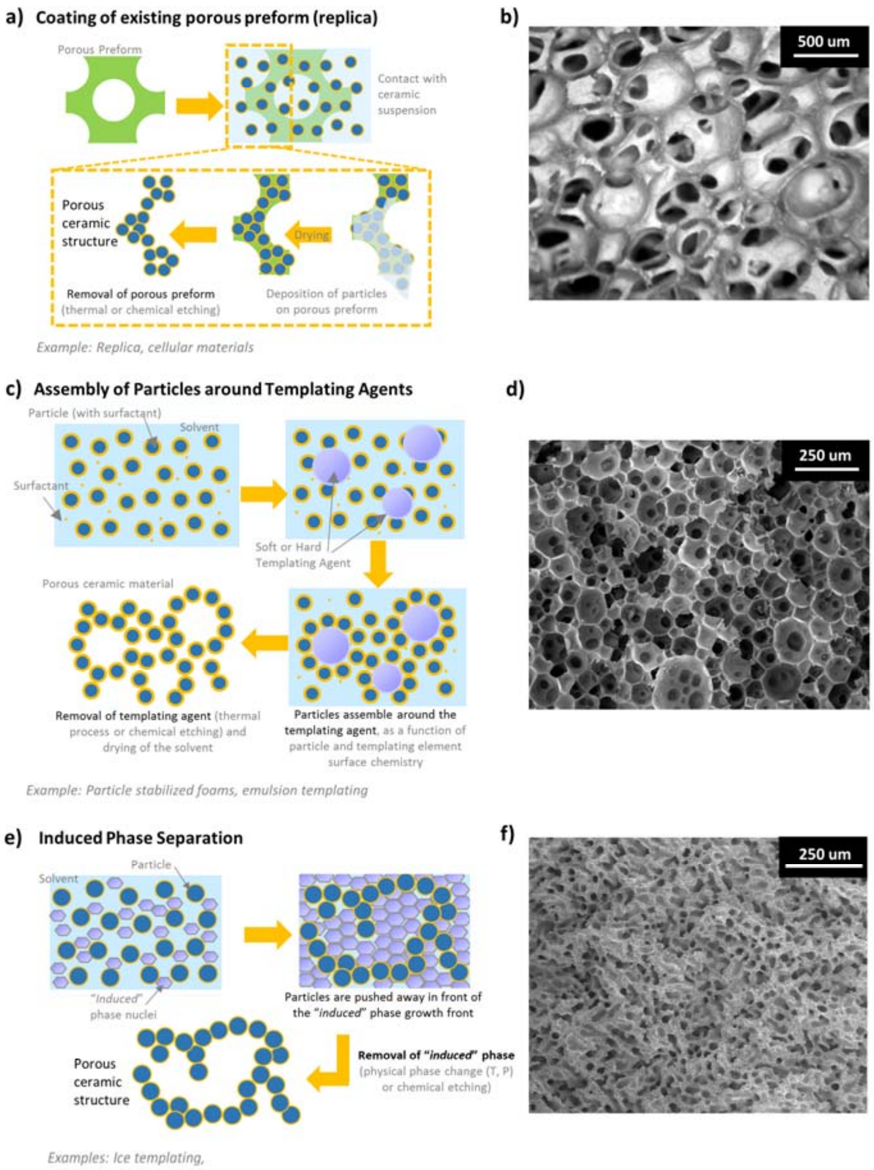


*Figure 5. Summary of different mechanisms used to create macroporous ceramics using colloidal processing techniques. a) The replica method involves coating of a porous preform, i.e., polymeric sponges or C-C structures, with a suspension then drying. b) Example of porous zirconium diboride ($ZrB_2$) produced with the replica technique with 85% porosity. c) The sacrificial template method involves assembly of particles around templating agents (air bubbles, emulsion droplets, polymeric spheres or carbon fibers) then drying. d) Example of porous alumina ($Al_2O_3$) produced with the particle stabilized foam method with 80% porosity. e) The induced phase separation approach relies on phase separation such as a frozen solvent or liquid to gel transitions to push particles into one phase leaving a particle free phase behind as a porogen. f) Example of porous $TiB_2$ produced by ice templating with 75% porosity. Most of these techniques require a stage to remove the preform, templating agent or the "induced" phase to create the porous structure. This removal stage is normally a thermal treatment (calcination), a physical transformation (sublimation) or a chemical etching. Finally, the green bodies are fired to strengthen and/or densify the struts.*

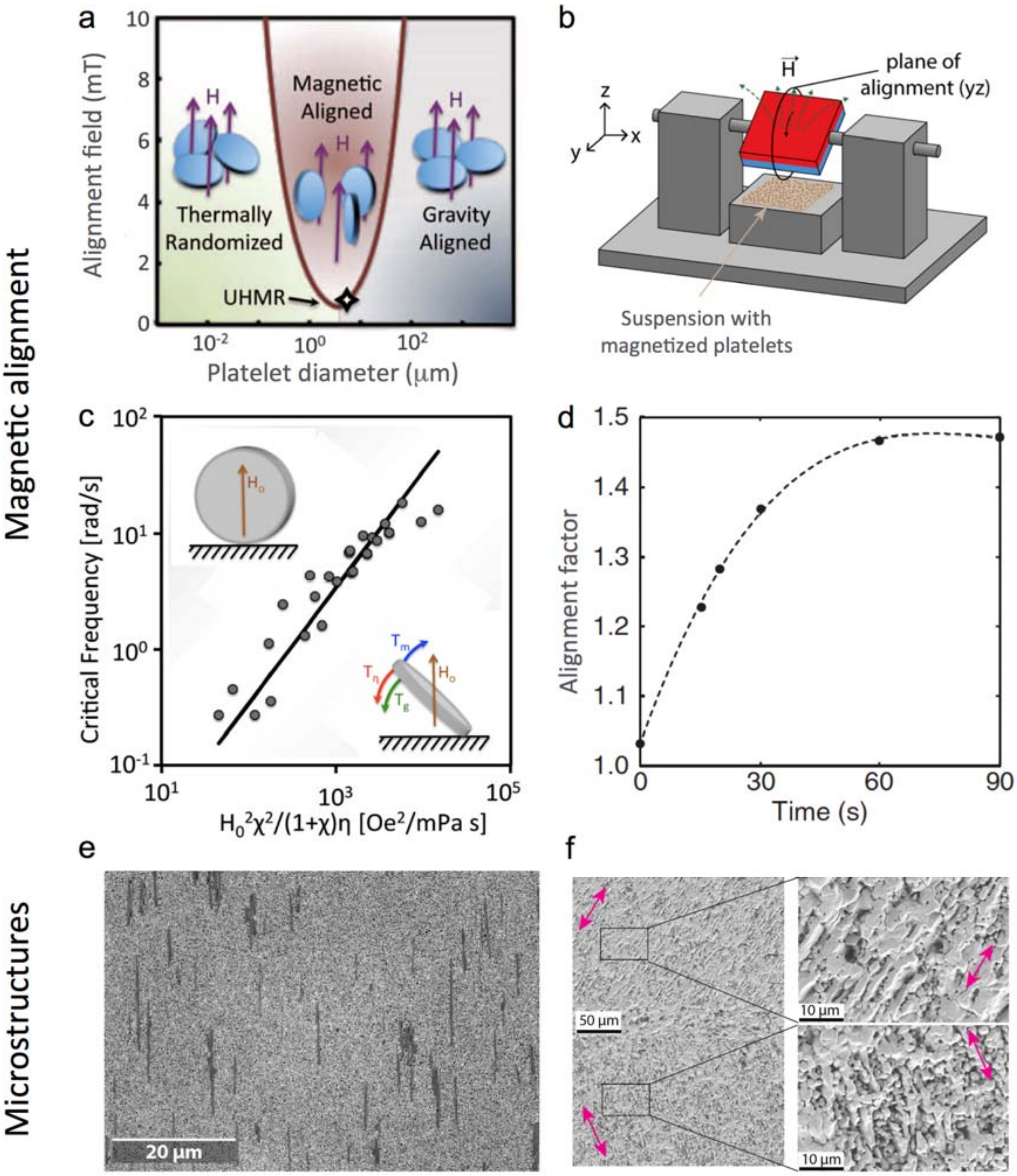


*Figure 6. Magnetically-assisted orientation control of anisotropic ceramic particles. (a) Magnetic field required for alignment as a function of the size of* $Al_2O_3$ *platelets coated with superparamagnetic iron oxide nanoparticles (SPIONs)* [274]*. (b) Setup typically utilized to apply a rotating magnetic field to a suspension of responsive anisotropic particles*[278]*. (c) Threshold frequency required to align disc-shaped particles within the plane of an external rotating magnetic field.* $H_0$, $\chi$ *and* $\eta$ *are the applied magnetic field, the particle magnetic susceptibility and the fluid viscosity, respectively.* $T_m$, $T_g$ *and* $T_\eta$ *are the magnetic, gravitational and viscous torques exerted at the edge of the disc. (d) Alignment factor extracted from optical microscopy images indicating the typical timescales required for the orientation of* $Al_2O_3$ *platelets under an external magnetic field*[161]*. (e) Microstructure of a green body containing* $Al_2O_3$ *platelets oriented in a specific direction within a matrix of* $Al_2O_3$ *nanoparticles*[278]*. (f) Sintered microstructure of a ceramic bilayer containing grains aligned in specific orientations in each of the layers*[278]*.*

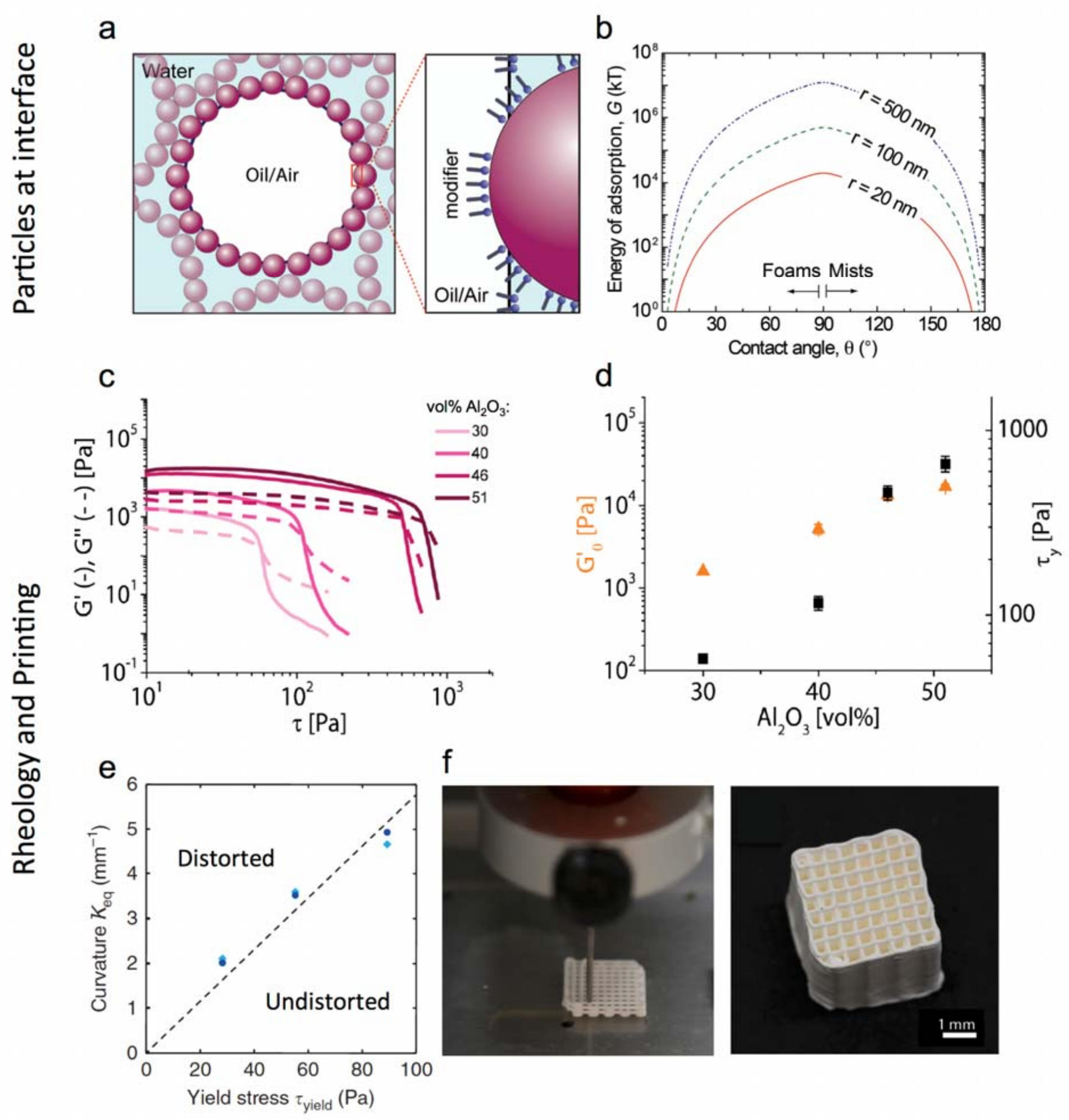


*Figure 7. 3D printing via direct ink writing (DIW) using particle-stabilized foams and emulsions as colloidal inks. (a) Schematics of the adsorption of weakly hydropohobic colloidal particles on the surface of oil droplets or air bubbles[241, 287]. (b) Estimated energy of adsorption of a colloidal particle at an air-water interface as a function of the particle size and interfacial contact angle[80]. (c) Rheological behaviour of Pickering emulsions containing different concentrations of alumina ($Al_2O_3$) particles modified with propionic acid[287]. (d) Effect of the $Al_2O_3$ content on the storage modulus ($G'$) and yield stress ($\tau_y$) of the emulsion[287]. (e) Yield stress required to print undistorted filaments with specific curvatures[161]. (f) 3D printing by DIW of a Pickering emulsion (left) and the resulting porous ceramic after drying and sintering (right)[287].*

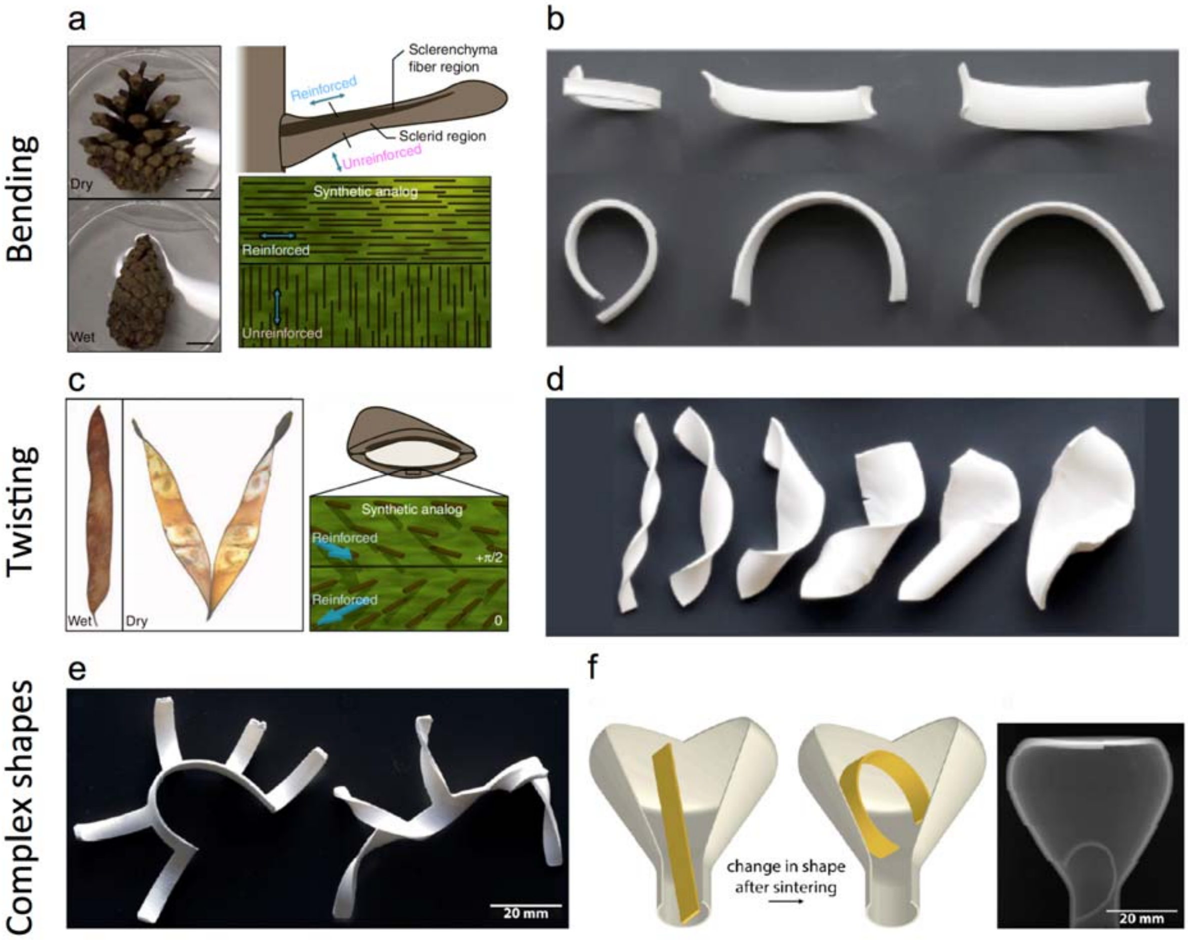


*Figure 8. Self-shaping ceramics with programmable microstructures inspired by plant seedpods. (a) Shape change of a pinecone upon humidity variations and the underlying bilayer reinforcement architecture of one scale of the cone*[299, 300]*. (b) Self-shaping ceramics that undergo programmable bending during sintering. The width of the ceramic bilayer increases from left to right*[278]*. (c) Chiral seedpod that twists upon drying and the reinforcement architecture leading to the shape change*[299, 301]*. (d) Self-shaping ceramics that twist during sintering, highlighting the strong effect of the bilayer width on the final twisted geometry*[278]*. (e,f) Examples of ceramics with unusual, complex geometries achieved through self-shaping effects*[278]*.*

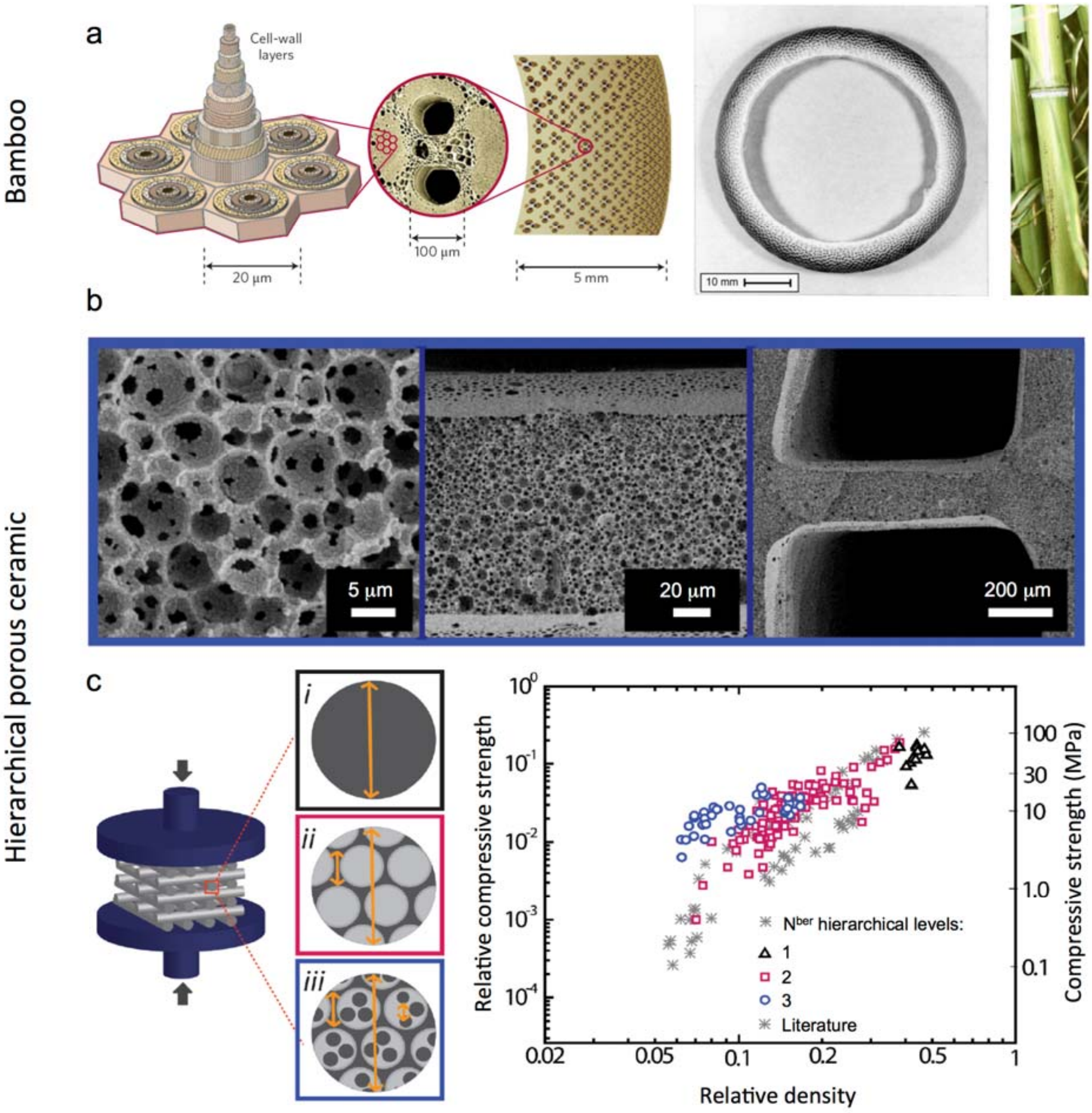


*Figure 9. Hierarchical structural materials with enhanced mechanical response using minimum material resources. (a) Hierarchical structure of bamboo. From left to right: multilayered cell walls, vascular and fiber bundles, radial gradient of bundles, transverse cross-section of bamboo culm, and picture of part of the bamboo culm*[307, 289, 308]*. (b) Synthetic hierarchical porous ceramic produced by 3D printing of a particle-stabilized emulsion*[287]*. (c) Compressive strength of porous ceramics with different number of hierarchical levels as compared to literature data for varying relative densities*[80, 287]*.*