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Metal-based conducive nano-inks: A review of synthesis and characterisation techniques

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Abstract

In the recent decade, metal-based conductive nano-inks comprising of nanometer-sized metallic particles of high electrical conductivity (mainly Ag and Cu) suspended in a polymer have revolutionized the field of printed electronics. The present review aims to provide an overview of the current state of research in synthesis and characterization techniques for metallic nano-inks and associated challenges. Moreover, the end of the review will discuss future perspectives in this field (from industrial and academic viewpoints).

1. Introduction

Optimization of efficient strategies to upscale different fabrication techniques from academic research to industrial applications is the main requirement for the commercial success of any manufacturing technology [1]–[6]. This imposes significant challenges on the cost, time, and labor (associated with material production. For instance, noble metal-based inks find applications in a number of printed electronics-based applications, which primarily include radiofrequency distribution (RFID) antennas, electrochromic devices, and touch panels [7]. For all the aforementioned applications, it is necessary to attain well-defined conductive structures combined with high resolution to enable high performance of the device [8]. To be more specific, line widths and spacings below 100 μm are desired, although the exact technical requirements are highly application-specific [9], [10]. The efficiency of printed electronic-based devices is highly deteriorated by printing defects which primarily include undesired discontinuities and connections necessitating high-quality printing [11]. In addition, the other critical parameters are the structural topology, electrical conductivity, and adhesion between metallic tracks and substrate material [12].

The conventional techniques for direct deposition of metallic nano-inks primarily include spin-coating, spray-coating, and drop-coating methods and a number of printing-based techniques such as flexo and gravure, etc. [11], [13]–[16]. Moreover, several physical and chemical reduction techniques for synthesizing metal-based conductive nano-inks have also been reported [6]. These techniques are based on the simultaneous application of solvent carrier with direct writing techniques to obtain nano-inks with the desired shape, size, and viscosity [6], [17]. The choice for a particular printing method to deposit conductive patterns is largely determined based on exact technical and commercial requirements for the specific product [6]. Continuous processing techniques are highly advantageous for large-scale industrial manufacturing [18]. For instance, Rotary screen printing of metallic pastes is a highly mature and well developed industrial technology, but the high layer thickness and surface roughness of the finished product has been reported to pose severe restrictions related to the compatibility with the architecture of a number of devices [19], [20]. Besides, most commercial metallic pastes are based on micrometer-sized metal flakes instead of nanoparticles, leading to limitations in electrical conductivities. For such cases, post-deposition processing conditions are required for the improvement of electrical conductivity [21]. However, the post-processing techniques tend to be incompatible with most of the low-cost substrates [22]. On the other hand, flexo and gravure printing of metal inks are also recorded to report (R2R) compatibility. They have been reported to provide excellent widths (of the order of nearly 10 μm and below) along with excellent electrical conductivities [23]. However, modifying the desired printed structures necessitates the acquisition of dedicated rotary screens or plate cylinders for each individual pattern, leading to a substantial financial investment, especially for small-scale production [24]. In this context, inkjet printing has been reported to be a beneficial alternative [25]. This is because a virtually unlimited variation of the produced structures is possible through a simple adjustment of the digital image input using inkjet printing [26]. Besides, inkjet printing, owing to its non-contact nature, also allows the deposition of materials on highly sensitive substrates [27]. Moreover, a suitable decision on the choice of printing technologies needs to be made on the basis of post-deposition treatment, which is required to render the electrically conductive nature of the printed ink through the removal of organic components (such as solvents, stabilizers, etc.) and subsequent sintering of particles [28]. Although a number of post-processing techniques (of organic components) based on exposure to chemicals, microwave and infrared radiation (IR) have been reported, however, at present, post-processing techniques based on exposure (of organic components) to laser beams and electric current are the only two techniques which have been developed for large scale

industrial manufacturing [7]. Although the traditional approach of thermal drying and sintering (using hot air ovens) is technically easy to achieve, however, the maximum temperatures (in these techniques) are limited by the thermal stability of plastic substrates, which makes these techniques slow [9], [29], [30]. In addition, the aforementioned limitation also leads to the massive energy consumption of these techniques, rendering them inefficient from the viewpoint of energy consumption [10], [31]. In recent times, photonic flash sintering has been reported as a promising alternative to conventional sintering techniques. The photonic flash sintering technique has been reported to rely on the localized heating of the ink through selective absorption of visible light, leading to high peak temperatures in a relatively shorter time span (compared to the conventional sintering techniques) and highly intense flashes. In other words, this technique is highly energy-efficient [32]–[34].

It is highly important to optimize the process parameters for deposition and post-deposition treatments for large-scale manufacturing of metallic nano-inks [6]. At present, this turns out to be a major scientific challenge [6]. The other challenge is to fine-tune the process parameters for the purpose of upscaling the experimental findings (in laboratory-scale) to bulk scale for industrial manufacturing in an economical way [18]. Moreover, among the metal-based conductive nano-inks, Ag-based conductive nano-inks are the most investigated and find widespread applications as antenna radio frequency identification (RFID) tags in electronic industries owing to their extraordinary electrical and mechanical properties [35]. The notion of synthesizing metal-based conductive nano-inks is based on utilizing the high surface area to volume ratio of nano-inks to control the flow characteristics, adhesion, and viscosity (of the ink) essential in determining the resolution of the printed part [35]. The efficiency of the nano-ink synthesis technique is primarily determined by the ability to produce nanoparticles (NPs) with uniform shape, size, and a high level of purity and the ability to capture radio frequency (RF) energy which is based on the density of the ink [35]. For instance, a non-appropriate synthesis technique may lead to high microstructural porosities and high resistance to electromagnetic energy in the cured component [35]. Hence, optimization of process parameters involved in nano-ink synthesis techniques is highly essential [35]. A systematic understanding of microstructural features in the fabricated NPs is necessary for optimizing the process parameters in the aforementioned techniques [35]. In the last ten years, there have been significant advancements in material characterization, which enable a systematic understanding of material properties, ranging from bulk to nanoscale [6], [35]. These characterization techniques may primarily be classified into two types: (i) Structural and (ii) Chemical characterization techniques [36].

Moreover, recent times have witnessed the emergence of a novel 'correlative' methodology of correlating the structural information with the chemical information from the same region in the microstructure, has also been developed and is being presently used to scientifically explore some previously unexplored features in a number of materials [18], [37]. However, the aforementioned methodology has not been used to investigate structure-property correlation in metal-based conductive nano-inks, primarily due to the complexity of sample preparation techniques. Therefore, the present chapter aims to provide an overview of the state-of-the-art research in synthesis and characterization techniques for metallic nano-inks through a few cutting-edge reports in this field. However, in view of the diverse nature of the field, the authors do not claim to address all the avenues of research in this field.

2. What are conductive inks?

Conventionally used conductive inks are composed of metallic flakes, mainly Ag or Cu, or carbon (C) flakes suspended in a particular matrix (also termed as retaining matrix) which is made of polymers [6], [23]. These polymers are also known as polymer thick films (PTFs) and are weakly conductive in terms of electrical conductivity) [6]. Removal of retaining matrix leads to curing in which metallic or C particles come in contact with each other, thereby rendering electrical conductivity to the ink [6]. In conductive inks, curing may be performed through several techniques (e.g., Ultra-Violet (UV) curing, heat curing, etc.) [20]. Typically, PTF inks have lower curing temperatures (~ 150 °C), which leads to a number of options for substrate selection and is particularly useful with flexible polymer films [1]. Water-based flexographic conductive inks typically undergo curing through evaporation of the solvent into the outer environment. Unsaturated polyester, acrylics, epoxy, and thiolene resins have been reported as potential matrices for UV curable inks [31], [38].

The difference between C- and metallic-based conductive inks is that C-based inks are generally less electrically conductive than metallic inks and thus provide a weaker signal in RFID applications [39]–[41]. However, C-based inks are more economical (from the viewpoint of production) and possess lower environmental toxicity as compared to metal-based inks [42], [43]. C-based inks typically find applications in electromagnetic interference (EMI)/RF shielding due to their lower electrical conductivity (compared to that of metallic inks). On the other hand, metallic inks are currently used in printed, electronic applications, including membrane switches and circuits, RFID tag antennas, etc. [6], [37]. At present, both metallic and organic conductive inks are designed to suit a particular substrate and printing process [19],

[44]. Recently, conductive inks have been developed for use in all forms of print methods (inkjet, screen, offset lithography, flexography, and gravure). However, at present, there is no report of metallic or C- based conductive inks fabricated using toner-based electrostatic printing [21].

2.1 Metallic inks

Metallic-based inks primarily find applications in membrane switches and circuits and RFID tag antennas owing to high electrical conductivity [35]. Moreover, in the context of metallic inks, curability can be performed at relatively low temperatures for short time periods (using a heated press) [6], [35]. Metal-based conductive inks are also being used to manufacture printed antennas for automotive applications at present [17]. For such applications, Ag particle-filled inks are initially printed on the thin-film substrate [18]. For the purpose of maintaining dimensional stability reasons, only pre-shrunk films are used for the aforementioned applications [37]. The films may be pretreated for the purpose of improving their adhesive properties. The drying parameters must be considered (in post-printed conditions) because an accurate thermal treatment is essential to enhance the conductivity and adhesion [6]. The overall performance of the antenna is largely dependent on its Ag content. Moreover, Ag content in RFID antenna has a huge influence on the price [6]. The other factors, such as particle geometry and the binder system, largely influenced the overall performance and cost of these antennae [6].

2.1.1   Metallic nano-inks: Synthesis

In recent times, research in conductive nano-inks mainly focuses on investigating electronic properties in nano-inks comprising of nano-sized metallic particles primarily due to a number of interesting electrical properties due to the high surface area to volume ratio of metallic NPs present in these nano inks [35]. Commercially available conductive inks typically comprise ~ 30–50 wt.% metal NPs (Au or Ag) (sizes ~ < 20 nm) suspended in a solvent [22]. After deposition, elimination of solvent leads to a high metal fraction (in the residue), rendering electrical conductivity to the ink. In addition, several applications also require the sintering of Ag particles (on the substrate) at elevated temperatures to obtain the desired electrical conductivity [20]. Through inkjet printing, metallic nano–inks can be used to form fine metal lines and features with high electrical conductivity [6], [18]. As the size of materials becomes < 100 nm, some properties, including electronic, magnetic, optic, catalytic, and thermodynamic properties of the materials, have been reported to be significantly different from those of relatively larger-sized materials [4], [10], [42], [45]. Metal NPs, in particular, exhibit unique properties owing to a large surface area to volume ratio due to a reduction in dimension (< 100

nm) [6]. More interestingly, the melting point (Tm) of materials has been reported to undergo a significant lowering due to the aforementioned size effect [6]. The low melting temperature of metal NPs, leads to a reduction in sintering temperatures and annealing temperatures (required to form low resistance conductive films), rendering metal NPs as potential candidates for use in printed electronics applications. Printable electronics manufactured using roll-to-roll (R2R) processes have been reported to offer a unique advantage in the mass production of inexpensive, flexible electronics [6]. Ag NPs, in particular, are considered to be the most suitable precursor candidates for printed conductors owing to a good balance of cost and performance [18]. On the other hand, Au NPs are desirable (for the synthesis of nano-inks) owing to good chemical stability and high work function [19]. Zhuo et al. [46] have reported a low-cost synthesis route of Ag-based nano-inks using chemical reduction technique. Results have shown that low room-temperature electrical resistivity (~ 3.9×10^{-7} Ω·m) and good electrical conductivity (~ 2.56×10^6 S/m) lead to the usage of these inks in printed electronics. Abou El-Nour et al. [47] have reported physical and chemical synthesis techniques to fabricate Ag-based nano-inks. In addition, the applications of Ag-based nano-inks have been summarised in Ref. [47]. On the other hand, Cu NPs are also quite attractive (for the fabrication of nano-inks) due to their lower costs than Ag and Au. Au NPs are generally fabricated (using liquid chemical methods) by the reduction of chloroauric acid ($HAuCl_4$) with a reducing agent (such as sodium boron hydride ($NaBH_4$)) [48]. The solution becomes supersaturated during liquid chemical methods during the formation of a neutral (or charge-free) Au atom [18]. Au gradually undergoes precipitation in the form of NPs [22]. To prevent further aggregation of Au NPs, stabilizing agents (mainly organic ligands) are added [49]. These lead to the formation of organic-inorganic hybrids with advanced functionalities [35]. These hybrid materials find widespread applications in electronics and (nano) biotechnology [50], [51]. The first report on the synthesis of ligand-stabilized Au NPs was from Schmid et al. [52], followed by the report on the preparation of monolayer-protected Au NPs by Brust et al. [53], [54]. Many organic compounds with reactive head groups, including thiol, sulphide, thiosulfate, etc. have been used to prevent self-agglomeration of different metal NPs, including Au, Ag, Cu, Pt, etc. [55]. The synthesis of metal NPs protected with various monolayers containing the different reactive head, and functional tail groups are of prime importance for the enhancement of chemical and biochemical applications of metallic NPs [25], [55], [56]. Owing to a combination of good electronic and optical properties of Cu NPs, there has been an increased amount of interest in the preparation of stable monolayer-protected Cu NPs [26], [57], [58]. Chu et al. [59] have

reported a hole connection process using pulsed light sintering with Cu micro/Ag nano-hybrid ink for applications in the field of printed electronics. Alkylamines, Alkyl xanthates, tetraalkyl ammonium complexes, and alkanethiol are some of the common ligands which have been reported to prevent self-agglomeration of Cu NPs [28]. However, there has been limited progress owing to the high instability of Cu NPs. Chen and Sommers [60] have used alkanethiolate to prevent the self-agglomeration of Cu NPs. The spherical Cu particle (prepared by Chen and Sommers [60]) bound hexanethiolate monolayers (nearly ~ 1–2 nm in diameter) have been reported to undergo oxidation of Cu core, morphological evolution, and irreversible aggregation process [60]. Long-chain alkanethiols have been reported to undergo self-agglomeration into compact monolayers (i.e., 3-D self-assembled monolayers) on metallic NPs leading to a significant reduction in electrical conductivity [60]. Bhat et al. [61] have fabricated and characterized steroid capped noble metal NPs (silver (Ag) and gold (Au)) through the method of reducing their precursors such as Au trichloride ($AuCl_3$) and Ag nitrate ($AgNO_3$) [61]. It has been demonstrated that metal NPs may be capped and stabilized by bile acid-derived thiols as effectively as long alkyl chain thiols [61]. The maximum particle sizes of Ag and Au NPs (reported by Bhat et al. [61]) are ~ 3 and 5 nm, respectively. Moreover, the capped NPs may be easily dispersed in a number of non-polar solvents in the presence of alcohol, with dispersions being stable for more than a year. Yang et al. [62] have reported a novel chemical process for the synthesis of hydrophobic Cu NPs with excellent anti-oxidation properties [62], [63]. Well-dispersed Cu NPs with good surface properties were obtained from the water/organic solution. In this process, oleic acid acts as a phase transfer agent and a particle protector leading to the coordination of carboxyl end groups on the newly generated surface of Cu particles with hydrophobic C tails (of oleic acids) pointed away from the surface of particles [62]. Moreover, this organic film has also been reported to prevent the self-agglomeration of newly formed Cu particles [62]. Foresti et al. [64] have synthesized copper 3-(6-mercaptohexyl)thiophene protected nanoparticles through the utilization of NaBH4/LiCl mixture using diglyme as the reducing reagent. Moreover, the study also revealed that the spherical shape of Cu T6SH NPs (~ 5–6 nm in diameter) does not undergo significant variations with time of storage [64]. Li et al. [65] have summarised the electrical resistivity of Cu-based nano-inks as a function of particle size, stabilizing agents, substrates, and sintering methods. Kanninen et al. [49] have studied the stability and oxidation of Cu NPs stabilized with different ligands. Cu NPs (capped with Lauric acid) were synthesized using a modified Brust–Schiffrin method [66]. Subsequently, ligand exchange with excessive amounts of different capping agents was performed [6]. Alkanethiols and oleic acid were observed to improve oxidation

resistance [6], [49]. The oxidation resistance of thiol-capped Cu NPs was found to increase with the increasing length of thiol chain [48], [49]. After oxidation, dissolution of ligand exchanged particles (due to excess ligand) was observed [49]. Moreover, Oleic acid was reported to be a better protective agent for Cu NPs (against oxidation) in comparison to the tested thiols (with ligand to copper ratio of 20:1). Murai et al. [67] have proposed a different approach for the purpose of capping Cu NPs with organic long-chain acids through evaporation of Cu wire in an oleic acid vapor/mist. The coating layer thickness was the order of a few nanometres powder diameter of nearly 25 nm [68]. The coating was reported to the growth of Cu NPs. Moreover, Cu NPs were found to be passivated [68].

Luechinger et al. [69] have fabricated Cu NPs coated with protective graphene shells using a bottom-up approach to synthesize a chemically inert metal nanopowder. They have used an amphiphilic surfactant and successfully printed it onto a polymer substrate through conventional inkjet printing [69]. The printed patterns (after drying) were reported to exhibit strong metallic luster and good electrical conductivity (>1 S/cm) without undergoing sintering or densification [69]. This electrical conductivity was reported to limit the use of printed patterns in low current applications. The high air stability of graphene-coated Cu NPs renders them as alternatives to Ag or Au nanocolloids [69]. Woo et al. [70] have reported the development of highly conductive tracks on a flexible substrate through low-temperature annealing of Cu/Ag-based mixed metal conductive ink [70]. Moreover, the addition of small Ag particles was reported to significantly improve the packing density by filling the interstices present between the large Cu particles, leading to an improvement in electrical conductivity compared to that of pure Cu film [70]. Besides, the particle size and volume ratio of Ag particles must be optimized for achieving maximum packing density [70].

In the context of Ag nano-inks, the fabricated printing inks must exhibit low curing temperatures [6]. In addition, the printing metal inks must not only exhibit good electrical conductivity but should also show good adhesion on the surface of the bulk substrate [18]. To achieve the desired ink properties, the main actors are the medium carrier, dispersing agent, and adhesion promoter (for fabrication of Ag ink) [6]. The printing metal track on polymer substrates may be produced using two different methodologies [19]. The first method is based on mixing metal nanoparticles (NPs) with a medium carrier for ink fabrication with diameters < 5 nm, leading to a significant reduction of the melting temperature (as compared to the bulk) [49]. This has been attributed to the reduced surface area to volume ratio, leading to the high surface energy of metal NPs [71]. The second method involves using Ag ion agent solution

with a low temperature-activated reduction agent, which leads to the conversion of the ionic solution into a metallic track [71]. Dearden et al. [28] have demonstrated the synthesis of printable Ag ink using Ag carboxylate by its dissolution into a non-polar organic solvent (for example, xylene), leading to an ionic solution. The chemical reduction process has been reported to form final organic Ag inks, which can be utilized for many printing methodologies [28]. The electrical resistivity of the printed Ag track has been reported to achieve two to three times the theoretically calculated electrical resistivity of Ag for high curing temperatures [28]. However, after fabrication, the metallic track may not be suitable for nano-chip-based applications due to the high porosity of the bulk structure. Liu et al. [58] have reported the dissolution of AgNO3 in a mixture of water and dimethyl sulfoxide (as a precursor) for the process of metallization. The electrical resistivity of Ag tracks has been observed to be higher (by order of magnitude) as compared to bulk Ag [58]. Moreover, the electrical resistivity of Ag tracks has been reported to be influenced by the amount of microstructural porosities and the amount of chemical additive residue retained within the printed bulk tracks [58]. Moreover, metallo-organic decomposition (MOD) Ag inks have been used for inkjet printing purposes by Perelaer et al. [22], [72]. The formation of the Ag printing track has been reported to be purely based on the chemical reduction process. MOD inks have been reported to resistant to agglomeration or clogging. However, the electrical resistivity observed by Perelaer et al. [22], [72] was nearly 89 times higher as compared to that of commercially pure Ag. Low-temperature sintered Ag inks with excellent electrical conductivity were fabricated by Walker and Lewis [4] using the modified Tollens process. The Ag inks fabricated using the modified Tollens method have been reported to offer many advantages compared to the other reported methodologies [4]. First, the inks synthesized using the above method possess low viscosities and are compatible with many printing techniques [4]. Second, only a low curing or sintering temperature is required for Ag ink fabrication using the chemical reduction technique [4]. Moreover, it is possible to stabilize the condition of the inks for about a month without particle precipitation due to room temperature storage [4]. As reported in Ref. [2], the electrical conductivity of printed Ag tracks (sintered at 90 °C) is comparable to that of bulk Ag. The formulation of the modified Tollens process to produce Ag inks is described by the following formula:

$$NH_4OH/H_2O + AgC_2H_3O_2 + CH_2O_2 = [Ag(NH3)_2]^+ [C_2H_3O_2]^- = Ag \qquad (1)$$

Curtis et al. have synthesized Ag printing inks through inkjet printing of hybrid NP- metal-organic inks. The fabricated Ag inks were reported to be suitable for several direct writing techniques, including spraying, inkjet printing, etc. In addition, a highly pure and dense Ag track was printed with (hexafluoroacetylacetonato)Ag(I)(1,5-cyclooctadiene) (Ag(hfa) COD) metal-organic precursors on heated substrates which include glass, kapton tape, and commercially pure Si. Besides, good adherence to the printed Ag track was observed without the application of an adhesion promoter [4]. Ginley [73] has fabricated self-reducing Ag inks by selecting an Ag organic precursor mixture with a reducing agent and subsequent dissolution of the mixture in the organic solvent [73]. The resulting mixture has been reported to be stable in the liquid phase (at room temperature), without any reduction process [73]. Fig. 1 shows a schematic of metallic particles used for NP synthesis for conductive nano-inks.
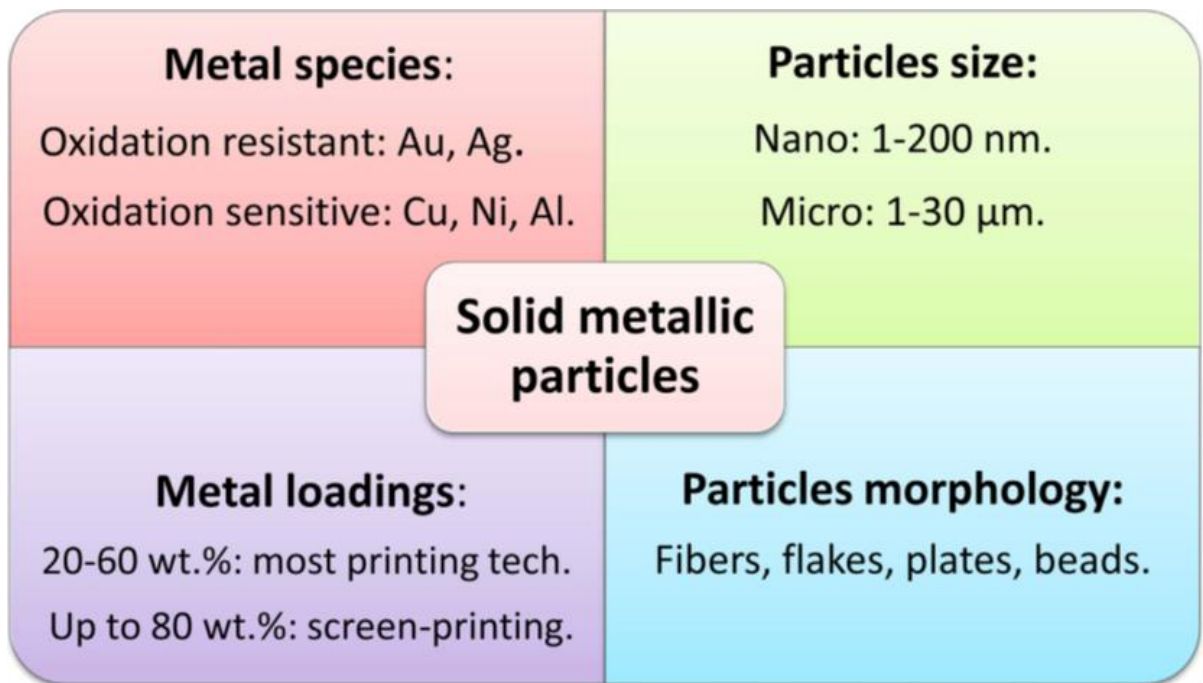

Metal species:

Oxidation resistant: Au, Ag.

Oxidation sensitive: Cu, Ni, Al.

Particles size:

Nano: 1-200 nm.

Micro: 1-30 μm.

Solid metallic particles

Metal loadings:

20-60 wt.%: most printing tech.

Up to 80 wt.%: screen-printing.

Particles morphology:

Fibers, flakes, plates, beads.

Fig. 1 Representation of metallic particles used for NP synthesis in the context of conductive nano-inks [74].

As described by Chou et al. [24], thermal sintering of Ag nano-inks using a heated oven with Nitrogen (N_2) gas flow has been reported as the most common method for curing Ag ink. N_2 gas is employed due to its inert nature and prevents oxidation of printed metal tracks [75]. Multiple-step sintering with a specific temperature step profile has also been reported to ensure effective curing [75]. This process is important to ensure that all the amount of solvent carrier, dispersing agent, and adhesion promoter with different evaporation temperatures is fully removed (through evaporation) from the printed bulk layer (before the process of metallization

between Ag NPs) [75]. Insufficient removal of the solvent leads to the formation of solvent residues in the printed metal track, which subsequently forms network formation between the NPs and degrades the electrical conductivity [75]. Yamasaki et al. [76] have applied a laser sintering method to cure printing Ag metal tracks. In the study (of Yamasaki et al. [76]), a continuous wave Nd: YAG laser with a wavelength of 1064 nm and power output used 150 W in the Ar gas environment to print the Ag layer. The irradiation of the laser beam on the Ag NPs leads to metallization. It enhances the occurrence of inter-diffusion between the printed Ag film and the interface between the film and bulk substrate, leading to high adhesive strength nano-ink [76].

Xie et al. [48] have introduced an electrical pulse sintering method for curing and melting metallic nanopowder ink in order to form an electrically conductive path. The advantage of this technique is that it provides localized heating of the nanometallic track leading to a rapid heating effect in milliseconds without the non-printed region getting heated up [48]. This technique has been reported to cure Ag, Cu, and Al NPs [48]. Radivojevic et al. [23] have reported the effectiveness of UV light for curing printing Ag metal tracks. In this technique, damage underneath the bulk substrate may be avoided by knowing the range of energy absorption of the material (for analysis) beforehand [23]. For instance, the maximum energy absorption range for Ag lies within the wavelength range of 400-425 nm [23]. Moreover, a substrate (bulk) with a different range of energy absorption may be used to prevent the collective heating up of materials during the sintering, lowering the risk of bulk substrate damage [23]. Perelaer et al. [22] have applied the microwave sintering method for printing Ag tracks on a polyimide substrate. The efficiency of this method has been reported to depend on the relative orientation between the plane of the microwave incidence source and the printed Ag track [22]. The penetration depth of microwave irradiation on bulk Ag has been reported to lie within the range of 1.3 μm, limiting this technique's usefulness on a relatively thick Ag printing layer [22]. In the context of photonic sintering, the basic principle is based on using the phenomenon of absorption of the photonic source (from an emission source such as Xe lamp source) to heat the printing Ag inks [22], [44]. **Fig. 2** shows Cu-based nano-ink ((composition: 20% Cu in a mixed solvent of ethylene glycol and 2-methoxyethanol, Poly-vinyl Propylene (PVP) as a stabilizer) at different sintering temperatures on a glass substrate followed by sintering for 1h in a vacuum. Reinhold et al. [23] have recently explored Ar plasma sintering for curing Ag metal tracks. Pre-heating of the printing substrate has been reported to be essential for ensuring the evaporation of the solvent from the printing metallic inks [44]. Plasma post-treatment was only performed to remove subsequent solvent residue and the

formation of networking Ag cluster [44]. **Fig. 3** shows a general flowchart of metal NPs synthesis and their applications as conductive nano-inks.
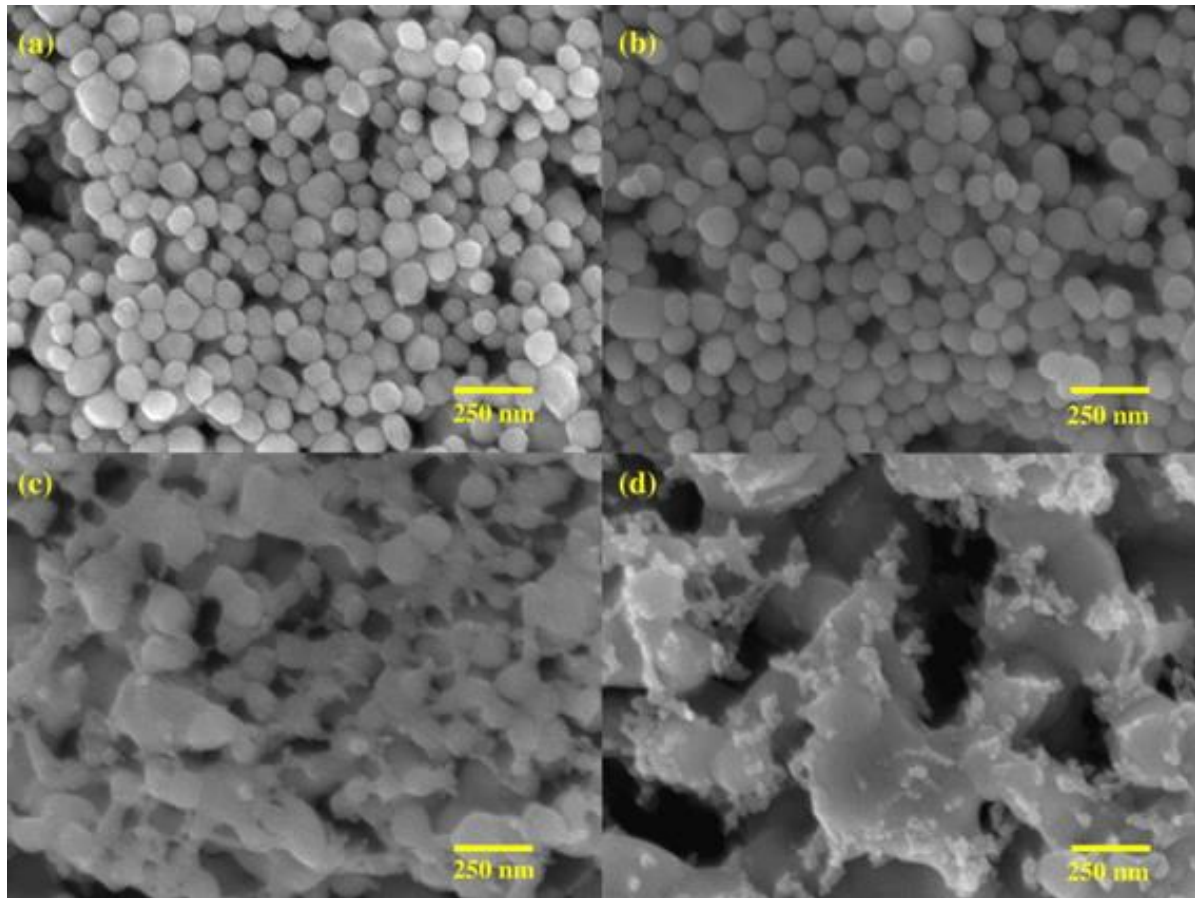

Fig. 2 SEM micrograph of 2D conductive structures at different sintering temperatures: Structures obtained by printing Cu nano-ink on a glass substrate and vacuum sintered for 1h [77].
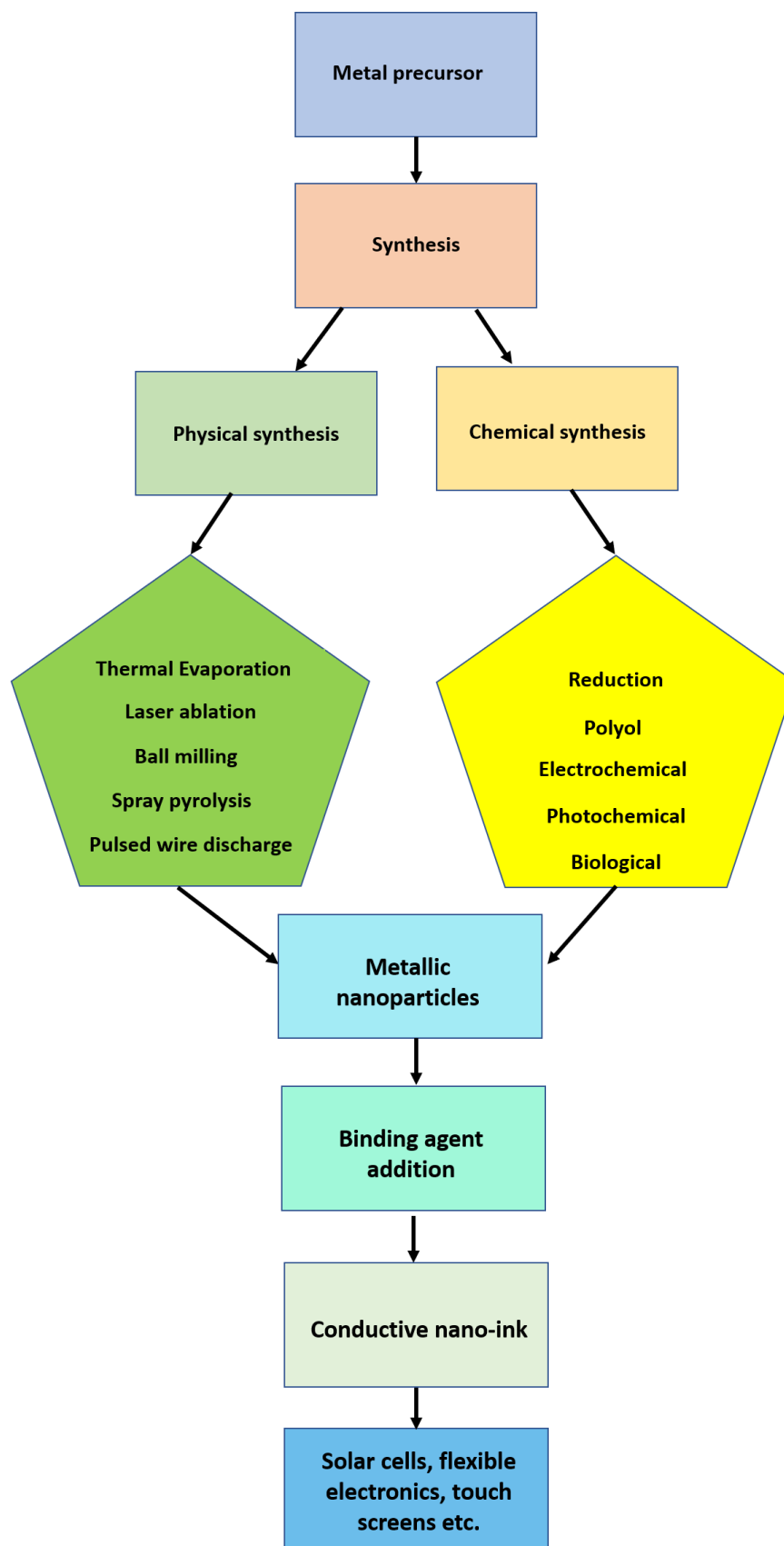
Fig. 3 Flowchart representing the synthesis of metallic nanoparticles (in general) and their application as inks.

2.1.2 Metallic nano-inks: Stabilisation

The stability of the fabricated metallic NPs is one of the most important properties of the metallic nano-ink. Aggregation followed by agglomeration and sedimentation occurs spontaneously due to the higher energy state of the metallic NPs compared to bulk metal. All the three aforementioned processes must be prevented from using additives to obtain stable dispersions. Selecting an appropriate stabilizer and composition of the NP are of prime importance since these components hugely influence the shelf-life and the overall performance of the ink [78]. According to the DLVO theory, the stability of a colloidal solution is determined by the balance between electrical repulsive and attraction energies. Electrical repulsion energy is a function of the surface electrical potential of the interacting particles, the medium permittivity, and the Debye–Huckel (D-H) parameter [79]. D-H parameter determines the thickness of the electrical double layer. The attractive energy (or van der Waals energy) is inversely proportional to (i) the distance between interacting particles, (ii) the Hamaker constant, and (iii) the particle diameter [80], [81]. In aqueous dispersions, the necessary condition for obtaining stable (or metastable) dispersions is the value of electrical potential [82], [83]. In other words, the higher the electrical potential, the stronger the electrostatic repulsion between the interacting particles. Strong electrostatic repulsion indicates high stability of the stable colloidal system [84]. The surface electrical potential of a particle is measured using zeta potential (ζ). ζ is defined as the potential at the boundary between the moving particle and the liquid. The dispersions of colloidal particle dispersions have been reported to be stable at zeta potentials > ~35–40 mV [85], [86]. Metallic NPs are usually stabilized (electrostatically) using adsorbed ionic surfactants. Typical examples are the cationic surfactant (cetyltrimethylammonium bromide) (CTAB) [85–87] and the anionic surfactants, such as sodium oleate [87], (sodium bis(2-ethylhexyl)sulfosuccinate) (AOT) [88] and (sodium dodecyl sulfate) (SDS) [87], [88].

Collision and flocculation of particles (with high electrolyte concentration) are common events due to a decrease in the electrical double layer thickness with increasing thickness. Dispersions with the high metal load required for the formulation of conductive ink contain a high concentration of the metallic ions during synthesis (of nano-ink), leading to the aggregation of the metallic NPs [85], [86]. In order to overcome the aforementioned disadvantage of electrostatic stabilization, steric stabilization of metal NPs is achieved by surrounding the particles with a sterically bulk molecule layer (e.g., molecules of a surfactant or a nonionic polymer) is commonly used [87]. The most effective steric stabilizers capable of interacting with both metallic NPs and dispersion medium are suitable for both aqueous and organic media

are nonionic amphiphilic polymers [84]. Among them, poly(N-vinyl-2-pyrrolidone) (PVP) of various molecular weights is the most frequently used for stabilizing metal NPs, such as Ag and Cu, in various liquids and the formulation of nano-inks [80]–[83]. Other nonionic polymers, which have been reported to stabilise metallic NPs such as Ag and Cu, are poly(oxyethylene)-poly(oxypropylene) copolymer (Pluronic F127) and poly(vinyl alcohol) (PVA) [78], [79], [84]. Table. 1 summarises the particle size, stabilizing agent, substrate, sintering technique, and electrical resistivity of Cu inks.

Table. 1 Particle size, stabilizing agents, substrates, sintering methods, and electrical resistivity of Cu inks (Abbreviations: DPM: Dipropylene glycol monomethyl ether; AMP: 2-amino-2-methyl-1-propanol; DEA-1, 2-PD: 3-diethylamino-1,2-propanediol; EG: Ethylene glycol; IPL : intense pulsed light.) [65]

Materials	Size (nm)	Stabilizing agent	Substrate	Sintering method	Electrical Resistivity ($\mu\Omega\cdot cm$)	Reference
Cu	40-50	PVP	Glass	325 °C, vacuum	17.2	[89]
Cu	35-60	PVP	PI	275 °C, vacuum	92.0	[90]
Cu	30-65	PVP	PI	200 °C, formic acid	3.6	[91]
Cu	5	NA	Glass/PI	IPL	5.0	[91]
Cu	5	NA	PI	250 °C, formic acid	NA	[92]
Cu	7	Oleic acid	BT	200 °C, formic acid	4.0	[93]
Cu	20	NA	Glass	200 °C, H_2	20.0	[94]
Cu	40	Oleic acid	PI	250 °C, vacuum	11.0	[95]
Cu	40.4	PVP	Alumina	300 °C, 5 MPa, air	86.0	[96]
Cu	30	PVP	PI	IPL	5.0	[97]
Cu	30	PVP	PI	Multi IPL	173.0	[98]
Cu	65	PVP	Glass	250 °C, formic acid	2.3	[99]
Cu	20-50	PVP	PI	IPL	NA	[100]
Cu	10	Lactic acid	Glass	200 °C, N_2	9.1	[101]

Cu	50-70	NA	PI	Laser-808 nm	NA	[102]
Cu	42/108	Oleic acid	Glass	200 °C, H_2	4.0	[103]
Cu	25	PVP	PI	Plasma	21.1	[104]
Cu	15-25	PVP	Paper	160 °C, Ar	13.4	[105]
Cu	100-120	NA	Glass	Laser-522 nm in air	5.3	[106]
Cu	135	PEG-2000	PI	250 °C, N_2	15.8	[107]
Cu	-	PVP	PET	Hydrogen plasma	15.9	[105]
Cu	3.5	1-amino-2-propanol	PI	150 °C, N_2	30.0	[104]
Cu	45	NA	PI	Laser/IPL	8.9	[108]
Cu	100	Oleic acid	PET	IPL	51.2	[107]
Cu	130	Gelatin	Glass	200 °C, 3% H_2	8.2	[103]
Cu	<100	PVP	PI	IPL	7.0	[104]
Cu	50	PVP	Glass/PEN	Laser-532 in air	NA	[101]
Cu	30	PVP	Glass	260 °C, 5% H_2	6.1	[100]
Cu	≤110	Oleic acid	PET	Laser-1064 nm in air	86.0	[109]
Cu	Micron	Ascorbic acid	PET	Chemical sintering	774.0	[99]
Cu	61.7	Trisodium citrate	Glass	200 °C, H_2	7.6	[99]
Cu	3.6/64.6	L-ascorbic acid	PET	IPL	96.0	[98]
Cu	10	Poly (VI-co-VTS)	Glass	Sinter-free	1200.0	[110]
Cu	150	PVP	PET	IPL	44.0	[109]
Cu	NA	NA	Glass/PET	150 °C, formic acid	6.9	[107]
Cu	5	Isopropylamine	Glass	250 °C, H_2	4.4	[104]
Cu	100-120	PGME	Glass	Laser-532 nm and 350 °C, N_2	1.8	[106]
Cu-G CS	45	NA	Polymer	120 °C, air	NA	[104]

Cu-Ag CS	42	PAAS	Glass	250 °C, N_2	32.0	[106]
Cu-Ag CS	13.5	Oleylamine	Glass	350 °C, N_2	12.0	[108]
Cu-Ag CS	13.5	TMAH	Glass	350 °C	13.7	[104]
Cu-Ni CS	56/147	Oleylamine	PI	IPL	-	[107]
Cu-Cu10Sn3 CS	20-60	Oleic acid	PET	IPL	16.0	[101]
Cu/Ag H	63/21	PVP	PES	175 °C, vacuum	38.6	[100]
Cu/Ni H	10-80	-	Glass	200 °C, H_2	599.0	[99]
Cu/Ag H	NA	PVP	PI	IPL	4.1	[109]

2.1.3 Metallic nano-inks: Characterisation

In the context of characterization of metallic nano-inks, the work done till date has primarily focussed on Ag nano-inks owing to the best combination of electronic properties (especially electrical conductivity), oxidation resistance, and cost as compared to the other metallic nano-inks (Ag and Cu nano-inks) [6]. The inks containing metallic NPs (sizes < 100 nm) have been reported to exhibit a significant reduction in melting temperatures [35], [111]. The melting temperature of Ag (nearly 1064 °C) can be reduced drastically below 300 °C when the size of the particles becomes less than 50 nm. Lai et al. [35] and Allen et al. [112] have reported the reduction in melting points of other metals, including Sn, Bi, and Pb in nano-regime (< 100 nm). The reduction of melting point in NP may be explained on the basis of reduction in cohesive energy per atom within the NPs [112]. For instance, the atoms present on the surface of NPs with spherical curvature exhibit smaller cohesive bonding energy with neighboring atoms compared to the atoms in bulk solid, leading to a significant reduction in melting temperatures of NPs [35]. The average cohesive bonding energy per atom (E) within NPs may be calculated according to the following relation: [35]

$$E = E_b(1 - \frac{d}{D}) \tag{2}$$

where D is the size of NP, d is the atomic radius, and Eb is the cohesive energy per atom of bulk-sized particle. Based on Lindemann's theory [50], [51], the cohesive energy of a surface atom within NPs is directly proportional to the melting temperature (of the material). The atoms on the surface of spherical NPs have lesser bonds (as compared to that for bulk-sized particles), which reduces the amount of energy required to free a surface atom from the solid-state [113]–[115]. Moreover, the theoretical size is dependent on the melting point of the material, which

can be determined using the following relation: [6], [18], [24], [113], [116]. $T_M(d) = T_{MB}(1 - \frac{4\sigma_{sl}}{H_f \rho_s d})$ **(3)**

where TMB is the melting temperature of bulk-sized particles, σ_{sl} is the solid-liquid interfacial energy, ρ_s is the density of the material, d is the diameter of the particle, and Hf is the heat of fusion (of bulk-sized particles) [6]. Applying the UV-vis spectroscopy technique has been reported as an alternative for the characterization of Ag NPs [6].

As reported by Elpidio et al. [22], Ag NPs formed using albumin as the reducing agent was characterized by stable Plasmon absorption spectra after nearly six months of storage. The surface plasmon resonance peak for Ag was found to be nearly 420 nm, the position of which remained unaltered even after re-measurement for various storage times. The printing Ag inks mostly contain solvents as a medium carrier, dispersing agent, and promoter (adhesion). An investigation performed by Perelaer et al. [72] has reported the utilization of non-polar solvents with a long alkyl chain and a polar head (such as amines, thiols, mercapto, carboxylic acids, or amide groups) for the stabilization of Ag NPs in the inks for relatively long periods of storage. Moreover, it was observed that the organic solvents exhibited a low bonding strength on the surface of Ag NPs and could be easily removed at low curing temperatures [117]. Greer and Street [117] have reported that increasing the curing temperature leads to grain boundary (GB) diffusion leading to the formation of microstructural pores that degrade electrical conductivity and overall mechanical strength compared to that of bulk-sized Ag. To this end, the characterization of Ag inks is highly important to ensure a suitable curing temperature and appropriate sintering techniques [117]. Such characterization has been reported using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis techniques [35]. Fig. 6 shows a TGA plot representing the variation of mass.% and resistance as a function of temperature. DSC is a useful technique for the detection of phase transformations in materials. In the context of Ag nano-inks, temperature profile plotting (using DSC) aids in understanding the ink properties, such as the amount of additives or solvent required for the fabrication of Ag inks [35], [118]. The evaporation of the solvent or additives requires kinetic energy for the transition from liquid to the gaseous phase. Boiling points of additives are dependent on their composition. In addition to TGA and DSC, structural characterization of NPs has been reported using different techniques such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) for phase identification, determination of particle sizes, and the morphology of NPs [49]. For instance, Kanninen et al. [67] have performed UV-vis spectroscopy, XRD, and TEM analysis

to investigate the oxidation resistance of Cu NPs stabilized with a number of different ligands and reported that alkanethiols and oleic acids improve air stability of Cu NPs. Murai et al. [67] have performed XRD and TEM analysis of Cu NPs with long organic chains synthesized by the evaporation of Cu wire in an oleic acid mist/vapor and reported that Cu NPs developed using this approach have high oxidation resistance. Moreover, Foresti et al. [64] have performed TEM investigations on Cu T6SH NPs (after different storage periods) and reported that Cu T6SH NPs show excellent resistance to self-agglomeration even after a storage period nearly six months. **Fig. 4** shows a TEM-Bright field (BF) and High-resolution TEM (HRTEM) images of Cu-based nano-ink (at pH=11) in the presence of ethylene glycol by the reaction of Cu(NO3)2 with varying concentrations of NaBH4 [119].

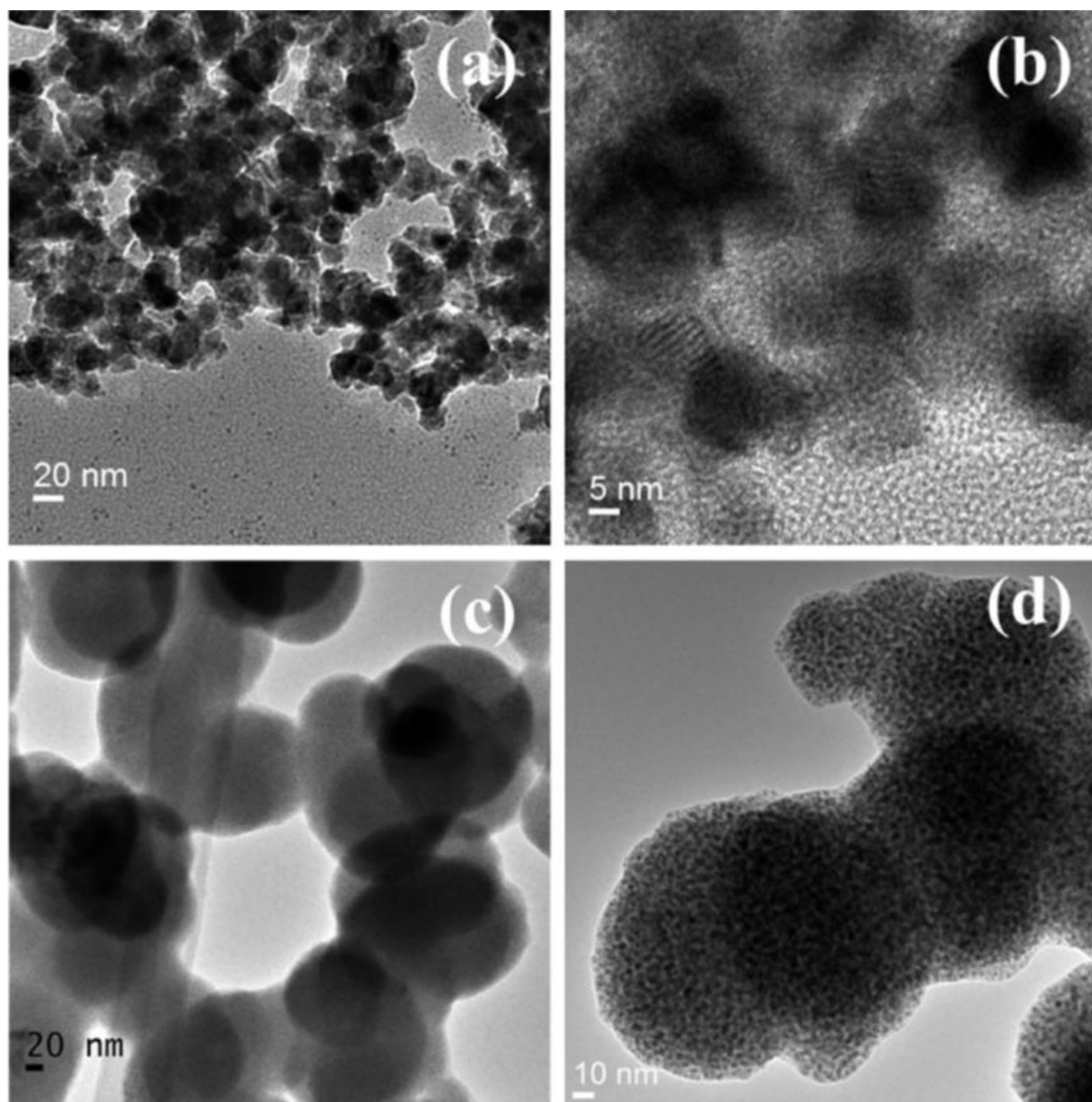**Fig. 4** Cu-based nano-ink synthesized at pH = 11 in presence of ethylene glycol Cu(NO$_3$)$_2$ with 0.05 M NaBH$_4$: **(a)** TEM-BF image, and **(b)** HRTEM image and 0.6 M NaBH4 **(c)** TEM-BF image and **(d)** HRTEM image [119].

3.   Challenges and future perspectives: From the viewpoint of industrial research

Currently, most of the commercially available metallic inks are Ag-based owing to a unique combination of low-cost and excellent electrical conductivity properties along with high oxidation resistance (as discussed previously in Section 2.1.3) [35]. Although, at present, there have been a number of attempts towards developing less expensive materials (including Cu and Al) for the replacement of Ag for the production of metallic inks [35]. However, the occurrence of oxidation (at room temperature) has been the major limitation in such attempts. In order to prevent room temperature oxidation (of Cu and Al inks), synthesis of a suitable solvent or reduction agent is required to decelerate the oxidation of Cu and Al inks [71], [72]. On the other hand, although Au has excellent room-temperature oxidation resistance, however, the primary limitation associated with the large-scale industrial manufacturing of Au in metallic printing technology is the tremendously high production cost (as compared to that of Ag) [50].

With regards to the present Ag nano-ink printing technology, there are a few major concerns that need to be systematically investigated for obtaining good printing metal tracks [51]. The selection of a suitable sintering method for curing printing tracks is one of the most important factors for obtaining good printing metal tracks [35]. An unsuitable sintering method may lead to a high electrical resistance and microstructural porosities after the curing process leading to a massive degradation in the electrical performance of nano-inks [72]. Moreover, for obtaining good conductive printed metallic tracks, a temperature-sensitive substrate should be applied using the lowest sintering temperature [71]. This also depends on the properties of inks. On the other hand, the organic additives, including the solvent, dispersing agent, and adhesion promoter, also determine the curing temperature of the printed metallic track [24]. The additives need to possess low evaporation temperatures to protect the temperature-sensitive substrates, such as paper, epoxy, fiberglass, etc. In addition, as described by Greer and Street [117], the formation of the networks between the Ag NPs at a low sintering temperature leads to GB diffusion leading to degradation in electrical conductivity and formation of microstructural porosities. In order to achieve bulk diffusion, a higher sintering temperature and lower sintering energy (as compared to that of GB diffusion) is required [35]. Bulk diffusion is highly important for application on a temperature-sensitive substrate since it does not degrade electrical conductivity, unlike GB diffusion [35]. However, the major limitation of

increasing sintering temperature is the formation of a porous microstructure leading to the high resistance of the metallic track [72]. Improvement of adhesion (of the printed Ag metal tracks) on various substrates is another major challenge that remains unaddressed. In this context, the selection of the adhesion promoter (applied to the ink) is highly dependent on the nature of the printing substrate [35]. For instance, selecting an unsuitable adhesion promoter (on the Ag ink) may degrade the electrical and mechanical properties of the printed tracks in addition to improving the adhesion [24]. Hence, proper selection of adhesion promoters ensures that chemical or ionic bonding may be formed between the cured Ag tracks and the surface of the printing substrate. At present, a number of adhesion promoters are commercially available, which include metal, organic, and polymer adhesion promoters [20], [35]. Understanding the physical and chemical properties of adhesion promoters is highly essential before their commercialization in the printed electronics industry [50]. For the commercially available Ag nano-inks (at present), there is a considerable volume of microstructural porosities, regardless of the ink synthesis technique [21], [23], [44], [76]. In other words, porosity turns out to be the main limiting factor for printed Ag tracks, disabling them to achieve electrical conductivities comparable with that bulk Ag [6]. The application of high sintering temperatures has been reported to be capable of eliminating microstructural porosities; however, this method may not be applicable on temperature-sensitive substrates [35]. This necessitates the development of novel Ag ink concepts applicable to heat-sensitive substrates and leads to minimum microstructural porosities [35]. This is a currently unaddressed avenue with a considerable amount of potential for future research.

Presently, Additive manufacturing (AM) technology offers the capability to construct 3D structures for a large number of materials [121], [122]. During continuous 3D solids, the parameters to be optimized primarily include (i) ink composition optimization, (ii) its rheological behavior, and fabrication parameters (during printing) [55], [123], [124]. In this regard, 3D inkjet printing has been reported as an alternative to photolithography, etching, and filament-based direct writing techniques. Two main types of conductive inkjet inks for printing 3D structures have been studied: metal NPs dispersed in (i) volatile solvents and (ii) UV-curable liquids [125].

During the first approach, metal pillars, helices, wires, etc., are initially deposited on heated glass, Si wafer, or polymer substrates using additive printing of Au NPs dispersed in organic solvents [125], [126]. The solvent immediately evaporates upon contact with the ink droplets with the heated substrate. This subsequently increases the metal load and the ink viscosity,

leading to the fixation of each drop with droplet volume shrinkage [127]. Thermal sintering (at 150 °C) of the fabricated structure (bridge-shaped interconnectors) has been reported to possess electrical resistivity ~1.5 times higher as compared to that of bulk Au [123]. Similarly, the electrical resistivity of Ag bridges was reported to be ~19 times as compared to that of bulk Ag [121]. UV-curable ink oligomers (e.g., acrylate derivatives) and photoinitiators can rapidly polymerize upon UV exposure. This enables immediate fixation of each printed droplet or layer and the formation of a 3D structure through layer-by-layer printing on the same spot [78], [122].

A combination of UV-curable composition with conductive NPs offers the advantage of synthesizing conductive 3D components [123], [125]. For instance, electrical resistors have been reported to be printed using UV-curable inks based on a poly(ethylene glycol) diacrylate (PEGDA) matrix and a dispersion of aqueous Ag NPs (~10–50 wt.%) [122]. For resistors, the presence of a large amount of oligomers (insulating material) is not very significant. In order to enhance the electrical conductivity of these materials, a two-phase oil-in-water-type emulsion ink has been recently reported, in which the oil phase (comprising of polymerized acrylate monomers and initiators) provides the 3D structuring. In contrast, the water phase (composed of Ag NP dispersions) provides the electrical conductivity [121]. The electrical conductivity of the resulting ink after layer-by-layer inkjet printing and subsequent room temperature chemical sintering with NaCl solution has been reported to be ~3% of that for bulk Ag [124]. The other recently proposed approach for fabricating 3D nano-inks is by the use of UV polymerizable oil-in-water emulsion by digital laser processing (DLP) method based on selective polymerization of individual pixels inside a thin layer [121]. This is followed by the evaporation of the aqueous phase post-polymerization, yielding a porous 3D component [121]. This is subsequently followed by the immersion of the fabricated component in Ag NP-based dispersion and penetration of the resulting dispersion into the pores (using vacuum). Finally, exposure of the 3D component to HCl vapor leads to chemical sintering [121].

4. Challenges and future perspectives: From the viewpoint of academic research

A nanostructured material (owing to its high surface area to volume ratio) has a significant fraction of GBs present in the microstructure [17]. The major challenges faced by the commercially available Ag-based nano-inks (at present) are the presence of microstructural porosities irrespective of the synthesis technique (as discussed in section 3), limiting the electrical conductivity consequently limiting the overall electrical performance of these inks. Besides, the paradox between electrical conductivity and microstructural porosities is largely determined by the mechanism of diffusion. For instance, although both GB and bulk diffusion

lead to microstructural porosities, bulk diffusion (at relatively higher sintering temperatures compared to that of GB diffusion) does not degrade electrical conductivity to the extent of GB diffusion [35]. In material science, porosities are 3-D (volume) defects, whereas GBs are 2-D (planar) defects. At present, there is limited information on the influence of microstructural porosities on the electrical conductivity of metallic inks (including nano-inks) and the influence of diffusion on the formation of microstructural pores [72]. In order to address these issues, the first step is to understand the influence of different types of defects on the electronic properties (especially electrical conductivities) of these materials, primarily due to lack of experimental evidence on the direct visualization of these microstructural defects in these materials [71]. In the context of metallic nano-inks, an additional defect needs to be considered for completely understanding electrical conductivity, viz. dislocations which are 1-D (line) defects. In addition, the dislocation-GB interaction in polycrystalline metallic materials largely influences the electrical conductivities of these materials. For instance, apart from acting as dislocation obstacles, GBs act as electron scattering centers, affecting electrical conductivities in nanostructured materials [12], [128]. The structure of a GB (comprising of a misorientation angle and GB plane) largely influences the electron scattering phenomenon and the nature of dislocation interactions with the GB [128]. Jose and Khadar [129] have proposed that GBs themselves contain a number of defects, including vacancies, dangling bonds, which can play an important role in the electron transport properties of nanostructured materials.

One of the avenues that remains unaddressed is the atomic arrangement at different interfaces (including GBs) in Ag nano-inks. Segregation at different interfaces (including GB segregation) may lead to a change in the interfacial energy and subsequently, alter the nature of interfacial interactions with dislocations and electron scattering tendency at different interfaces. In recent times, the evolution of a number of defect characterization techniques, including Electron Backscatter Diffraction (EBSD) (both 2-D and 3-D) for orientation imaging and Electron Channeling Contrast Imaging (ECCI), has paved the way for many different research avenues in the field of nano-inks. For instance, the nature of a GB coupled with the arrangement of dislocations (near an interface) may be investigated through a crystallographic orientation-based investigation (using EBSD on either side of an interface) coupled with direct visualization of defects (such as dislocations near different interfaces) using ECCI technique may provide useful information on the influence of GB structure on the arrangement of pile-up dislocations near the GB. Coupling the aforementioned characterization techniques with in-situ sintering studies may be able to address the mechanism of diffusion on the defect

interactions and formation of microstructural voids. However, such equipment is highly challenging to build.

On the other hand, positron annihilation spectroscopy may be used to determine the distribution of vacancies in nano-inks since the mobility of vacancies is largely affected by the mechanism of diffusion (during sintering). In addition, at present, there exists no experimental technique for direct visualization of electrons undergoing scattering from GB. For most electron interaction studies with GB, Mayadas-Shatzkes (MS) model [128] for electron scattering is used. However, the MS model is based on electron scattering from columnar GBs. However, the aforementioned model does not consider the GB structure for the electron scattering phenomenon. The reason as to why the present chapter intends to address the unaddressed avenues in the field of nano-inks is that there exist neither any experimental evidence nor any theoretical calculations to account for the change of GB structure during diffusion and its associated influence on the electron scattering tendency and that of dislocation interaction with GBs in the context of nano-inks.

In the context of interfacial segregation, Atom Probe Tomography (APT) technique serves as an extremely powerful tool for determining the exact chemical composition within individual grains and at different interfaces (such as GBs) [36], [130]. This is particularly helpful in understanding the change in localized composition near GB during GB diffusion and compositional variation within individual grains during bulk diffusion. Moreover, the influence of interface composition on Ag NPs and substrate (in nano-inks) has not been reported to date. Therefore, the determination of local composition at substrate/NP interface may be highly useful in understanding the influence of local composition at substrate/NP interface on the adhesive properties of printed metal track. Moreover, in recent times, the evolution of correlative methodology of defect characterization involving the correlation of different structural characterization techniques with chemical characterization techniques has been extensively used to address structure-property correlation in metallic materials. However, such a methodology has not been used to address the aforementioned correlation in nano-inks. This offers enormous potentials for future investigations. Moreover, the emergence of Artificial Intelligence (AI) and machine learning (ML) guided material selection concepts [131] also seem to offer a huge potential in the selection of nano-inks for specific purposes. This may aid material researchers in tailoring the electronic properties of nano-inks through microstructural modifications based on AI and ML-guided design concepts.

5. Conclusions

There is absolutely no doubt that the field of metallic nano-inks (especially Ag nano-inks) offers countless research possibilities, both industrially and academically. However, addressing the aforementioned challenges (especially microstructural porosities) through scientific investigations is necessary to render nano-inks closer to being considered more exclusively for printed electronics-related applications.

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