Robocasting of ceramic-based composites

Abstract

Robocasting, also known as direct ink writing, is a layer-by-layer nozzle-based material deposition 3D printing technique that can form customizable 3D shapes and designs. This technique involves the extrusion of an ink paste through a small nozzle orifice before deposition onto a controlled spatial position of the stage. Out of all classes of materials, manufacturing of ceramics proves to be difficult due to its high melting point and inherent brittleness. However, with suitable rheological properties, ceramic-based composites can be used as the ink paste, such that geometrically complex 3D ceramic structures can now be formed. From the discovery of this new fabrication method in forming ceramic structures in 1999 till today, many applications based on this technique have been illustrated, ranging from its uses in creating biomedical scaffolds, ceramic structural models, and piezoelectric devices.

In view of potential widespread use of this technique, it is thus of interest to discuss and understand more of the technological advancement in robocasting of ceramic-based composites. This paper first introduces the principles of this technique and the properties required by the ceramic-ink. This is then followed by a discussion on the advantages and the applications of this technique. Finally, a review of future work and the challenges of this method will be presented.
1. Principles of robocasting

In robocasting, the ink paste located within an ink reservoir is fed into a nozzle. It is then extruded/squeezed through a small cylindrical nozzle orifice by a pressurized system (such as a plunger), thus creating a filamentary structure, and thereafter it is deposited at specific positions on the printing bed to form a 3D layered structure. A schematic of robocasting is shown in Figure 1.

![Figure 1: Schematic of robocasting](image)

One important characteristic required by robocasting inks is a controlled viscoelastic property. Here, viscoelasticity refers to dual properties of the ink where its viscosity determines the difficulty in the flow of the ink and the elasticity affects the deformation of the ink upon application of stress. First, the ink flows through a nozzle with a small diameter, overcoming any resistive shear stress acting on the ink by the walls of the nozzle. Upon extrusion, the ink then “sets” immediately in order to retain its shape and prevent excessive wetting of the printed lines. Lastly, the ink should be able fuse to previously deposited material to form a homogeneous 3D structure.
One form of ceramic composite that possess such viscoelastic property is colloidal gel-based ink [2], which contains a high concentration of attractive ceramic particles in a dispersing medium. The gel (Figure 2b) displays shear thinning behaviour and acts as a fluid (Figure 2a) when stressed/pressured beyond its yield point. This meant that when stressed, the ink has lower viscosity and thus its flow in the nozzle can be increased. As this ink exits the nozzle, the fluid-like ink experience no stress, and it returns to its solidified gel-like properties such that its cylindrical shape can be retained. At the same time, during this transformation from a fluid-like ink to a gelled state, particles bonds are re-forming and thus fusing between adjacent extruded lines can take place at their contact point. After the print, the ink is often heated/sintered to high temperatures to remove the solvent or dispersing medium, leaving behind the ceramic particles.

Figure 2: Schematic illustration [3] of (a) fluid colloidal ink, which has dispersed particles above its yield stress and (b) gel-like colloidal inks, which has interconnected attractive particles below its yield stress

Fabricating new types of ceramic-based ink requires understanding about how different physical parameters - such as the sizes and fraction of the particles and different interparticle forces - may influence the viscosity, yield stress and viscoelastic properties of the ink. A scaling relationship [4] relating these parameters is shown in Equation 1:
\[ y = k \left( \frac{\varnothing}{\varnothing_{gel}} - 1 \right)^x \]  

(1)

where \( y \) represents an arbitrary elastic property such as the elastic modulus or shear yield stress, \( k \) is a proportionality constant, \( \varnothing \) is the colloid volume fraction, \( \varnothing_{gel} \) is colloid volume fraction at gel point, and \( x \) is the scaling exponent which is approximately 2.5. Here, \( \varnothing_{gel} \) is inversely related to the bond strength, in which higher bond strength between particles indicates that the gel state can be attained much more easily. It is noted that the bonding between particles can come in many forms – van der waals, electrostatic, and ionic. The colloid volume fraction, \( \varnothing \), is commonly kept at a high constant value to minimize undesired drying shrinkage during the heating/sintering process after the print.

One example of this process is the printing of Alumina (\( \text{Al}_2\text{O}_3 \)) based ink presented by Rao and co-workers [6]. In their work, a high concentration of alumina particles are dispersed by poly(acrylic acid) (PAA). The polymeric structure of PAA contains a negative ionisable carboxylic acid group (COO\(^-\)). The alumina particles are then coated with polyethleneimine (PEI), which contains a positive NH\(_2\)\(^+\) group. By doing so, they can introduce attractive bonding between the oppositely charged ions, thus triggering the fluid-to-gel transition.

**Figure 3:** (a) Effects of the ratio of NH\(_2\)\(^+\) to COO\(^-\) ions on the elastic modulus- shear stress relationship. (b) Shear thinning behaviour after shear stress exceeded the yield shear stress. Figure adapted from Rao [6].
Figure 3a shows that the effects of the different ratio of \( \text{NH}_4^+ \) to \( \text{COO}^- \) ions on the Elastic Modulus-Shear stress relationship. Beyond a shear yield stress, rupturing of the inter-particle attractive forces take place and thus the elastic modulus of the ink drops dramatically by orders of magnitude. From Figure 3b, it is shown that there is a drop in its viscosity with increasing shear rate. This facilitates an ease of flow of the ink through the nozzle simply by pressurizing the ink through the nozzle. Upon exiting the nozzle, the ink solidifies back to its gel-like state, retaining the cross-sectional shapes of the nozzle orifice (Figure 4). This approach of a gel-based ink thus creates new opportunities in designing and fabricating a larger range of printable ceramic composite inks. Some other ceramic-inks that have been presented are Silica (\( \text{SiO}_2 \)) [7], Metal Titanate [8, 9] and Hydroxyapatite [10].

![Figure 4: (a)-(c) Micronozzles with different cross-sectional orifices. (d)-(f) Extruded ink which retains the cross-sectional shape. Figure adapted from Rao [6].](image)
2. Advantages and Applications of Robocasting

a) Piezoelectric devices:

One use of ceramic material is in the formation of piezoelectric devices. Using 3D printing techniques such as robocasting, offers a quick and easy way to form complex 3D piezoelectric structures. A study showing how 3D structural variation can enhance the piezoelectric strength is described by Smay [11]. In this study, composites containing a ceramic piezoelectric material, lead zirconate titanate (PZT), and a polymer phase are printed via robocasting. Printing PZT composites proves to be less laborious and offers higher design customizability as compared to conventional manufacturing techniques such as extrusion [12], holes-drilling in PZT blocks [13], and physically stacking PZT layers [14,15]. Here, structural variation, determined by the connectivity and symmetry of the PZT phase within the polymer, affects the overall performance of the printed device. By optimizing the composite structures, one may redirect the stress distribution onto the PZT phase while the polymer phase helps to reduce the overall dielectric constant. This enhances the voltage output of the device. Figure 5 shows 3 different PZT-polymer composite structures with different piezoelectric constants obtained from the 3 structures, allowing us to have a tunable piezoelectric effect based on structural variation. These printed piezoelectric ceramic composites can thus be used in applications such as hydrophone, ultrasonic imaging, and sonar systems [16-17].
Figure 5: (a) Printed lattice with alternating printing directions for each layer. (b) Printed lattice similar to a but with capping layers at its ends. (c) Printed lattice similar to b but with extra sidewall along its circumference. (d) Piezoelectric constant for increasing fraction of PZT within the composite. Circle- Lattice a, Square- Lattice b, Triangle- Lattice c. Adapted from Smay [11].

b) Bone Implants and scaffolds:

One commonly used material for scaffolds is calcium phosphate, also known as Hydroxyapatite (HA). HA, being a main material in natural bone itself, displays biocompatibility and osteoconductivity to allow for the growth of bone. Structurally, it is desired that a scaffold contains pores to promote growth of the bones and support vascularity within itself. Robocasting of HA-based inks can not only create a customizable 3D -shaped scaffold that fits perfectly into a damaged bone (Figure 6 ) but also help create porosity [18] necessary for bone growth. Figure 7 shows that different length scales of porosity can be achieved in a single scaffold [19,20].The continuous porous pathways created by the periodicity of the
printed structure has the ideal dimensions for bone growth, while smaller micropores can serve as reservoirs for drug delivery [21].

**Figure 6:** Processing steps to achieve a customized hydroxyapatite (HA) scaffold for a patient jaw bone. First, a computed tomography scan of the jaw bone is taken. Next, a solid 3D model is developed. Lastly, a periodic HA structure is robocasted from the 3D model. Adapted from Ref. [18].

**Figure 7:** (a) Robocasted Hydroxyapatite periodic scaffold. (b) Scaffold contains macropores denoted as 1. (c) The individual printed lines contains micropores of bimodal sizes denote by 2 and 3. Adapted from Cesarano [22].
c) Electrochemical Applications:

Another common use of oxide-based ceramic materials is in the electrodes (anodes and cathodes) of our batteries. One example is that of Lithium Titanium Oxide (LTO) and Lithium Iron Phosphate (LFP) that serve as the anode and cathode materials [23], respectively.

![Figure 8: (a)-(d) Steps involved in printing a battery. First, the conductive collector gold electrode is printed on a substrate. The LTO and LFP are later printed next to each other. A packaging material is used to contain the battery. (e) Scanning Electron Microscopy Image of the robocasted battery. Adapted from Sun [24].](image)

In a recent work [24], researchers utilized the same gel-ink approach as mentioned in this report to fabricate a printing ink that contains Lithium-based ceramic particles. This leads to the ability to design and print/robocast high aspect ratio, multilayer electrodes that takes up small areal space (Figure 8). The researchers then show that their printed miniscule battery has energy and power density that are competitive and similar to commercial batteries (Figure 9). Having the capability to print the cathodes and anodes with high resolution give rise to more opportunities to fabricate much smaller and customizable batteries which has potential applications in powering microdevices.
3. Future work and Challenges

a) Novel Ink design:

A future aim for many researchers in this field is to achieve novel types of inks that contain new ceramic materials for varying applications. However, the fabrication of new forms of ink are always impeded by the agglomeration of the nano or micro ceramic particles within the dispersing medium. Such agglomeration usually increases the viscosity of the ink, thus resulting in the clogging of the nozzle. In addition, agglomeration of these particles creates inhomogeneity of its composition across the structure of the final printed objects. To overcome agglomeration, one may functionalize these particles [25] with organic linker molecules to keep the particles separated from each other.

In addition, it is often desired for the ink to contain high loading fraction [25] of the ceramic particles, so that first, the desired functionality of the ceramic component can be further enhanced and secondly, the porosity of the final sintered product can be reduced to
improve its structural strength. However, there is a limit to the fraction of ceramic particles that can be added into a dispersing medium, since an increase in ceramic particles results in a rise in viscosity which may cause nozzle clogging. Lastly, to achieve higher resolution, the diameter of the nozzle orifice should decrease. An externality is that the required viscosity of the printing ink should be reduced to facilitate smooth extrusion through the nozzle orifice. The concentration of ceramic particles and material viscosity thus constrain the loading fraction of the ceramic particles. Given these challenges, one strategy is to rethink the design of the print head [26] coupled with more simulation work on the ink flow through potentially re-designed nozzles. In doing so, it is possible to determine the optimized shape of a nozzle, hence preventing nozzle clogging.

b) Moving from prototypes to commercial production:

Since robocasting is an additive manufacturing technique in which materials are deposited layer by layer, printing of products may be slower compared to parallel techniques such as injection moulding. One solution to increase the manufacturing speed of printed objects is to implement multiple print heads on a single printing platform to print many objects simultaneously.

Another factor impacting realization of the commercial use of robocasted objects is the reliability [27] of the printed objects in the various applications. For example, biomedical scaffolds, which are robocasted, often contain unnecessary morphologies such as edges, grooves or discontinuities in topography. These morphologies may create undesired topography-driven changes in the adhesion and migration of cells [28]. In addition, such discontinuities in topography may also be detrimental as they act as stress intensifying sites. This may result in crack formation, which is highly undesirable in robocasted ceramic products.
that are being used as structural support. As such, further studies and research are required to investigate the reliability of these robocasted products, such that robocasting of ceramic-based composite can be a ubiquitous tool to produce commercial ceramic objects.

(* Note: Total number of pages excluding Figures and References is 8)


