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<th>Review of 3D printed electronics: metallic nanoparticles inks</th>
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ABSTRACT: There are growing interests among researchers to use additive manufacturing technologies for on-demand fabrication of functional electronic components and circuitries. The conductive ink is one of the most important components in 3D printed electronics, in which the material properties of the ink determine the mechanical and electrical properties of the printed patterns. Therefore, there is great importance to look into and understand the different types of ink used in 3D printed electronics. In this review paper, we discuss the overview of the metallic nanoparticles inks used for 3D printed electronics.

KEYWORDS: Additive Manufacturing; Metallic Nanoparticles Ink; 3D Printed Electronics; 3D Printing.

INTRODUCTION

Printed electronics technologies have been around for many decades, but it has only gained much attention over the recent years for on-demand fabrication of 3D printed electrical components and circuitries. The 3D printed electronics sector in the additive manufacturing (AM) industry had generated $681 million of revenue in 2015, and its market size is expected to grow and exceed $1 billion by 2025 [1, 2]. AM experts also predicted that 3D printed electronics have the potentials of revolutionizing product innovations. One of the main advantages of 3D printed electronics is to allow the manufacture of electrical components and circuitries on a wide range of substrates with different properties (for instance, transparent, stretchable, low cost, flexible, eco-friendly, wearable substrates) [3].

Currently, most electronic components and circuitries are mass produced through a series of additive and subtractive fabrication process (for example, additive processes, laser ablation and photolithography etching). This approach is also known as the conventional ‘mixed subtractive-additive’ approach and it gives many undesirable disadvantages such as time bottlenecks in the prototyping stages and polluting wastes from the subtractive processes [4-6]. Therefore, 3D printed electronics is commonly seen as an alternative for mass production of electronic components and circuitries by the industries to mitigate the shortfalls in conventional manufacturing of electronics. 3D printed electronics’ printing technologies can allow on-demand deposition of conductive inks on various substrates, especially for the fabrications of highly customisable, low-volume and low-cost electronics [4, 7, 8]. 3D printed electronics technologies can also help to reduce prototyping time in designing printed circuit boards (PCBs), in which conventional PCBs prototyping processes face long time bottlenecks. Furthermore, digital printing techniques, such as the aerosol jet and inkjet printing, can be integrated into other additive manufacturing systems for fabricating embedded electronics within 3-dimensional (3D) structures [4, 7-15].

The ink is one of the most important components in 3D printed electronics, in which the material properties of the ink determine the mechanical and electrical properties of the printed patterns. Therefore, there is great importance to look into and understand the different types of ink used in 3D printed electronics as they have different specialised functionalities and properties. The inks can be further categorised into these categories: metallic nanoparticles ink, metallic-organic decomposition (MOD) ink, conductive polymers ink, dielectric ink, semiconductor ink, carbon nanotubes (CNT) ink and graphene ink. This paper presents an overview of the metallic nanoparticles inks used for 3D printed electronics and discusses the different parameters that affect the metallic nanoparticles inks’ materials and electrical properties.

METALLIC NANOPARTICLES

Metallic nanoparticles inks are one of the most commonly used inks in 3D printed electronics applications and they are widely available in the market commercially. Metallic nanoparticles inks are suspensions of metallic nanoparticles in liquid mediums and these nanoparticles typically have diameters ranging from 1 to 100 nm [16]. They are usually preferred over metal-organic decomposition (MOD) inks of their higher metal loadings [16] which give better electrical conductance. In addition, the electrically conductive nature of the metallic nanoparticles omits the need for additional chemical reduction processes [17]. However, undesirable coffee ring effects are prominent and inevitable
on deposited metallic particles inks, in which metallic nanoparticles tend to concentrate on the perimeters [18]. Note that the freshly deposited metallic nanoparticles inks are not electrically conductive as the metallic nanoparticles are enveloped in organic additives and stabilising agents. These organic additives and stabilising agents help improve the inks’ printability and stability and prevent agglomeration of nanoparticles in the ink suspension. Therefore, the deposited inks require a post-processing process called sintering, in which energy is introduced to decompose the organic additives and stabilising agents so that the metallic nanoparticles can form contacting points with each other.

An ideal metallic nanoparticles ink should possess good printability and ink stability. In addition, it should ideally require low sintering temperature and short sintering time (especially in thermal sintering process) to achieve its best optimal electrical conductivity [17]. This section looks into the different parameters that affect the metallic nanoparticles inks’ materials and electrical properties. These parameters can be categorised into two broad categories: metallic nanoparticles and liquid medium. Metallic nanoparticles can be further separated into material composition, particles concentration, particles size and particles shape, whereas liquid medium can be optimised according to its carriers, dispersants and additives used (see Figure 1) [17].

Figure 1: Parameters of the metallic nanoparticles inks.

A) Material Composition

The liquid medium is removed from the metallic nanoparticles inks through various sintering techniques after they are deposited onto the substrates’ surfaces [4], so that neighbouring metallic nanoparticles can form contacting points with adjacent particles to conduct electricity. The printed patterns mainly consist of metallic nanoparticles after the decomposition of the liquid medium. Therefore, the material composition of these nanoparticles determines the main characteristics of the metallic nanoparticles inks and electrical properties of the final printed patterns.

There are several factors of consideration that affect the choice of material composition: electrical conductivity, oxidation stability, costs, and unique electrical and magnetic properties. The first factor that affects the choice of the nanoparticles’ material composition is the electrical conductivity of its bulk materials. For instance, materials with high electrical conductivity (such as silver, gold and copper) are preferred especially for the fabrication of electrically conductive tracks in 3D printed electronics applications. High conductivity materials help to reduce the Joule heating effects in circuits and promote efficiency. The second factor that affects the choice of the nanoparticles’ material composition is their oxidation stability. Some metals tend to form metal oxides when exposed to air at elevated temperatures, and hence making them electrically non-conductive. For instance, copper nanoparticles rapidly oxidise in the atmosphere at elevated temperatures and these undesirable copper oxides are found to be less conductive than pure copper nanoparticles [19]. As 3D printed electronics aim to decrease fabrication costs, the choice of material must both possess good electrical properties and low-cost price. Therefore, the material cost is a crucial factor in deciding the metallic nanoparticles’ material composition. For instance, highly conductive silver exhibits excellent electrical properties but it has an expensive price tag. Hence, it may not be cost-effective in using silver nanoparticles inks for mass fabrications of 3D printed electronics. Therefore, ongoing research has been looking into using copper nanoparticles inks for the fabrications of 3D printed electronics due to their good electrical properties and their significantly cheaper cost price. Lastly, materials with unique electrical and magnetic properties may also be a factor of consideration for the choice of material composition. For instance, cobalt nanoparticles inks have high permeability and these inks are suitable for fabricating radio frequency absorbers, antennas, magnetic sensors, filters, resonators and phase shifters [20, 21].

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B) Particle Concentration

The solid loading of metallic nanoparticles ink directly affects the electrical conductivity of the printed patterns. Ceteris paribus, inks with higher metallic nanoparticles solid loading theoretically tend to have better electrical conductivity as compared to those with lower solid loading [22]. Printing conductive patterns with higher solid loading metallic nanoparticles inks tends to have thicker cross-sectional areas and hence reducing the electrical resistance. Furthermore, when higher solid loading metallic nanoparticles inks are being used, a lesser amount of organic additives are present within the printed patterns and minimising the effects of contact resistance between the nanoparticles caused by these additives [22]. Wang et al. [22] demonstrated that by using silver nanoparticles ink with 80 wt% solid loading of silver nanoparticles, it was possible to produce conductive tracks with a very low electrical resistivity of $3.92 \times 10^{-8} \cdot \Omega \cdot \text{m}$ (approximately 2.45 times of silver’s bulk resistivity). The metallic nanoparticles inks currently available in the markets have a fairly high concentration of metal particles, ranging from 20% to 80% [23].

C) Particle Size

Metallic nanoparticles have significantly lower melting temperatures than its bulk counterparts [24] and this interesting phenomenon allows the sintering of nanoparticles at lower temperatures. Buffat et al. [25] demonstrated that it is possible to decrease the melting temperature of gold significantly by shrinking the particles into the nanometre scale. For instance, gold nanoparticles with diameters below 5 nm have melting temperature below 300°C, which is substantially below the melting temperature of bulk gold at 1064°C [16]. Allen et al. also demonstrated that there is an approximately linear relationship between the melting temperature and the reciprocal of the particle’s radius [24]. This unique and interesting property of the metallic nanoparticles can be explained by the surface effects phenomenon [26]. The surface effects phenomenon explains the reason behind nanoparticles’ lower melting temperatures [24, 27, 28] and correlates their melting temperatures to be directly proportional to their particle’s sizes [29]. Nanoparticles have higher surface-to-volume ratios when compared to larger bulk materials, in which the surface-to-volume ratio is inversely proportional to the particle’s size. On the one hand, nanoparticles are mostly made up of surface atoms [28]. There is a significant lack of chemical bonding on the surfaces, which causes the surface atoms to have lesser stability as compared to those in the body of the particles. Hence, lesser energy is required to break down chemical bonds between individual surface atoms. On the other hand, bulk materials have lesser percentages of surface atoms. The atoms in the body of bulk materials naturally have more neighbouring atoms, which in turn increases the strength of their chemical bonding, mechanical stability and eventually their melting temperatures. Therefore, it can be concluded that the particles size directly affects the nanoparticles’ sintering and melting temperatures [24, 26, 27]. Ceteris paribus, inks with small particles size theoretically require a lower sintering temperature than inks with larger particles size. Due to the nanoparticles’ large surface curvatures [16], organic additives and stabilising agents are formulated into metallic nanoparticles inks to prevent agglomeration and improve the nanoparticles’ dispersion stability and printability [16, 30]. Steric repulsion forces are introduced between individual particles by the enveloping organic additives around individual nanoparticles. These steric repulsive forces reduce the Van der Waals forces between nanoparticles and prevent agglomeration [16]. Organic additives also help to promote better adhesions of the nanoparticles to the substrates [16, 31] and maintain the mechanical integrity of the printed patterns [31]. The stabilising agents help to maintain stable dispersions of nanoparticles in ink formulations. Although smaller nanoparticles can significantly lower the sintering temperatures, the need for organic additives and stabilising agents in formulating the metallic nanoparticles inks may further increase the required sintering temperatures [32]. On the one hand, reducing the amount of organic additives presents in the metallic nanoparticles inks may reduce the sintering temperatures required, but on the other hand, the printability and stability of the inks may be in return be sacrificed. Therefore, the metallic nanoparticles inks have to be optimised to the appropriate amount of organic additives needed according to the different applications and printing techniques used.

D) Particle Shape

The electrical, magnetic, optical and catalytic properties of metallic nanoparticles are affected by their shapes and sizes [33]. Many research has been using unconventional metallic nanoparticles’ geometries (for example, nanowires, nanocube, nanorod, prism and multifaceted nanoparticles) for many interesting applications. In the market, spherical nanoparticles are commonly used for the formulation of metallic nanoparticles inks as they are easier and cheaper to
manufacture. Among all geometries, spherical shapes possess the least energy shape and hence requiring minimum dispersants to achieve dispersion stability. Spherical nanoparticles also have the least effects on the thixotropy and shear thickening. However, spherical nanoparticles face challenges in packing efficiency and are unable to achieve high-density packing. For spherical nanoparticles, assuming all size equal, the maximum achievable packing density is merely 74%. In order to achieve higher packing density, other non-spherical geometries or polydispersed nanoparticles can be employed. The spherical geometry is also not optimal for electrons to migrate over long linear distances and thus not maximising the maximum electrical conductance of the printed patterns [17, 33]. Literature has recently indicated strong interests in silver nanowires, as silver nanowires have interesting material properties. Apart from silver’s anti-bacterial properties, silver nanowires have good electrical conductivity and as well as high optical transparency (up to 90% transparency). Hence, silver nanowires are often employed in applications to fabricate transparent electrodes [33]. However, silver nanowires have the tendency to clog inkjet printers’ print heads due to their unique geometries and this presents a challenging technical issue to overcome [34, 35]. Nanoplatelets are also known to give very good electrical conductance due to their flat geometries, which can enable them to form very dense microstructures [33, 36].

E) Carriers

Carriers are the main liquid mediums vehicles that encompass and stabilise the metallic nanoparticles, which forms the volumetric bulk of the metallic nanoparticles inks. Carriers in metallic nanoparticles inks should exhibit fast evaporation rates without undesired residues after evaporation, as residues may increase the final electrical resistivity of the printed patterns. These carriers should also be free of contaminants to preserve the intended chemical properties of the metallic nanoparticles inks. These carriers may be solvents such as water, hydrocarbons, alcohols, aromatics, amides and esters [17, 33].

F) Dispersants

The Van der Waals forces between particles increase as the particle size gets smaller and hence increasing the probability of flocculation in metallic nanoparticles inks where nanoparticles agglomerate. Agglomeration of these nanoparticles causes undesirable effects such as clogging of nozzles especially in inkjet printing and inhomogeneous dispersions of the nanoparticles in the inks. Hence, dispersants come into play in the formulations of metallic nanoparticles inks to prevent flocculation by introducing repulsive forces to each individual nanoparticle. Dispersants are chemical agents (for example, surfactants and other moieties) that promote dispersion stability to increase the metal loading of the metal nanoparticles inks through methods such as electrosteric, electrostatic and steric stabilisation [17, 33].

G) Additives

Other than carriers and dispersants, additives are also required to be added to metallic nanoparticles ink formulations. Additives are required to tailor the inks to the desired surface tension and improve its printability, wettability and dispersion stability. Additives can also promote good adhesions to the substrates and prevent the growth of bacteria and fungi in the ink. Additives typically consist of surfactants, humectants, adhesion promoters, biocides and fungicides and they will be further discussed individually in this chapter [17, 33].

CONCLUSION

It is important to look into and understand the different parameters of the metallic nanoparticles inks for 3D printed electronics as they directly influence their material and electrical properties. Therefore, the parameters should be individually optimized to tailor the metallic nanoparticles inks to possess good printability, ink stability, low sintering temperature, short sintering time and the desired material and electrical properties.

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