Systematic Ink Design and Solubility Enhancement via Genetic Algorithm for Nanoparticle-based Inkjet Inks

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Abstract

Metal nanoparticle inks are the most commonly used material for creating conductive contacts via inkjet printing. While there are many commercial inks available, these inks may not be well-matched to individual systems or process flows. As such, the custom design of metal nanoparticle inks is a possible solution. However, the creation of a highly-loaded metal nanoparticle ink that exhibits reliable jetting behavior is a non-trivial process. In this paper we discuss a systematic method for designing metal nanoparticle inks using the fluid properties of both the unloaded and loaded ink to achieve reliable jetting behavior. In addition, we discuss the application of non-traditional experimental optimization methods, namely multi-objective genetic algorithms, to the search for highly soluble metal nanoparticles.

Introduction

There are multiple issues one must consider when designing a nanoparticle-based ink for inkjet printing. These may include controlling ink spread on various substrates, reducing the curing temperature required to transition the deposited nanoparticles into a functional state, guaranteeing reliable jetting behavior from the nozzle, and increasing the solubility of the nanoparticles being deposited, to name a few. This work will discuss progress made in designing metal nanoparticle inks with regard to the final two issues listed.

First, stable droplet formation from an inkjet nozzle is required in order to reduce the variation both within and across printing runs. Unstable drop formation may manifest itself in a number of ways such as satellite droplet formation, nozzle clogging, and volume or trajectory variation. Because stable drop formation is integral to pattern fidelity, there have been numerous efforts to quantify and predict jetting performance, commonly using a physically-based dimensionless parameter called the Z number [1-4]. However, there is general disagreement on the acceptable range of the Z number for inkjet applications, and more recently a combination of Reynolds, Weber, and Capillary numbers has provided additional insight [5, 6]. These three parameters dictate the jetting performance of inkjet inks through a balance of surface tension, viscous, and inertial forces. Using these parameters, we have previously shown that by assuming the surface tension of solvents commonly used to print organic-soluble metal nanoparticle inks is constant, then the control of viscous and inertial forces can be used to define a window of expected reliable jetting performance [7].

In addition to guaranteeing stable drop formation, the enhancement of nanoparticle solubility is an important thrust for ink design. Increased solubility results in a reduction of the required number of droplets for feature formation on a substrate, improving the overall throughput of the process. Some of the most commonly synthesized metal nanoparticles are gold and silver nanoparticles encapsulated by carbon-based alkane chains [8, 9]. While standard syntheses involve alkanes of uniform length, the incorporation of multiple alkane chain lengths has been shown to improve the solubility of metal nanoparticles [10]. However, the nature of the relationship between encapsulant composition and solubility is neither smooth nor well understood. Due to the non-smooth relationship, the exploration for highly soluble nanoparticles is well-suited for heuristic experimental optimization techniques as opposed to traditional statistical design of experiments. Genetic algorithms have been adapted to numerous chemical systems such as phosphor optimization for LEDs [11]. Using this methodology in combination with high-throughput synthesis made possible via robotic control [12], we report here on a multi-objective function genetic algorithm that aims to optimize both the solubility and conductivity of metal nanoparticles as a function of ligand composition.

Experimental

Jetting Experiments

All jetting experiments were performed using MicroFab MJ-AT piezoelectric nozzles with a 60 µm orifice and a custom-built drop-on-demand inkjet printer. The inks studied were either hexanethiol-encapsulated gold nanoparticles or dodecylamine-encapsulated silver nanoparticles and were jetted using typical bipolar trapezoidal waveforms as described in [10]. Both droplet volume and velocity were determined using stroboscopic image capture. A Brookfield LVDV III rheometer was used to determine ink viscosity and surface tension measurements were performed using a custom-built pendant drop measurement tool.

Solubility Experiments

Solubility enhancement studies were confined to the silver nanoparticle synthesis only due to the more simple, single-pot synthesis involved. A robot typically used for semiconductor nanoparticle synthesis was adapted to perform metal nanoparticle syntheses based on the procedure described in [9]. In order to successfully adapt the synthesis to the robot, liquid precursors were used to dispense controlled volumes and compositions of alkylamines with carbon chain lengths varying from 12 – 18 carbons. UV-Vis absorption and thermogravimetric analysis (TGA) were used to quantify nanoparticle solubility and the silver:carbon ratio of synthesized silver nanoparticles.

Results and Discussion

Jetting Performance and Loading Effects

The primary performance goal of a reliable nanoparticle ink is to establish jetting conditions that avoid breakdown mechanisms such as satellite droplets and nozzle clogging over extended periods of time. Because multiple solvents were explored in this work, each requiring different pulse waveform conditions in order to produce stable droplets, it is necessary to determine jetting criteria that enable for a direct comparison between one ink and the next. This is

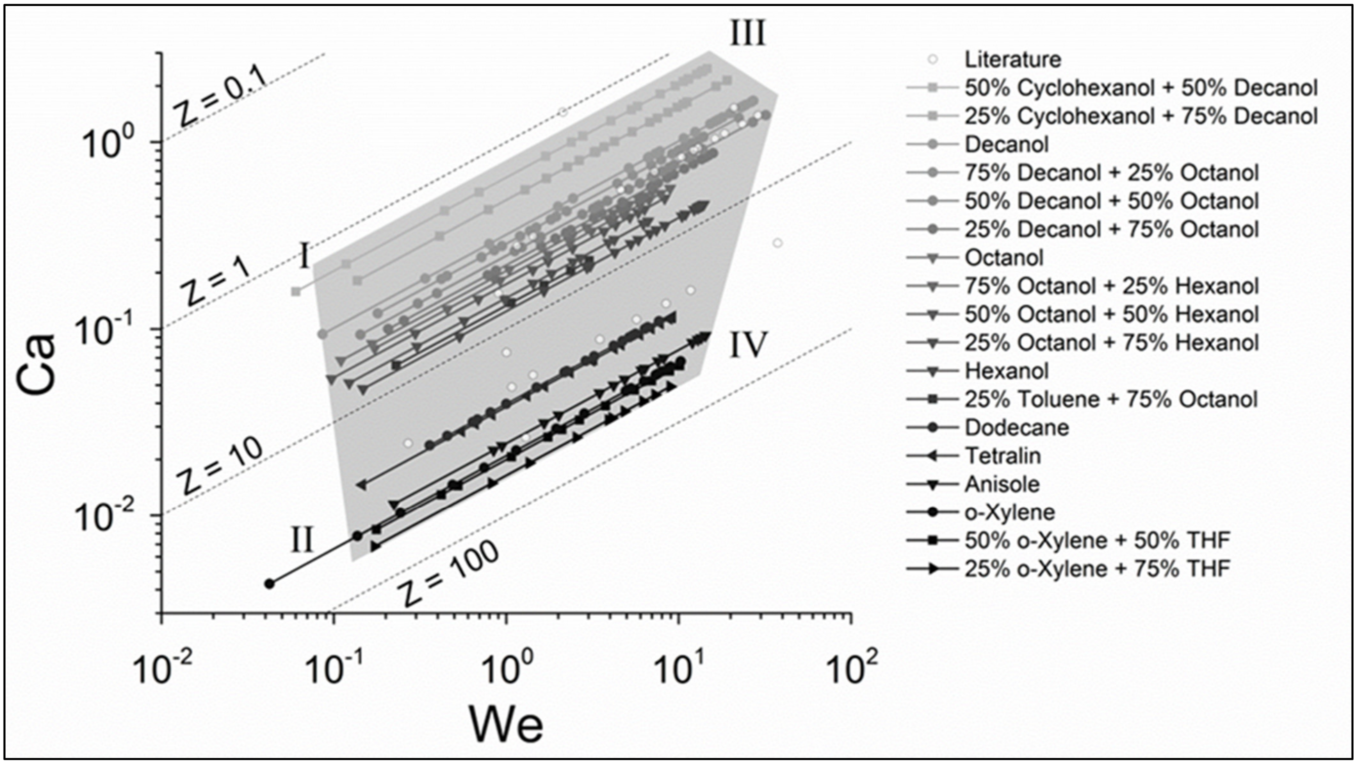

Figure 1. Ca-We stable jetting window and jetting performance for single and binary solvent systems tested in this work. The bounds of the stable window are labeled I – IV, indicating the failure mechanism observed when the conditions extend beyond the stable window.

traditionally accomplished by maximizing drop velocity as a function of dwell time used in standard bipolar waveforms. While velocity maximization is traditionally targeted, drop momentum maximization has been shown to more clearly produce the expected periodic trend with respect to bipolar pulse dwell time. This is largely due in part to the fact that the applied pressure can strongly affect the volume and therefore velocity of the droplet. Therefore, to eliminate this effect, drop momentum maximization is preferred.

As previously mentioned, the effect of surface tension forces was considered null because the solvents used our work all had primarily the same surface tension values. Therefore, the two dimensionless fluid parameters that normalize by surface tension, the capillary number (Ca) and Weber number (We) were used to determine the region of reliable jetting conditions for both unloaded and loaded inks. **Figure 1** depicts this Ca-We space and plots the performance of both single and dual solvent systems tested in this work. Each data point represents a stable jetting condition for the given solvent system and each line connecting these data points represents a series of droplet velocities tested, i.e. varying We, for the given system. Because Ca is proportional to velocity and We is proportional to the square of velocity, these contours exhibit a slope of ½ when plotted on a log-log plot, as shown. The boundaries of this plot are labeled with breakdown mechanisms I – IV, which correspond to no drop formation (I and II), satellite drop formation (III), and multiple droplet formation (IV). In addition, Z number contours are overload on the plot, showing a jetting region that spans Z number values from 1 – 100.

As expected, inks with higher viscosity values fall in the upper portion of the stable jetting window and inks with lower viscosities are in the lower portion. In addition, we observe the successful adjustment of ink viscosity via the addition of co-solvents, indicating that co-solvent addition is a viable route to modifying ink performance and achieve stable jetting performance. We can also extend this concept to inks loaded with nanoparticles. We see in **Figure 2a** that the addition of high viscosity solvent (alpha-terpineol) to a low viscosity solvent (hexane) ink loaded with 10% gold nanoparticles by mass results in imparting stability to the ink. This occurred when the alpha-terpineol fraction reached 30% of the overall solvent system composition.

In addition to imparting stability via the addition of co-solvents, it is also possible to adjust the loading of nanoparticles in the ink in order to tune the viscosity for stable jetting conditions. As nanoparticle loading increases, the viscosity of the ink will likewise increase. Therefore, in the same way that adding a high viscosity solvent moved an unstable low viscosity ink up into the stable jetting region, increasing nanoparticle loading has been shown to increase the ink viscosity and force the ink out of the stable jetting region (see **Figure 2b**).

General Ink Design

Using these two principles, we can describe a systematic method of formulating reliable custom nanoparticle inks for inkjet printing. First, one should select two solvents that each impart reasonable solubility to the nanoparticles being used. One solvent should be high viscosity and the other should be low viscosity. Next, a mixture of these two solvents should be formulated such that the jetting performance of the pure solvents lies somewhere near the middle of the stable jetting region. Jetting performance should be based on the maximization of drop momentum in order to clearly determine the optimal dwell time. Finally, the nanoparticles should be loaded into the solvent system such that the resulting ink viscosity does not push the ink outside of the stable jetting window.

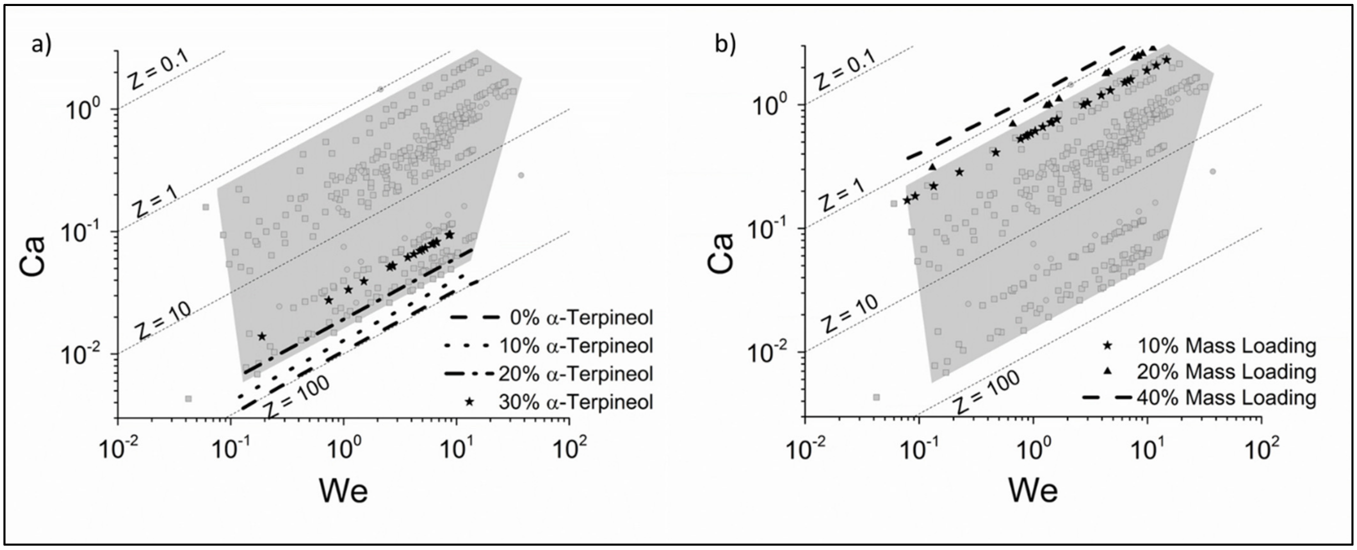

Figure 2. Modification of jetting performance via a) the addition of co-solvent (alpha-terpineol) to hexane inks and b) increased nanoparticle loading in alpha-terpineol inks. Conditions depicted with dashed lines indicate non-stable conditions. Conditions depicted by individual symbols are stable jetting conditions.

Silver Nanoparticle Ink for 3D Printing

The use of metal nanoparticle inks in inkjet printing applications is typically confined to planar interconnects or fabrication of passive components [13]. However, we have also recently developed fabrication processes for creating three-dimensional interconnect structures using similar metal nanoparticle inks [14]. In an effort to develop and demonstrate our custom ink formulation strategy, we also developed a custom silver ink to fabricate three-dimensional structures. Using dodecylamine-encapsulated silver nanoparticles, we formulated an ink based on a single solvent system with moderate viscosity, dodecane. When loaded up to 30%, the stable printing jetting conditions were a dwell time of 16 µs and +/- 32V. Pillars were printed with a total of 50 drops. While pillar fabrication was possible over a range of temperatures and drop frequencies, **Figure 3** shows a sample pillar printed substrate temperature of 80 °C and a drop ejection frequency of 1 Hz.

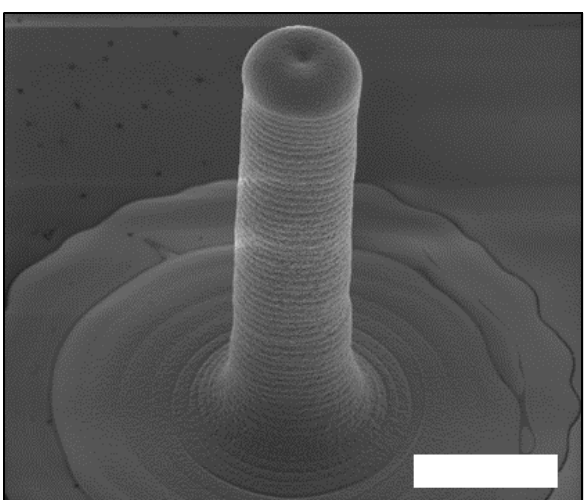

Figure 3. High aspect ratio three-dimensional structure fabricated with custom silver nanoparticle ink formulation. Pillar printed with a total of 50 droplets ejected at 1 Hz frequency on a silicon substrate at 80 °C. Scale bar is 50 µm.

Genetic Algorithm Conditions

Improving the solubility of nanoparticles is beneficial for two key reasons. First, as nanoparticle solubility increases, the concentration of functional material per droplet increases, which in turn decreases the total number of droplets required for printing functional features. In addition, because increasing the loading of nanoparticles can be used to adjust the viscosity and therefore jetting behavior of the ink, access to higher possible mass loading expands the general window within in which an ink designer might wish to design an ink. More specifically, it allows an ink designer to use lower viscosity solvents as the base solvent material and to bring the jetting behavior up and into the stable jetting window.

In this work, a multi-objective function genetic algorithm was developed to optimize for 1) increasing the solubility of silver nanoparticles and 2) decreasing the mass ratio of bound encapsulant carbon to core silver content. In the design, we allow for the variation of overall encapsulant:silver molar ratio during the synthesis, the reducing agent:silver molar ratio during synthesis, the concentration of the reaction, and most importantly the composition of the encapsulant used. Four encpaulants are selected for the study: dodecylamine, tetradecylamine, hexadecylamine, and octadecylamine. The bounds of the system are described in **Table 1**. The sum of the amine fractions was kept constant at 1 for each reaction, and the initial generation has 30 members whereas subsequent generations were comprised of 33 members each.

Table 1. Genetic algorithm conditions for silver nanoparticle solubility study

Condition	Range
Ag Concentration [mM]	37.5 – 87.5
Mole Reducing Agent : Mole Ag	1.0 – 1.5
Mole Encapsulant : Mole Ag	10 – 15
Dodecylamine fraction	0 – 1
Tetradecylamine fraction	0 – 1
Hexadecylamine fraction	0 – 1
Octadecylamine fraction	0 – 1

Initial Solubility Enhancement Results

In order to quantify the solubility of the nanoparticles generated, nanoparticles are collected, purified, and dissolved in tetradecane at mass loading conditions approaching 50% by mass, assuming full solubility. A series of subsequent dilutions of each highly loaded condition is then prepared and tested using UV-Vis absorption. The dilution series is wide enough such that it will, at some subset of dilution conditions, cover the linear response range for UV-Vis peak absorption. These conditions are extracted and the concentration of the nanoparticles is determined by extrapolating back to the non-diluted condition. **Figure 4** shows a sample set of UV-Vis curves for a set of six reactions prepared at varying initial concentrations.

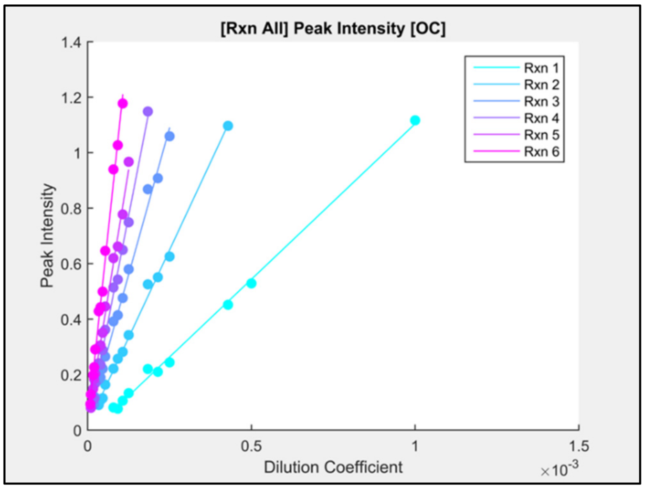

Figure 4. UV-Vis peak intensity versus dilution for six reactions prepared at varying initial concentration. Extrapolating each condition to a dilution coefficient of 1 is representative of the non-dilute condition, therefore steeper slopes represent higher initial concentration.

To date, only two generations of the algorithm have been completed. However, the initial results indicate an improvement of nearly 5% for the maximum solubility observed from the first two second generation. The second objective function, reducing the mass ratio of bound carbon to the mass of the nanoparticle core also showed improvements. The average condition improved by 15% from one generation to the next.

Conclusion

The ability to formulate and control the behavior of nanoparticle inks is critical for inkjet-printed electronics to be realized at manufacturing scales. We have reviewed the important principles of stabilizing jetting conditions via the addition of co-solvents as well as nanoparticles in order to tune the viscosity of the ink. In addition, we have demonstrated how this systematic process can be used to formulate relatively simple nanoparticle inks suitable for the fabrication of complex, high aspect ratio structures relevant to electronics packaging applications. However, because stable jetting is only a single piece of the larger puzzle, we have also begun exploring the solubility enhancement of silver nanoparticles by using a combination of heuristic experimental design as well as high-throughput robotic control. Our initial results indicate that, indeed, nanoparticle solubility enhancement as a function of encapsulant composition is observed. Using this technique, we aim to discover nanoparticles with even higher solubility values in future generations, in order to formulate nanoparticle inks with extremely high loading capabilities.

Acknowledgement

The authors would to acknowledge Ultratech, Inc. for funding and The Molecular Foundry at Lawrence Berkeley National Laboratory for access to invaluable research tools and staff.

References

[1] J. Fromm, "Numerical Calculation of the Fluid Dynamics of Drop-On-Demand Jets," *IBM J. Res. Dev.,* vol. 28, no. 3, pp. 322-333, 1984.

[2] N. Ries, B. Derby, "Ink Jet Deposition of Ceramic Suspensions: Modeling and Experiments of Droplet Formation," *MRS Proc.*, vol. 625, pp. 117-122, 2000.

[3] D. Jang, D. Kim, J. Moon, "Influence of Fluid Physical Properties on Ink-Jet Printability," *Langmuir*, vol. 25, no. 5, pp. 2629-2635, 2009.

[4] J. Tai, H. Gan, Y. Liang, B. Lok, "Control of Droplet Formation in Inkjet Printing Using Ohnesorge Number Category: Materials and Processes," *10th Electronics Packaging Tech. Conf.*, pp. 761-766, 2008.

[5] B. Derby, "Inkjet Printing Ceramics: From Drops to Solid," *J. Eur. Cer. Soc.*, vol. 31, no. 14, pp. 2542-2550, 2011.

[6] E. Kim, J. Baek, "Numerical study on the effects of non-dimensional parameters on drop-on-demand droplet formation dynamics and printability range in the up-scaled model," *Phys. Fluids*, vol. 24, no. 8, pp. 082103-082103-12, 2012.

[7] H. Nallan, J. Sadie, R. Kitsomboonloha, S. Volkman, V. Subramanian, "Systematic Design of Jettable Nanoparticle-Based Inkjet Inks: Rheology, Acoustics, and Jettability," *Langmuir*, vol. 30, no. 44, pp. 13470-13477, 2014.

[8] M. Brust, M. Walker, D. Bethell, D. Schiffrin, R. Whyman, "Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid-Liquid sysem," *J. Chem. Soc., Chem, Commun,*, vol. 7, pp. 801-802, 1994.

[9] Y. Li, Y. Wu, B. Ong, "Facile Synthesis of Silver Nanoparticles Udeful for Fabrication of High-Conductivity Elements of Printed Electronics," *J. Amer. Chem. Soc., Comm.*, vol. 127, pp. 3266-3267, 2005.

[10] A. Centrone, E. Penzo, M. Sharma, J. Myserson, A. Jackson, N. Marzari, F. Stellacci, "The role of nanostructure in wetting behavior of mixed-monolayer-protected metal nanoparticles," *Proc. Nat. Acad. Sci.*, vol. 105, no. 29, pp. 9886-9891, 2008.

[11] K-S. Sohn, D. Park, S. Cho, B. Kim, S. Woo, "Genetic Algorithm-Assisted Combinatorial Search for a New Green Phosphor for Use in Tricolor White LEDs," *J. Comb. Chem.*, vol. 8, no. 1, pp. 44-49, 2006.

[12] E. Chan, C. Xu, A. Mao, G. Han, J. Owen, B. Cohen, D. Milliron, "Reproducible, High-Throughput Synthesis of Colloidal Nanocrystals for Optimization in Multidimensional Parameter Space," *Nano Lett.*, vol. 10, pp. 1874-1885, 2010.

[13] D. Huang, F. Liao, S. Molesa, D. Redinger, V. Subramanian, "Plastic-Compatible Low Resistance Printable Gold Nanoparticle Conductors for Flexible Electronics," *J. Electrochem. Soc.*, vol. 150, no. 7, pp. G412-G417, 2003.

[14] J. Sadie, V. Subramanian, "Three-Dimensional Inkjet-Printed Interconnects using Functional Metallic Nanoparticle Inks," *Adv. Func. Mater.*, vol. 24, no. 43, pp. 6834-6842, 2014.

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Jacob Sadie received his B.S. in electrical engineering from Clemson University in 2010, He is now pursuing his Ph.D. in electrical engineering at the University of California, Berkeley. In addition to inkjet jetting performance and metal nanoparticle solubility enhancement, his research in the Printed Electronics Research group has focused on the process development and characterization of three-dimensional inkjet-printed metal nanoparticle structures for semiconductor packaging applications.