

**Ligand-mediated stabilization of low temperature metal eutectics
and their use in composite systems**

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Lauren R. Finkenauer

B.S., Mechanical Engineering, University of Maryland, College Park
M.S., Mechanical Engineering, Carnegie Mellon University

Carnegie Mellon University
Pittsburgh, PA

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Abstract

The objective of this thesis is to contribute to the understanding of the behavior of the liquid metal eutectic gallium/indium (EGaIn) in composite systems and provide a platform for the development of functional hybrid nanocomposites. Contributions are regarding (i) the investigation of the electromechanical coupling performance of EGaIn as electrodes in a soft electrostatic transducer and (ii) the effectiveness of organic surfactants to stabilize EGaIn nanoparticles in organic solvents. For the first portion, a completely soft dielectric elastomer actuator (DEA) using EGaIn electrodes was fabricated and evaluated. Experimental actuation of the DEA showed high agreement with a generalized NeoHookean constitutive law, assuming uniaxial pre-stretch and considering the device saddle deformation. The expected conductive behavior of the liquid alloy was confirmed, and further efforts have focused on the development and stabilization of EGaIn nanodroplets, which do not exhibit the problems associated with larger pools of EGaIn (such as leakage) and can be applied to soft multifunctional materials. A computational procedure was developed for calculating suspended EGaIn nanoparticle mass in order to determine reaction yields using applied Mie theory and optical characterization techniques (dynamic light scattering and UV/Vis spectrophotometry). This method calculated total mass to within 20% when applied to a known system. A systematic study evaluating particle yield as a function of aliphatic surfactant composition and concentration (and solvent type) revealed a pronounced dependence of nanodroplet formation on the solvent type as well as surfactant structure. Ethanol (EtOH) was found to be the most effective solvent for the formation and stabilization of EGaIn nanodroplets, in which only thiol-based surfactants were found to improve nanodroplet yield. Results suggest a stabilization mechanism other than the expected self-assembled monolayer (SAM) formation. The research has been extended to alternative (*e.g.* plant based) surfactant systems.

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1. Introduction

1.1. Motivation

The possibility to alter the electronic, optical or thermal properties of polymeric elastomers without affecting their soft mechanical response has rendered low temperature metals or alloys an intriguing platform for nanocomposite materials in areas such as soft robotics. For example, liquid metal embedded in polymers has been used to create “soft” electronic devices such as flexible sensors¹⁻⁵ and actuators^{6,7} and conductive or high-k dielectric composites.^{8,9} However, challenges exist that prevent a more pervasive use of this emerging class of material. One major difficulty is the absence of strategies that enable the dispersion of nanometer-sized droplets and the formation of nanocomposites with uniform morphology. Rather, current methods involve mechanically forced dispersion of liquid metal droplets – a process that results in micron-sized inclusions with irregular distributions of size and shape,⁸ shown in Figure 1-1. This limitation constrains both the

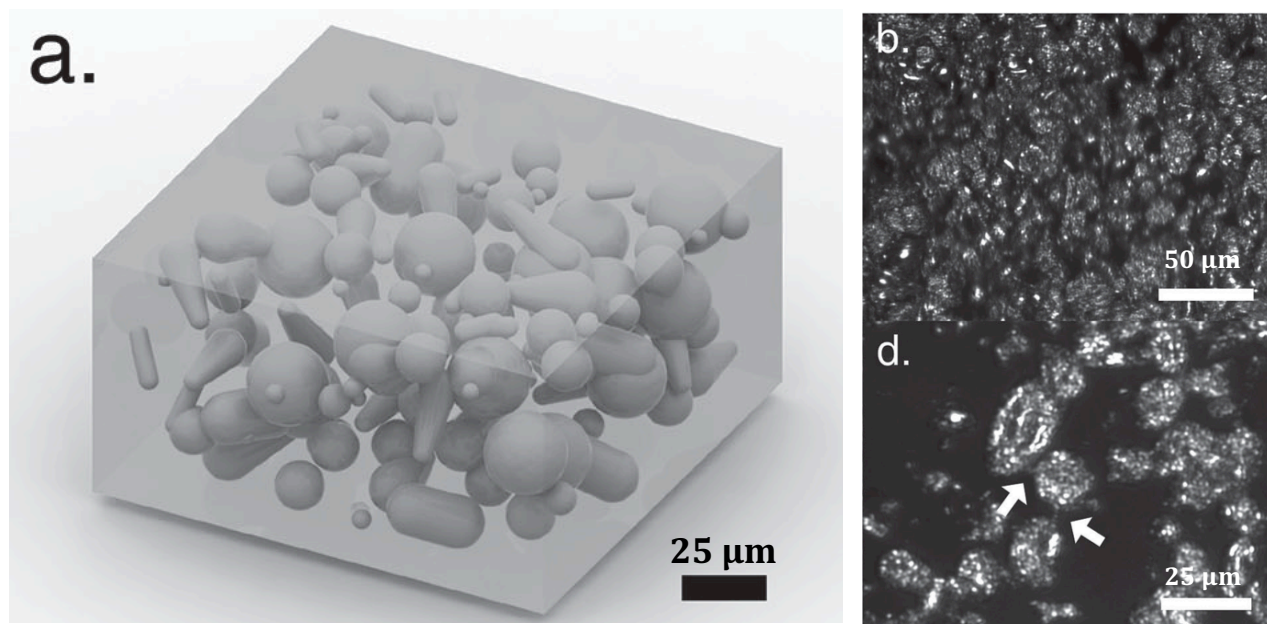


Figure 1-1. (a) Representation of 50% volume fraction of Galinstan in poly(dimethyl sulfoxide) (PDMS); (b) & (d) cross sections of composite demonstrating heterogeneity of dispersion. [Fassler 2015].

control of properties of composite materials as well as potential applications, and controlled dispersion of these low temperature metals, as illustrated in Figure 1-2, has yet to be demonstrated.

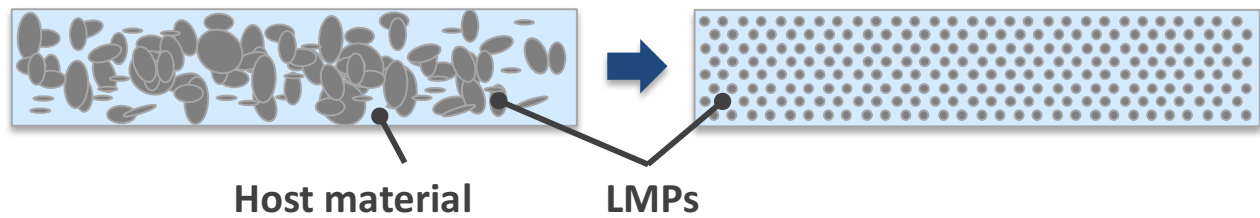


Figure 1-2. Illustration of (left) current morphologies of liquid metal-polymer composites versus (right) uniform distribution representing tailored morphology.

Insight for overcoming the challenge of controlling both the size and dispersion morphology of liquid metal particle (LMP) inclusions can be drawn from the field of classical polymer nanocomposite materials, where surfactants are used to prevent particle coarsening as well as to facilitate their compatibility in a polymer matrix. Current attempts to create low melting temperature and nanoscale LMPs involve stabilization with surfactants, and have resulted in particles ranging from tens of nanometers to over a micron in diameter.^{10–18} To facilitate the application of this concept to nanocomposites with LMPs, research has to elucidate surfactant coupling chemistries that enable strong binding to particle surfaces as well as the role of surfactant modification on the interaction between LMPs in solution and polymeric media. Additionally, there is a gap in the literature regarding the efficiency or yield of such solutions, which is usually either not reported, or mentioned as an approximate concentration range without further explanation. This is likely due to the difficulties in quantifying what is typically a very small amount of material. Gravimetric analysis methods are impractical and not repeatable when quantities are within the last decimal of the measurement equipment. Thus, the purpose of this research is (i) to demonstrate functioning soft robotic devices through the implementation of low temperature metal alloys and (ii) to contribute to both the better understanding of surfactant modifications on LMPs and the efficiency of surfactant systems to enable development of methodologies for the effective dispersal of LMPs in polymeric based or other materials.

1.2. Research objectives

As stated in 1.1, significant efforts have focused on developing flexible electronics using liquid metals as well as identifying surfactant strategies for stabilizing EGaIn ‘nanodroplets’ in organic media. A Web of Science search on the queries ‘surfactant’, ‘EGaIn’ reveals that at least 18 articles have been published on the subject of surfactant stabilization of EGaIn in the past 20 years. However, to date research has been mostly Edisonian in nature rather than systematic and hence an understanding of the role of surfactant structure in the ability to stabilize EGaIn nanodroplets remains outstanding. One of the major challenges has been the absence of efficient means to determine the ‘efficiency’ of dispersion processes. This has likely been due to the practical difficulties in applying established ensemble methods such as gravimetry (due to the small mass of material that is being used in the literature) and measuring scattered/transmitted light intensity (which assume monodisperse solutions and require that all optical constants are known).

The objectives of the research conducted within this thesis are twofold. First is to examine the electro-mechanical interplay of liquid metal (LM) and elastomers in soft dielectric systems, and validate the use of this material as an electrode in soft actuators (thus proving that LM behaves as expected). However, because the use of liquid metals incurs some unique challenges (such as leaks and contamination of other surfaces), a second objective is to produce stabilized LM nanodroplet dispersions and composites. Unlike liquid metal films and channels which can leak or pill, nanodroplets circumvent these issues and introduce opportunities for surface functionalization as well as applications where pools of liquid metals would be undesirable or impractical. This objective includes developing an efficient method of droplet synthesis and a strategy to determine particle yield of EGaIn surfactant systems, to employ the method to determine the interrelation between surfactant microstructure and composition on its ability to bind to and stabilize low

temperature metal nanoparticles, and then apply this understanding to enable controlled, tunable nanoparticle dispersion in a variety of host materials (such as polymers).

1.3. Hypothesis

This study tests the following hypotheses:

1. Liquid metal is a feasible material for electrodes in soft dielectric transducers (such as dielectric elastomer actuators) and should behave like a soft conductor where electromechanical coupling matches theoretical predictions, and also increased deflection compared with other conductive materials due to lack of mechanical resistance. If the electrodes are sufficiently thin compared to the composite device, it is expected that a model of the actuator can neglect the thickness contributions of these layers.
2. Metal nanoparticles are known to strongly interact with light by both absorption and scattering and thus the quantitative analysis of the optical spectra of EGaIn particle solutions (taking into account particle size distributions) should provide a means to determine the mass concentration of EGaIn nanodroplet solutions and consequently the yield of surfactant dispersion processes.
3. The extent to which surfactants bind to and stabilize the low liquid metal particles will depend on the coupling chemistry, surfactant structure and particle surface composition.

2. Background

2.1. Eutectic Gallium Indium

Eutectic Gallium-Indium (EGaIn) and composites of Gallium, Indium and Tin (GaInSn) (having various elemental ratios) are the main room temperature liquid metal alloys that have been utilized for micro- and nanoparticle formation. EGaIn is approximately 75.5% Ga and 24.5% In by weight, with a melting temperature of 15.3 °C^{19,20}. Figure 2-1 shows the phase diagram of the Ga-In system. Both alloys spontaneously form a protective oxide skin when exposed to air.¹⁹ In general, this is true of all liquid metals comprising Ga, for which an oxide forms very quickly in

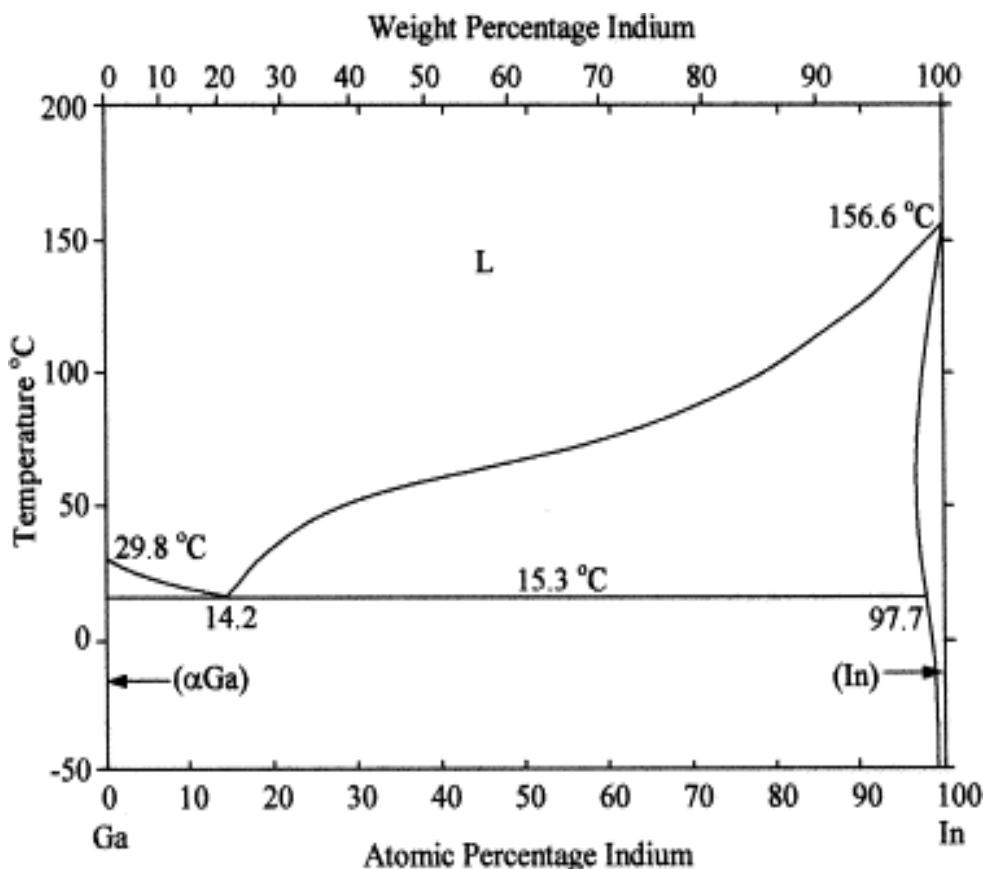


Figure 2-1. Phase diagram of gallium and indium. The eutectic composition is 75.5% Ga and 24.5% In (by weight) and at temperature 15.3°C. Image adapted from Anderson, et al.¹⁸

air²¹⁻²³ and instantaneously with direct exposure to oxygen.²⁴ Using x-ray reflectivity, Kawamoto et al. demonstrated the oxide layer to have a thickness of 5 Å in high vacuum conditions,^{25,26}

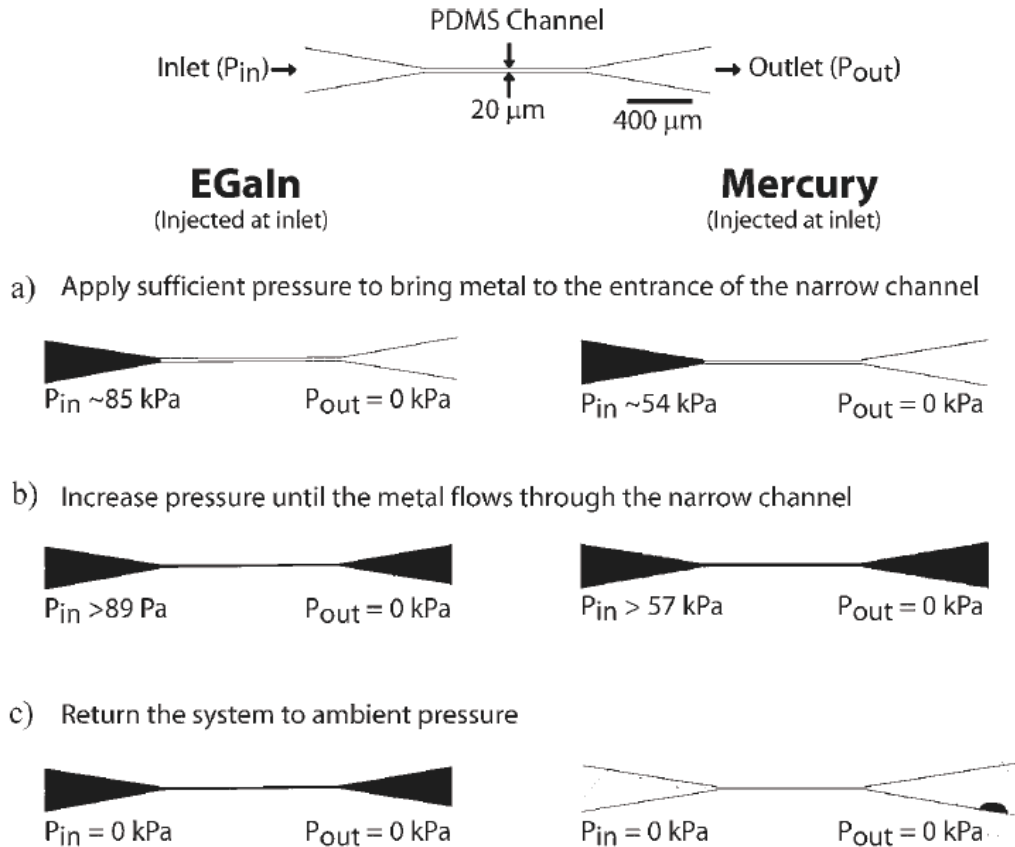


Figure 2-2. Demonstration of EGaIn wetting properties to PDMS and thus its ability to behave as a liquid wire. [Dickey 2008]

though as Dickey remarks, it is “likely thicker in ambient conditions.”^{22,23,25} As demonstrated in Figure 2-2, the skin formation provides some “moldability” of the materials, and enables spreading across a surface or within a channel (unlike mercury, which does not exhibit volumetric filling of a hollow channel geometry without sustained pressure)¹⁹. The oxide layer also affords some structural stability to the alloy, even allowing for 3D structures built of purely liquid metal droplets (demonstrated by Figure 2-3). Rheological experiments suggest that the mechanics of the oxide dictate flow behavior in response to applied stresses (at least for sub-mm scales).^{19,27,28} Larson et al. explored the viscoelastic nature of the oxide, which demonstrated both apparent elasticity and yield stress during testing in a parallel plate rheometer, and noted a strong dependence of the outcome on strain history.²⁷ Excluding the presence of oxide, EGaIn has a relatively low viscosity

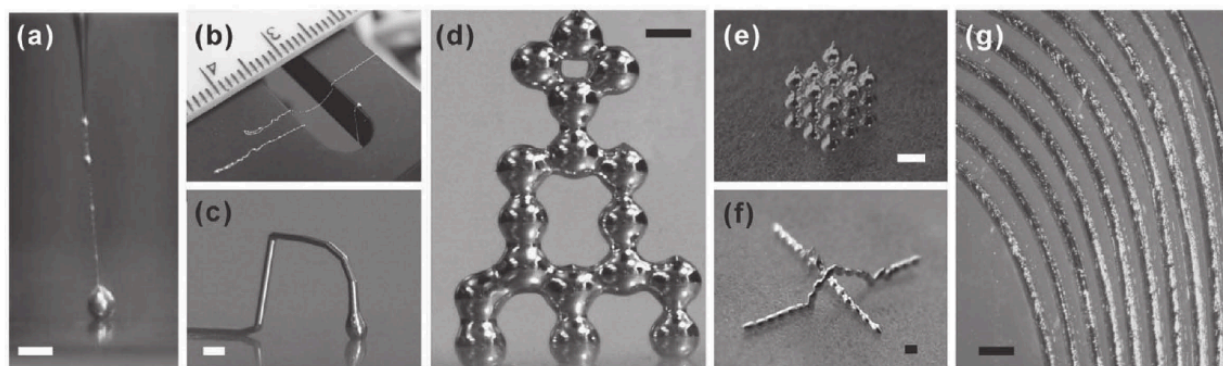


Figure 2-3. Demonstration of various structures and geometries possible to "print" due to EGaIn oxide layer. Scale bars are 500 μm . [Dickey 2013]

of $1.99\text{E-}3 \text{ Pa}\cdot\text{s}$ (only about twice that of water) – it readily flows within the limitations of its oxide skin on non-level substrates.¹⁹ See Table 2-1 below. EGaIn also has the advantage of a bulk electric conductivity of approximately $3.4\text{E}4 \text{ S/m}$, which approaches that of metals traditionally used in electronic hardware (within an order of magnitude), though the oxide is less conductive than the bulk alloys ($5\text{E-}3 \text{ S/m}$).^{19,29} The eutectic alloy has shown maintained conductivity up to about 700% strain (while still matching theoretically predicted resistances) when injected into a hollow extruded polymer resin.³⁰

Auger spectroscopy and x-ray photoelectron spectroscopy (XPS) have shown this layer to be oxides of gallium, predominantly Ga_2O_3 .^{16,19,31} For very small particles with a much higher surface to volume ratio, this could affect the alloy composition inside the core. However, for

Table 2-1. Comparison of selected physical and electrical properties of several low-T melting materials (including EGaIn) and water. Reproduced from "Stretchable Bioelectronics for Medical Devices and Systems." [Dickey 2016]

	Ga	EGaIn	Galinstan	Water
Melting point ($^{\circ}\text{C}$)	29.8	15.5	10.7	0
Boiling point ($^{\circ}\text{C}$)	2402	2000	>1300	100
Density (gm/cm^3)	6.91	6.36	6.36	1
Viscosity (10^{-3} kg/m s)	1.969	1.99	2.09	1
Surface tension (mN/m)	750	632	718	72.8
Thermal conductivity (W/m K)	30.5	26.4	25.4	0.6
Electric resistivity ($\mu\Omega \text{ cm}$)	27.2	29.4	30.3	20×10^8

particles with diameters on the order of a hundred nanometers, behavior is quite consistent with bulk material properties.¹⁸

2.2. Liquid metal + polymer composites

The rapidly growing fields of soft robotics and biocompatible electronics have required continued improvement of flexible circuitry. In contrast to traditional rigid electronic components, soft-matter counterparts must be bendable, stretchable or both depending on the application. Liquid metal alloys are an attractive option and have become an increasingly popular choice for such technologies as they are inherently compliant (while in the liquid phase) and highly conductive (see Figure 2-4 and Figure 2-5 for material comparisons).

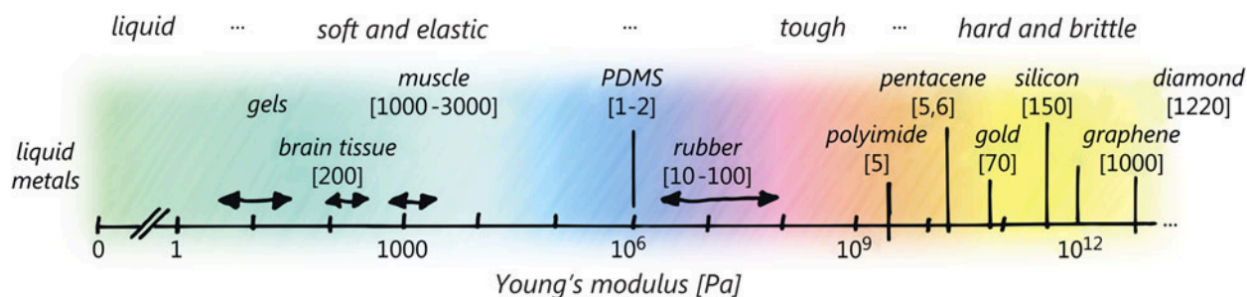


Figure 2-4. Elastic moduli for a variety of materials shown on a logarithmic scale, including liquid metals and some polymers. Adapted from Wagner et al. [MRS bulletin]

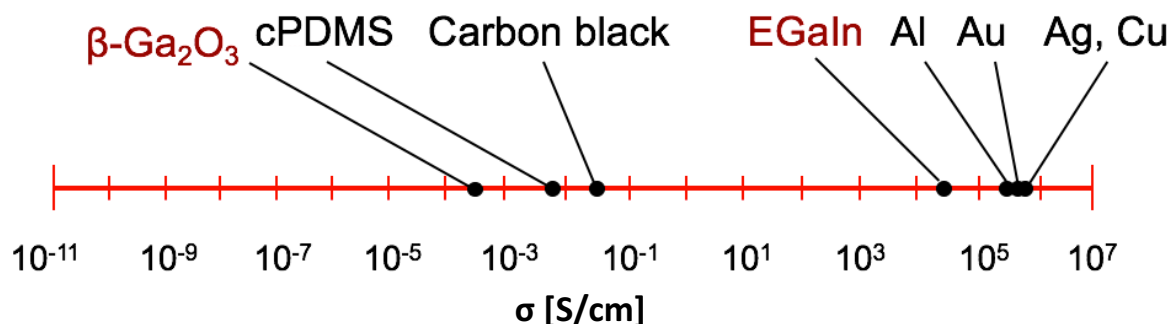


Figure 2-5. Conductivities of some common metals compared to popular materials for soft electronics.

These alloys, specifically EGaln, have been implemented into numerous types of devices: a variety of antennas to include patch,³² coil^{1,33} and reconfigurable^{3,34,35} structures, as well as a tunable split-ring resonator³⁶; compliant electrodes^{37,38,32,39–42} for circuits and actuators^{6,7,43} which have demonstrated self-healing behavior⁴⁴; a multitude of compliant and robust pressure^{2,4} and strain sensors.^{1,2,45,46} This has been accomplished through the use of several EGaln deposition and patterning techniques including transfer contact printing^{47–49} (sometimes in conjunction with photolithography^{36,48,50}), 3D printing,^{10,51,52} laser patterning,⁵³ stencil lithography^{6,54}, and perhaps most commonly, direct injection of pre-configured geometries.^{1,2,5,33,35,36,45} Self-healing capabilities have been demonstrated for extensible wires⁵⁵ and electrodes,⁴⁴ as well as soft composites utilizing EGaln capsules with urea-formaldehyde shells that were deposited onto imbedded conductive substrates.⁵⁶ Figure 2-6 showcases this and other example applications.

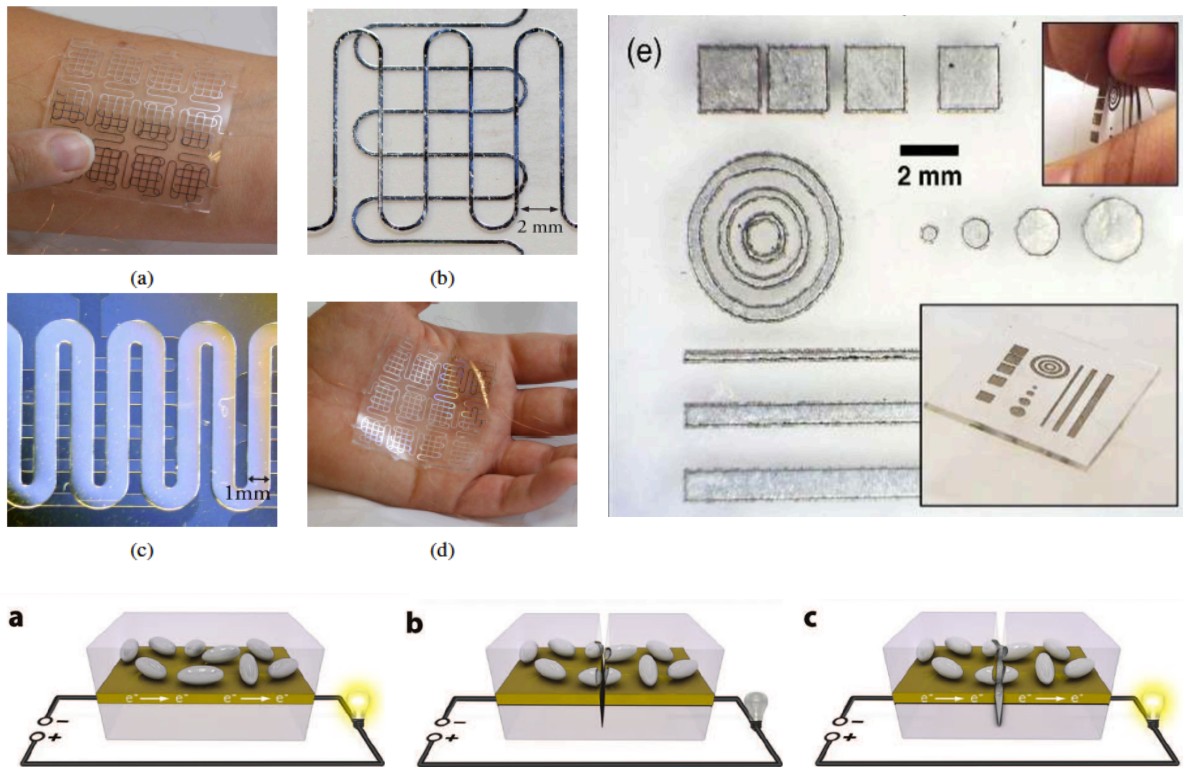


Figure 2-6. (Top left) Example of compliant strain sensors made from EGaln imbedded in PDMS[Kramer 2011]; (top right) demonstration of various discontinuous shapes made via laser patterning of the same materials[Lu 2014]; (bottom) demonstration of self-healing composite circuit using encapsulated EGaln, adapted from Blaisik et al. [Blaisik 2012].

More recently, direct mechanical mixing (mortar and pestle) of polymer and liquid metal has led to elastic composites with liquid metal inclusions. Such composites were shown to either have permanent conductance upon application of a critical pressure⁸ or demonstrate a high bulk dielectric constant through the combination of conductive droplets in both silicone and polyurethane based elastomers.⁹ For both cases however, the fabrication methodology resulted in poor control of particle shape, size and dispersion formation. As highlighted in Figure 2-7, EGaIn droplets were oblong, irregular, rough and on the order of 20 – 30 μm or larger.^{8,9} For such composites and other applications, conductive fluids as an example, uniform droplets with sizes on the nanometer scale is desirable in order to maximize the benefits of high particle surface area. The creation of liquid metal-polymer composites with tailored morphologies has yet to be demonstrated.

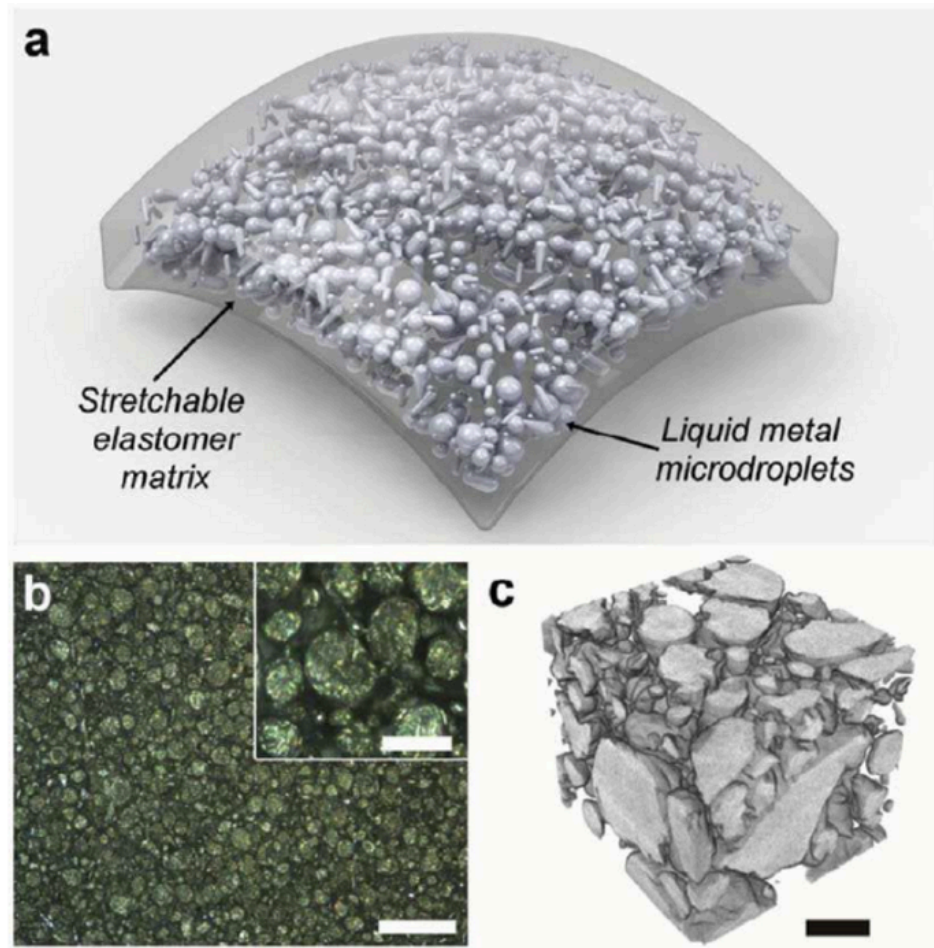


Figure 2-7. (Top) Rendering of EGaIn droplets in cured PDMS elastomer; (bottom left) cross-section of EGaIn-PDMS composite, scale bar = 100 μm and inset scale bar = 25 μm ; (bottom right) Nano-CT scan of composite, scale bar = 25 μm . [Bartlett 2016]

2.3. Approaches to droplet formation

2.3.1. Sonication in solution

Sonication techniques, specifically ultrasonication (>20 kHz), have been used for emulsification since the early 1920s, mostly for oil in water (O/W) systems.⁵⁷ Willert et al. demonstrated pure gallium nanoparticles down to 150 nm using an ultrasonic bath to further reduce a mini-emulsion of gallium in cyclohexane with a block copolymer surfactant (TEGO EBE45).¹¹ Gedanken's widely cited work of 2004 generalized the use of "sonochemistry" for creating nanoparticles and nanomaterials, and led to ultrasonication as the technique of choice for the synthesis of low melting temperature and liquid metal micro- and nanospheres.⁵⁸ Shown in Figure 2-8, Friedman et al. obtained 100 μm microspheres of Pb and the Au-Si eutectic in hot silicone oil ($T > T_m$) with a bath sonicator, and later Ga, In, Sn, Bi, Pb, Zn, Hg and eutectics of Au-Ge and Au-Si.^{59,60} Both Raabe and Hessling and Han et al. used probe ultrasonication with Field's metal (51% In, 32.5% Bi, 16.5% Sn).^{61,62} Raabe and Hessling synthesized particles in deionized (DI)

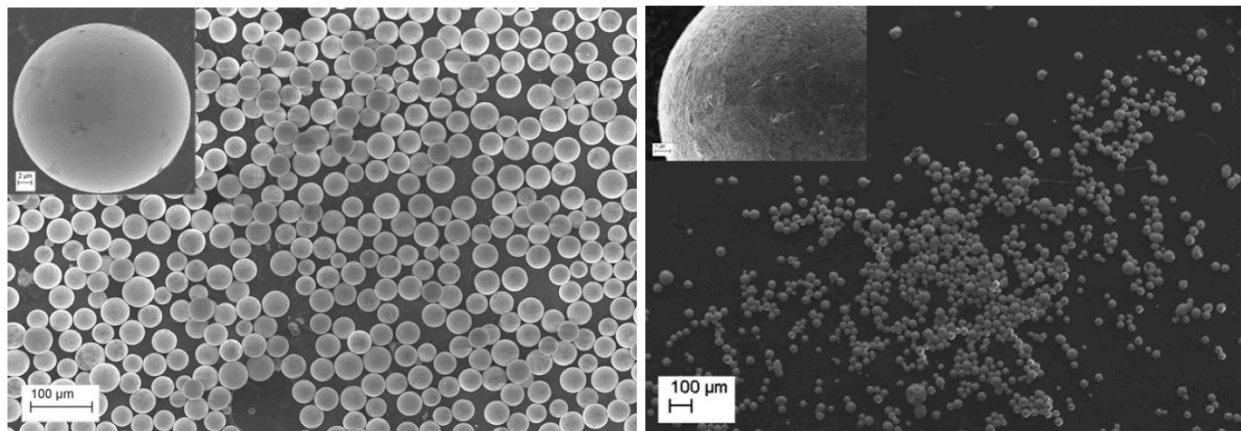


Figure 2-8. Microspheres produce by sonication of (left) Pb above T_m and (right) Au-Si. Inset scale bars are 2 μm (Pb) and 1 μm (Au-Si). [Friedman2010]

water ranging from a few nm to several microns.⁶² Kalantar-zadeh and coworkers instead treated droplets of Galinstan (the eutectic of GaInSn having weight percent Ga 68.5%, In = 21.5%, Sn = 1%) with WO_3 powder after ultrasonication in DI water to obtain WO_3 coated spherical particles

down to a couple microns.⁶³ While the resultant spheres were still quite large, many more droplets were produced. Galinstan was also utilized by Hayashi et al. to make metallic nanoemulsions in both DI water and 6% HCl solutions, for which the average size was determined from light scattering to be about 480 nm and slightly over 310 nm, respectively.⁶⁴ Han sonicated in polyalphaolefin (PAO) oil, and observed Field's metal droplets down to 15 nm and indium down to 30 nm.⁶¹

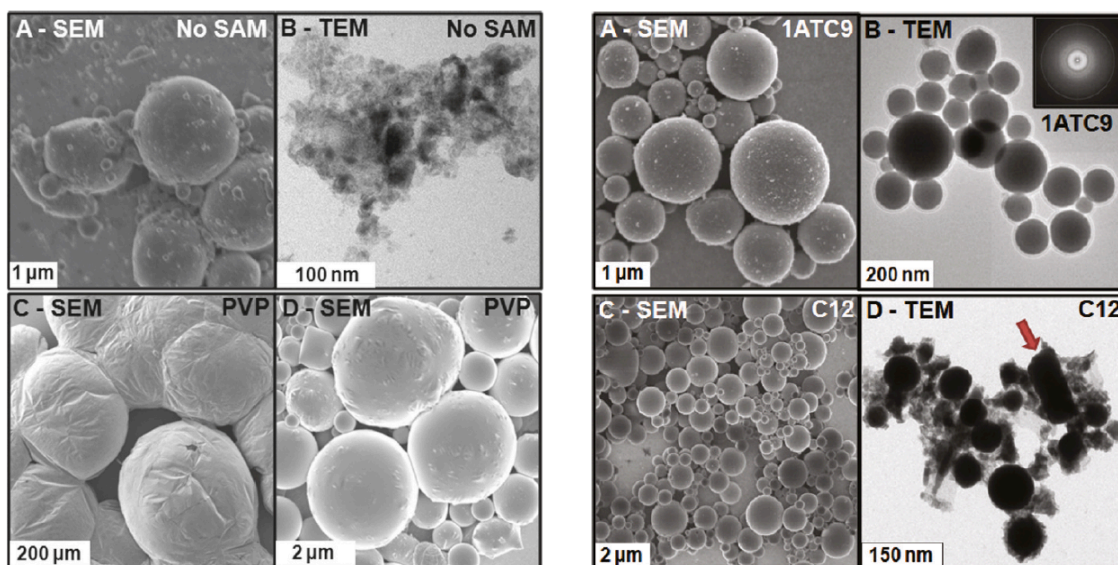


Figure 2-9. (Left square) Comparison of nanoparticles ultrasonicated (*top*) without the presence of SAMS and (*bottom*) in the presence of PVP. (Right square) Comparison of nanoparticles ultrasonicated (*top*) with 3-mercapto-N-nonylpropionamide and (*bottom*) 1-Dodecanethiol. Left column and right column in each square show SEM and TEM micrographs, respectively. Images adapted from [Hohman et al.]

Hohman et al. pioneered the use of ligands with ultrasonication of liquid metal to aid in particle size reduction and nanoparticle stabilization through self-assembled monomers (SAMS).¹³ They compared two SAM forming thiol surfactants, 1-Dodecanethiol (C12) and 3-mercapto-N-nonylpropionamide (1ATC9), and PVP against no added surfactants. All surfactant solutions were made with neat, degassed ethanol (EtOH). Figure 2-9 illustrates how the presence of any surfactant – especially those forming SAMS – affects EGaIn particle size, shape and surface morphology. The authors claimed that chemisorption of sulfur atoms with either gallium or indium on the particle surface for thiol self-assembly was the mechanism for inhibiting oxide skin formation,

evidenced by the smooth particles obtained when C12 and 1ATC9 were used (Figure 2-9, right) versus the wrinkled oxide skin which was still present in the control sample (neat EtOH only) and PVP (Figure 2-9, left). They also stated the necessity for the presence of the oxide layer (and therefore oxygen) during sonication, as the wrinkles and instabilities of the skin helped to further cleave particles. Without surfactants present, agglomerates clearly formed (and potentially coalesced). Nanoparticles synthesized using C12 ranged from 100 – 1000 nm, while those from 1ATC9 were smaller at 10 – 100 nm.¹³ The authors report a yield of 50 – 150 µg/mL for particles capped with C12, and 300 – 500 µg/mL for 1ATC9-capped particles, though provide no explanation as to how these concentrations were determined (most likely by gravimetric analysis).

Similarly, Kramer and coworkers sonicated EGaIn particles in neat EtOH with and without the presence of SAM forming 1ATC9.¹⁰ Drop casted particles subjected to “mechanical sintering” tests revealed that thiol capped particles ruptured more easily than oxide covered particles (no thiol), suggesting a lower surface tension of thiol capped to gallium oxide coated particles. Ren et al. utilized a conical probe tip to directly sonicate various compositions of GaInSn in EtOH with ethyl 3-mercaptopropionate to create passivated nanoparticles with diameters mostly 50 – 150 nm.¹⁸

Sudo et al. sonicated gallium in chloroform with both dodecanoic acid and dodecanamine as a surfactant, resulting in TEM observed particles of approximately 20 nm.¹⁵ Consistent with observations by Hohman et. al, no surfactant resulted in aggregated structures. It was also observed that higher sonication temperatures formed larger particles. Gallium was also examined by Kumar et al., who sonicated the melt in Ar-purged DI water, hexane or n-dodecane.¹⁴ Nanoparticles were observed when using hexane (300 – 1200 nm) and dodecane (200 – 500 nm and 700 – 1300 nm) as solvents. Yamaguchi and colleagues ultrasonicated with a conical probe tip a mixture of gallium

and C12 in 2-propanol to observe a particle size range of 10 – 400 nm.¹⁷ As with Sudo and coworkers, they noticed that higher temperature during sonication led to larger mean particles. Tevis et al. emulsified EGaIn and Field's metal in DI water and acetic acid, and reported an average particle size ranging from 6.4 nm to 10 μm .¹⁶

In summary, there exists ample evidence that surfactants can promote the stabilization of EGaIn nanodroplets. However, very little is known about the role of the surfactant chemistry (i.e. the nature of the “head group”) on the strength of the surfactant – particle bonds and particle size nor on the effect of surfactant binding on the compatibility characteristics of LMPs in polymeric host materials. Additionally, the effect of surfactant systems on dispersion efficiency (particle yield) has not been sufficiently discussed or explored. As such, there is an incomplete understanding of how such systems behave and their usefulness.

2.3.2. Alternative formation methods

Solution-based methods for the preparation of spherical colloids of low melting point metals fall in either of two categories: bottom-up or top-down. Wang and Xia demonstrated the preparation of spherical bismuth particles ($T_{\text{m, Bi}} = 271.4^{\circ}\text{C}$) with controllable diameters ranging from 100 to 600 nm using each type of approach.⁶⁵ For the bottom-up approach, bismuth acetate was thermally decomposed in ethylene glycol and then quenched in cold ethanol; using the top-

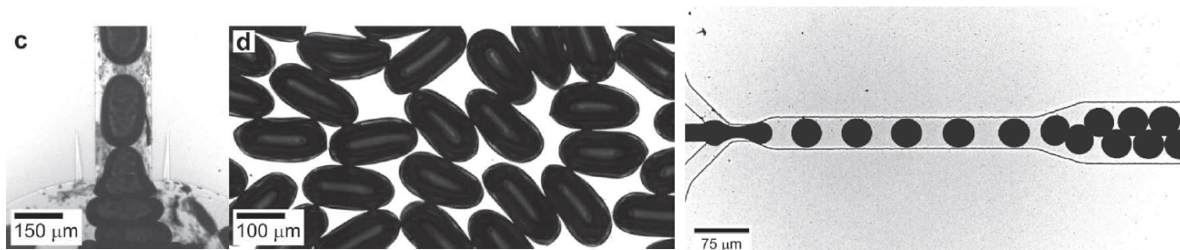


Figure 2-10. (Left, c and d) Oblong particles of EGaIn formed in oxygenated silicone oil with oxide layer still intact post forming, and (right) Spherical EGaIn particles made in deoxygenated oil without presence of the oxide layer. Images adapted from [21].

down method, molten drops of bismuth were instead emulsified in boiling di(ethylene glycol).⁶⁵ While both schemes resulted in the same product with the aid of poly(vinyl pyrrolidone) (PVP) as an emulsifier, the top-down method was less dependent on knowledge of chemical reactions and slightly more straightforward. The overwhelming majority of literature regarding the creation of low temperature or liquid metal particles examines top-down approaches.

Hutter and coworkers demonstrated microfluidic channels in deoxygenated and oxygenated silicone oil as a means of creating spherical and oblong droplets down to 30 μm , respectively.⁶⁶ As can be seen in Figure 2-10 above, the oxide layer that forms on the EGaln particles due to the oxygenated silicone allows the droplets to retain their oblong shape, while the particles in deoxygenated oil have no oxide layer and reform to the minimum energy structure (a sphere). Dickey and his colleagues similarly took advantage of the EGaln oxide layer to form droplets down to 1 μm .⁶⁷ As shown in Figure 2-11, EGaln was spread across a poly(dimethylsiloxane) (PDMS) template, possible because the oxide layer readily wets to PDMS, followed by treatment with hydrochloric acid (HCL) vapor to remove the oxide layer and cause the alloy droplets to bead into spheres.⁶⁷

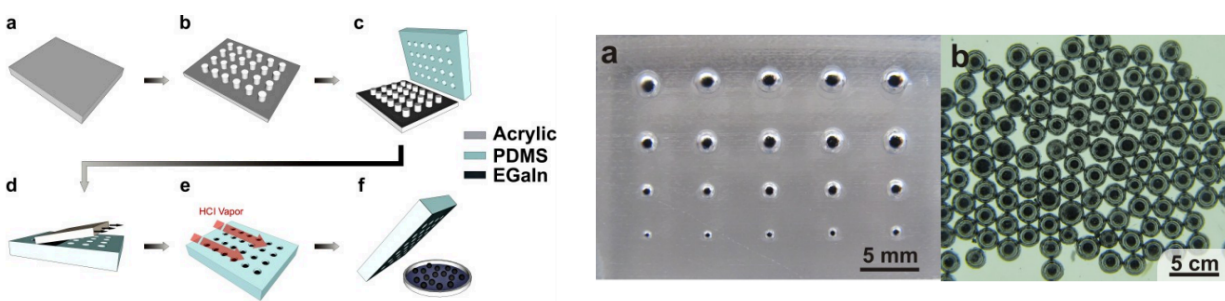


Figure 2-11. Micro-molding technique of EGaln using PDMS template and resulting uniform spherical droplets (Dickey 2014).

In these examples, uniformly sized colloidal particles were demonstrated, albeit in very small yields compared with sonication and with sizes much larger than nanoscale. While the

techniques described above appear attractive for the resulting monodisperse particles, such processes are not suitable or practical for large scale production.

2.4. Surfactants for particle stabilization

2.4.1. Surfactant introduction

According to the Encyclopedia of Colloid and Interface Science, surfactants or “surface active agents” are amphiphilic molecules comprising both a hydrophobic and hydrophilic portion (when in water).⁶⁸ They are often pictured having a head-tail structure as shown in Figure 2-12.

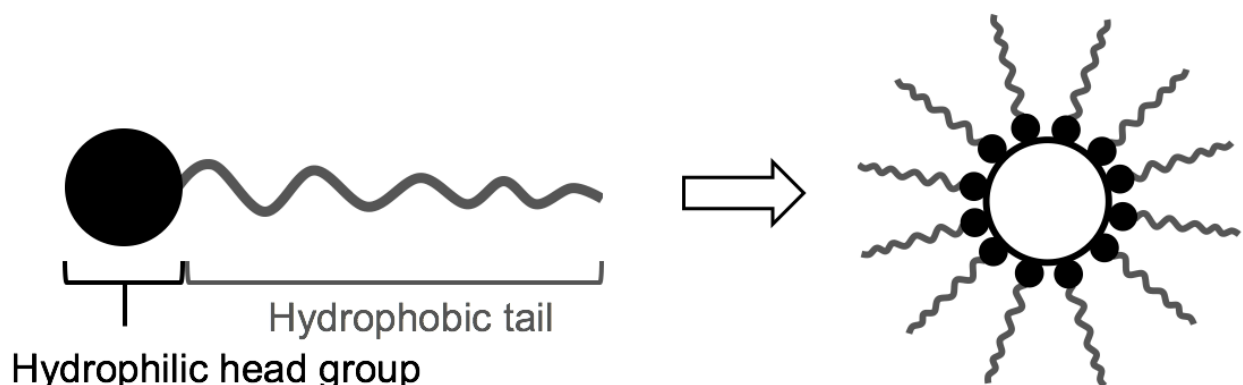
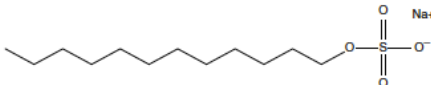
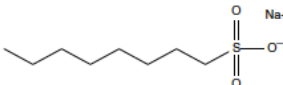
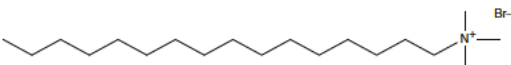
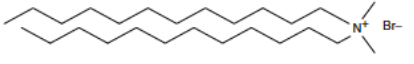
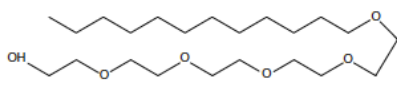
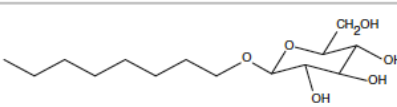
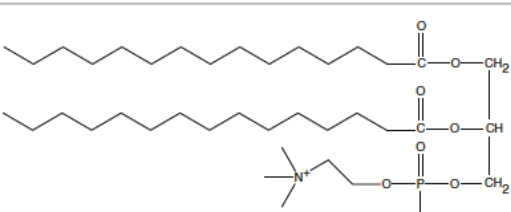
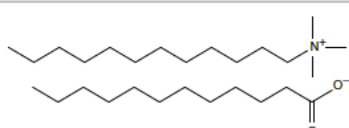


Figure 2-12. (Left) Generic two-component surfactant structure having hydrophilic head and hydrophobic tail; (right) potential orientation of surfactant molecules absorbed on particle.

Surfactants lower the surface tension at an interface (liquid-liquid, solid-liquid), and have numerous applications such as dispersants, wetting agents, emulsifiers and foaming agents.⁶⁹ The absorption of surfactants to a surface reduces its surface tension (proportionally to the amount of absorbed surfactant), which is an energetically driven process that lowers the free energy of the phase boundary. They are ubiquitous across every major industry. Examples of their applications include paints, detergents, cosmetics, plastics, pharmaceuticals, etc. Surfactants are typically classified by their head group (the hydrophilic portion), and are divided into four major classes: anionic, cationic, amphoteric (sometimes called zwitterionic) and nonionic.⁷⁰ As the names

suggest, anionic and cationic surfactants have negative and positive charged associated with their hydrophilic head, respectively. Amphoteric surfactants have both anionic and cationic components, and anionics have hydrophilic groups which do not ionize in water.⁷⁰ A list of common surfactants based on head group type can be found in Table 2-2. Of the four main classes,

Table 2-2. List of common surfactants organized by head group classification. Image from Marques, E.F. et al.

Type	Name	Structure	General class
Anionic	Sodium dodecylsulfate		Alkylsulfates
	Sodium octylsulfonate		Alkylsulfonates
Cationic	Hexadecyltrimethylammonium bromide		Alkyltrimethylammonium halides
	Didodecyldimethylammonium bromide		Dialkyldimethylammonium halides
Nonionic	Dodecylether pentaethyleneglicol		Poly(ethylene oxide) surfactants
	Octylglucoside		Alkylglucosides
Zwitterionic	Dimyristoyl-phosphatidylcholine		Dialkyl-phosphatidylcholines
Catanionic	Dodecyltrimethylammonium dodecanoate		Catanionic surfactants

anionic surfactants are the most common type of synthetic surfactants, specifically single-chained amphiphiles having either carboxylate (R-COO^-), sulfate (SO_4^{2-}), sulfonate (R-SO_3^-) or phosphate (PO_4^{3-}) with alkyl tails ranging in length from 12 to 16 carbons.⁶⁹ Surfactants also

demonstrate interesting behavior at or above a certain concentration known as the “critical micelle concentration” or CMC, in which they self-assemble to form structures called micelles. The concentration at which this occurs is dependent on individual surfactant, the media in which it is dispersed, and other factors (such as temperature and pressure). Shapes of these micelles can be spherical, cylindrical, lamellar or some combination (determined by surfactant structure as well as surround solvent).⁶⁹ Figure 2-13 shows various types of surfactant configurations (including micelle assembly) that can occur in aqueous solutions.

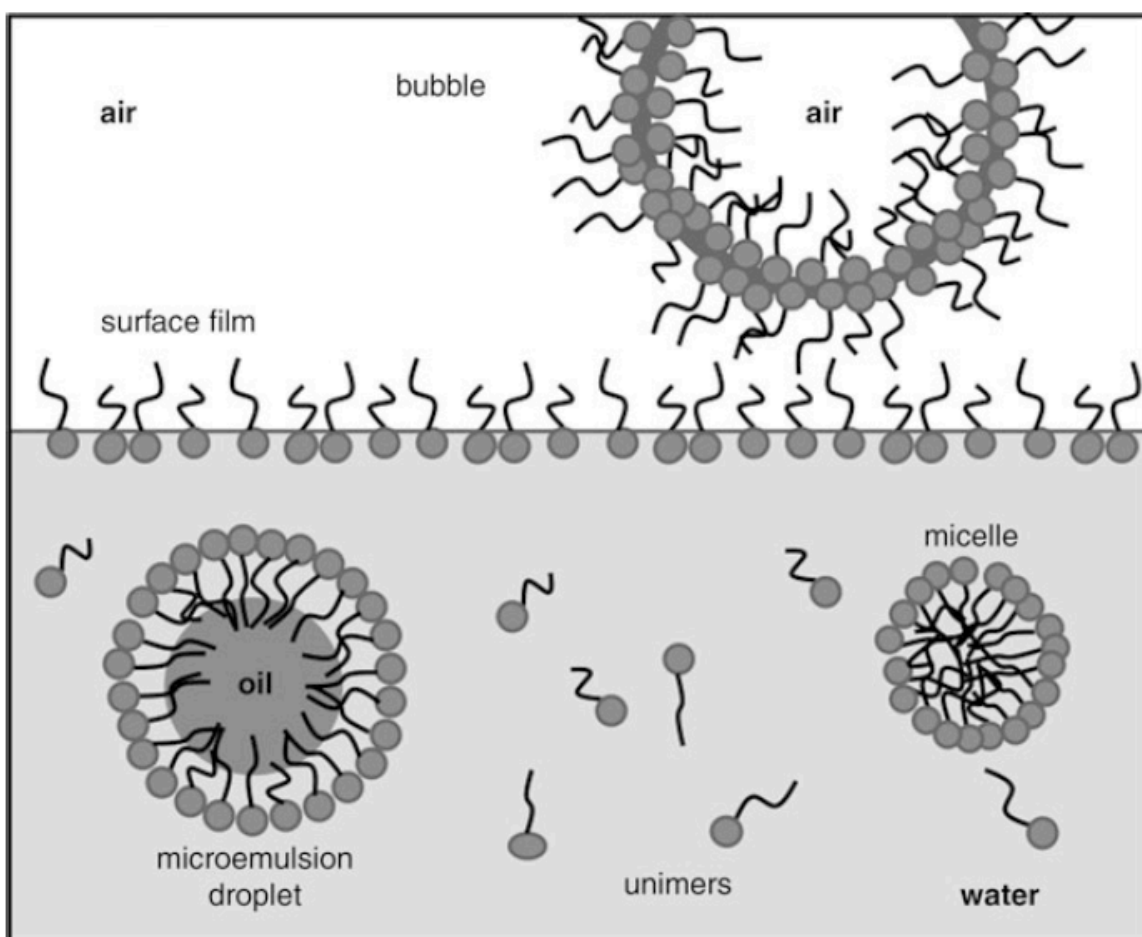


Figure 2-13. Illustrative schematic of potential surfactant arrangements depending on boundary conditions and surface properties. [Marques]

The micelle configuration adopted by a given surfactant is dependent on several parameters such as temperature, surfactant concentration and most importantly, surfactant packing parameter.

The packing parameter P_s is a non-dimensional term defined as the ratio of volume of the fully extended hydrocarbon tail to the product of the tail length and effective area of the head group: $P_s = V_{hc}/a_{hg} * l_{hc}$.⁷¹ Alternatively, preferential aggregate structures may be argued on the basis of a “spontaneous curvature” H_0 or the mean curvature preferred by a surfactant film, defined as $H_0 = \frac{1}{2}(R_1^{-1} + R_2^{-1})$ where R_1 and R_2 are radii of curvature for perpendicular directions.⁶⁹ The relationship of surfactant packing parameter P_s to micelle shape, as well as spontaneous curvature H_0 in an aqueous solution are highlighted in Figure 2-14.

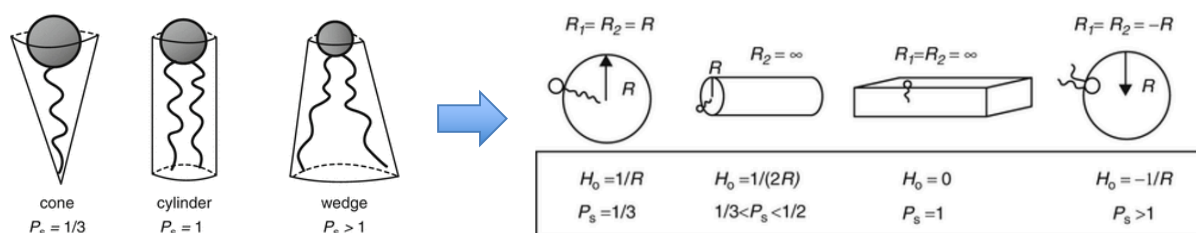


Figure 2-14. Packing parameters (P_s) for some common surfactant morphologies and corresponding micelle geometries formed in an aqueous solution.

2.4.2. Self-assembled monolayers

Self-assembled monolayers or SAMs are highly ordered and oriented assemblies of surfactants which absorb onto a surface.⁷² They form spontaneously due to surfactant head group affinity to a particular substrate,⁷³ and readily absorb due to the overall lowering of surface free-energy.⁷⁴ Experimental evidence points to a step-wise nucleation and growth process of these monolayers, and for temperatures below T_{triple} , it is explained as having three main phases: (1) random molecular dispersion at the surface (low-density phase), (2) disordered configurations or surfactant molecules lying flat on the surface (intermediate-density phase) and (3) an ordered and densely-packed conformation with surfactant molecules extended normal to the surface (high-density phase).⁷⁵ Quite often, SAMs are formed from functionalized long-chain hydrocarbons.⁷²

Though the first recognition and explanation of SAMs is often attributed to Bigelow et al.⁷⁶ for their 1946 publication on hexadecane and solutions of eicosyl alcohol, surely the best known and explored example in the literature is thiol based SAMs on gold nanoparticles (since Nuzzo and Allara's 1983 paper⁷⁷) – the first example in Table 2-3 – followed by trichlorosilanes on silicon dioxide.⁷⁵ While the bulk of SAM literature discusses variations of thiol- and silane-based SAMs, other coupling chemistries have been demonstrated over a broader range of substrates (such as metal oxides and semiconductors).⁷⁸ They are also summarized in Table 2-3.

Table 2-3. Various SAM forming adsorbates for specific substrate materials. Adapted from Jadhav.

Surface	Substrate	Adsorbate(s)
Metal	Au	R-SH, R-S-S-R, R-S-R
	Ag	R-NH ₂ , R-NC, R-COOH
	Pt	R-NC, R-SH
	Pd	R-SH
	Cu	R-SH
	Hg	R-SH
Semiconductor	GaAs (III-V)	R-SH
	InP (III-V)	R-SH
	CdSe (II-VI)	R-SH
	ZnSe (II-VI)	R-SH
Oxide	Al ₂ O ₃	R-COOH
	TiO ₂	R-COOH, R-PO ₃ H
	YBa ₂ Cu ₃ O ₇	R-NH ₂
	ITO ^a	R-COOH, R-SH, R-SiX ₃
	SiO ₂	R-SiX ₃

^a Indium titanium oxide [tin-doped indium oxide: solid solution of indium(III) oxide (In₂O₃) and tin(IV) oxide (SnO₂)].

2.4.3. Surfactants for dispersions

A dispersion of one liquid in another is usually called an emulsion (if the two liquids are immiscible). Common examples are oil-in-water (abbreviate o/w) emulsions, and the opposite of water-in-oil (w/o) emulsions. When surfactants are added to these mixtures they act as “emulsifiers” (i.e. they stabilize the otherwise immiscible droplets). Figure 2-15 shows the typical orientation of surfactant molecules for both o/w and w/o emulsions. For o/w, the molecules orient at the interface so that their hydrophobic tails are immersed in oil, while the hydrophilic head interacts with the surrounding water. In the case of w/o, the opposite is true.

There are two main means by which surfactants stabilize emulsions: electrostatic and steric.⁷⁹ The use of ionic surfactants usually results in electrostatically stabilized emulsions, while nonionic surfactants contribute to sterically stabilized particles.^{79–82} Most colloidal particles carry a charge, so oppositely charged ionic surfactants adsorb to the surfaces and create an electric double layer comprising a tightly bound layer of ions (Stern layer) and a surrounding diffuse layer

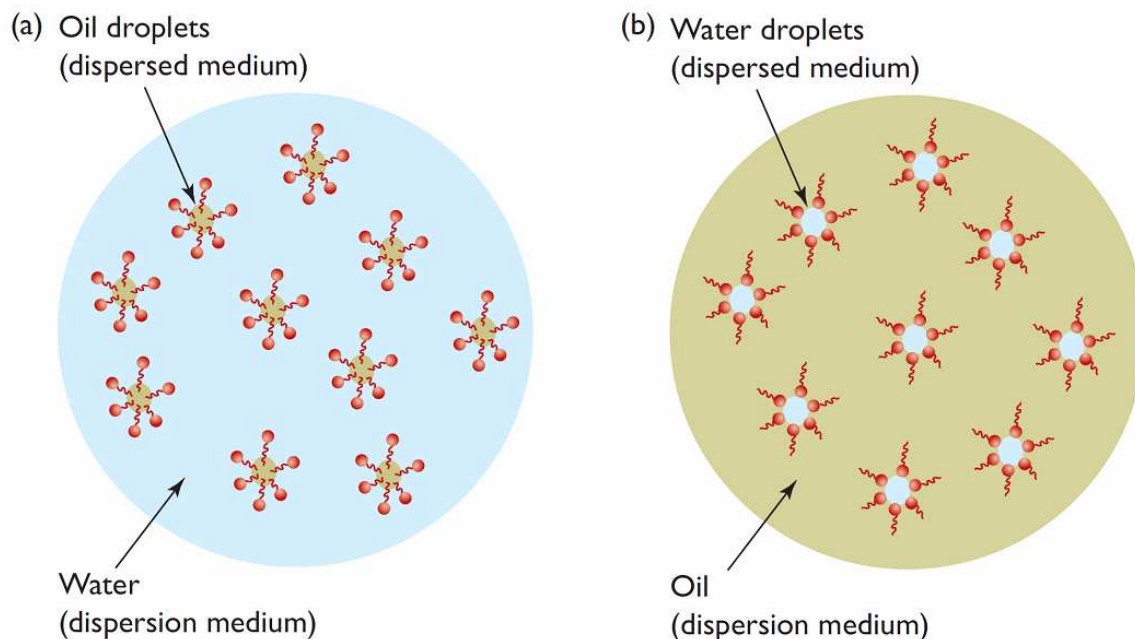


Figure 2-15. Comparison of surfactant behavior for (a) an oil-in-water (o/w) emulsion and (b) a water-in-oil (w/o) emulsion. Image source: <http://nsb.wdfiles.com/local--files/c-9-5-5-4/Emulsion%202.jpg>.

(see Figure 2-16). Repulsion occurs when charged colloidal particles approach so that the electric double layer overlaps (i.e. distance between particle surfaces is less than twice the distance of particle surface to edge of slipping plane), as the confinement of the layers no longer allows for complete decay of electrostatic potential.⁷⁹

Steric stabilization is due to dense coverage of nonionic surfactants bound to particle surfaces by their head groups and whose aliphatic chains physically repel other (in a configuration such as Figure 2-15 (b)). From an energy perspective, repulsion is entropy driven, and any overlap of surfactant chains between colliding particles would result in the loss of configurational entropy.⁷⁹

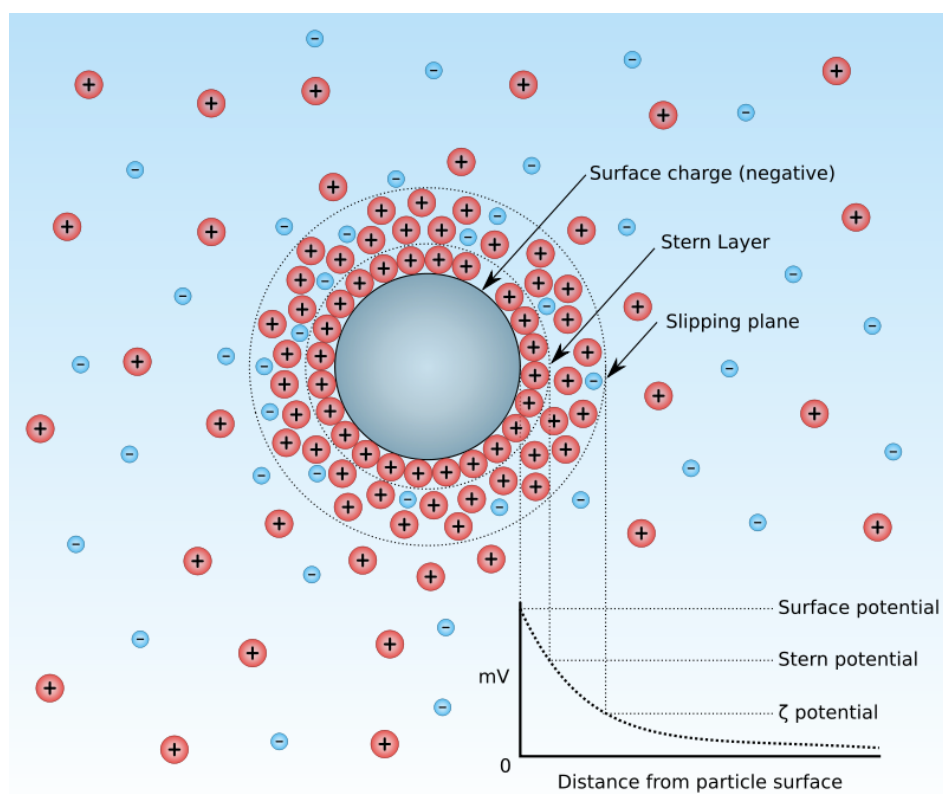


Figure 2-16. Illustration of electric double layer comprising the stern layer of tightly bound ions and a surrounding diffuse layer, the edge of which is called the slipping plane. Electrostatic potential dependence on distance from particle surface is also shown. (Modified and converted to SVG by Mjones1984. Original work by Larryisgood. - Modified image based upon <http://en.wikipedia.org/wiki/F>).

2.4.4. Surfactants for green chemistry

Techniques for the biological synthesis of metallic nanoparticles, specifically through the use of plant-derived molecules, have become increasingly popular within the last two decades for their potential as less toxic and more cost-effective methods.^{83–86} Since the first demonstration of metal nanoparticle biosynthesis or bio-precipitation by Gardea-Torresdey et al. in 1999 producing gold(0) nanoparticles from solutions of gold(III) ions with the aid of alfalfa biomass⁸⁷, a variety of other metallic (Ag and Au especially⁸⁸) and metal oxide particles have been produced with “phytosynthesis.” Table 2-4 highlights just a few examples.

The precise mechanism by which plants extracts are able to reduce and stabilize is not completely understood, though experimental parameters such as plants type, concentration (of both extract and metal ion), pH and temperature have been to have important contributions to final particle size and morphology.^{83,88} Possible chemical constituents responsible for this stabilizing behavior are illustrated in Figure 2-17.

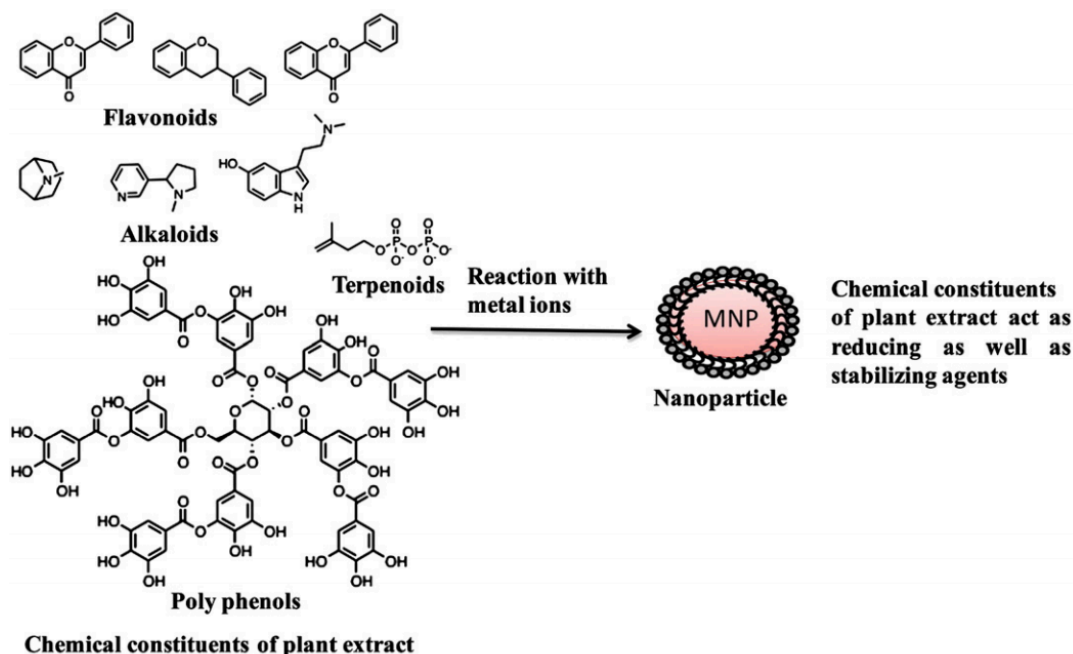


Figure 2-17. Likely chemical components of plant extract responsible for metallic bioreduction. Image adapted from [Mittal et al. 2013].

Table 2-4. Examples of phytosynthesized metallic nanoparticles and their applications. Image modified from [Singh et al. 2016].

Plants	Plant Tissues for Extraction	Types of Nanoparticle	Shapes	Size (nm)	Applications
<i>Euphorbia prostrata</i>	Leaves	Silver and titanium dioxide (TiO ₂)	Spherical	Silver 10–15; TiO ₂ , 81.7–84.7	Leishmanicidal
<i>Sargassum algae</i>	Alga	Palladium	Octahedral	5 –10	Electrocatalytic activities towards hydrogen peroxide
<i>Ginkgo biloba</i>	Leaves	Copper	Spherical	15–20	Catalytic
<i>Panax ginseng</i>	Root	Silver and gold	Spherical	Silver, 10–30; gold, 10–40	Antibacterial
Red ginseng	Root	Silver	Spherical	10–30	Antibacterial
<i>Cymbopogon citratus</i>	Leaves	Gold	Spherical, triangular, hexagonal and rod	20–50	Mosquitocidal
<i>Azadirachta indica</i>	Leaves	Silver	–	41–60	Biolarvicidal
<i>Nigella sativa</i>	Leaves	Silver	Spherical	15	Cytotoxicity
<i>Cocos nucifera</i>	Leaves	Lead	Spherical	47	Antibacterial and photocatalytic
<i>Catharanthus roseus</i>	Leaves	Palladium	Spherical	40	Catalytic activity in dye degradation
<i>Pistacia atlantica</i>	Seeds	Silver	Spherical	27	Antibacterial
Banana	Peel	Cadmium sulfide	–	1.48	–
<i>Nyctanthes arbortristis</i>	Flower	Silver	–	–	Antibacterial and cytotoxic
<i>Anogeissus latifolia</i>	Gum powder	Silver	Spherical	5.5–5.9	Antibacterial
<i>Abutilon indicum</i>	Leaves	Silver	Spherical	5–25	Antibacterial
<i>Pinus densiflora</i>	Cones	Silver	Oval in shape, few triangular shaped	30–80	Antimicrobial
<i>Artocarpus gomezianus</i>	Fruit	Zinc	Spherical	> 20	Luminescence, photocatalytic and antioxidant
<i>Citrus medica</i>	Fruit	Copper	–	20	Antimicrobial
Orange and pineapple	Fruits	Silver	Spherical	10–300	–
<i>Lawsonia inermis</i>	Leaves	Iron	Hexagonal	21	Antibacterial
<i>Gardenia jasminoides</i>	Leaves	Iron	Rock like appearance	32	Antibacterial

2.5. Optical methods

2.5.1. Dynamic light scattering

Dynamic light scattering (DLS) is an optical technique based on the scattering of light (typically a monochromatic laser) by small particles suspended in solution. As the name implies, DLS is used to capture fluctuations in intensity over a set period of time (whereas static light scattering measures the intensity of light at a single time).⁸⁹ Figure 2-18 provides a representative sketch of the effect that suspended particle size has on these intensity fluctuations: smaller particles resulting is faster fluctuations (and shorter correlation times). As light interacts with a material, the electric field induces oscillation in the electrons of that material, which then scatter light – the

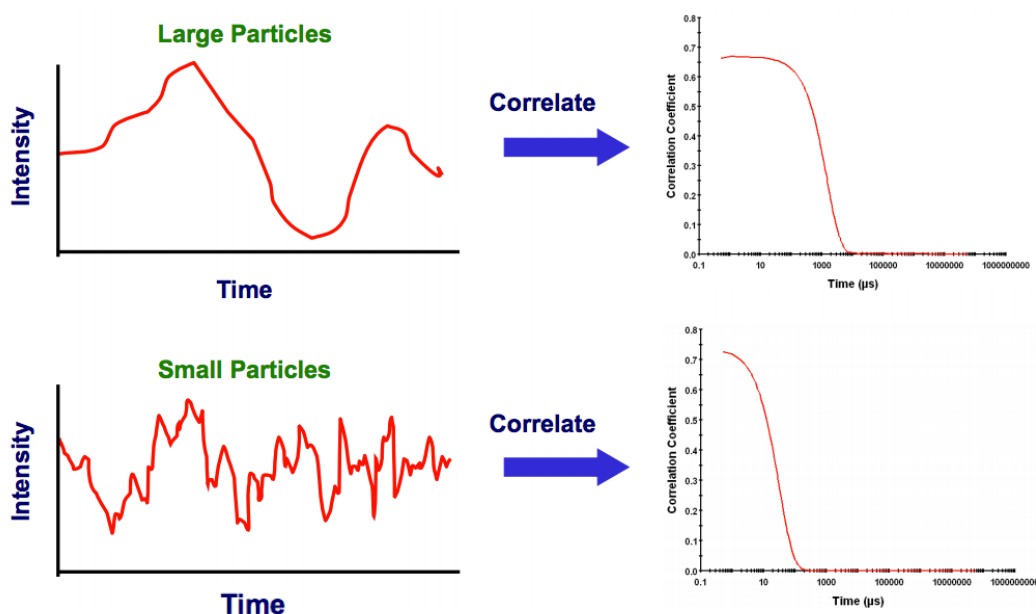


Figure 2-18. Representative intensity fluctuations and corresponding correlation functions measured by DLS for relatively large and small particles. Image adapted from <http://149.171.168.221/partcat/wp-content/uploads/Malvern-Zetasizer-LS.pdf>.

properties of which (e.g. polarization, angular distribution, intensity) are dependent upon the material characteristics (such as size, shapes and molecular interactions).⁹⁰ Thus, using DLS one can measure time dependent properties such as translational diffusion coefficient and

correspondingly, hydrodynamic radius.⁹¹ The normalized intensity autocorrelation function^{89,92} measured by DLS is a function of wave vector q and delay time t :

$$g_2(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I(q, 0) \rangle^2} \quad (2.1)$$

can be rewritten in terms of electric field using the Siegert relationship:

$$g_2(q, t) = 1 + f^*[\alpha g_1(q, t)]^2 \quad (2.2)$$

where $g_1(q, t)$ is the field autocorrelation function, f^* is a correction factor determining the intercept-to-baseline ratio and α represents intensity to due large correlation times.^{89,92} This so called field autocorrelation function can then be analyzed using several approaches to obtain useful information, namely the relaxation time (τ_r) or decay rate (Γ), where $\tau_r = 1/\Gamma$.⁹² The simplest and most straightforward approach is to fit a single exponential decay the correlation curve (assuming the displays a single, fast decay). Another technique is to use a stretched exponential called the Kohlrausch-Williams-Watts (KWW) function given as $g_1(t) = A \exp\left(-\left(\frac{t}{\tau_r}\right)^\beta\right)$ where here, β is a stretching factor ($0 < \beta < 1$) with τ_r is the relaxation time.⁹² The KWW fitting function has been well established in the literature and used to describe nonlinear relaxation of proteins, polymer isomers and SAM covered spherical metal nanoparticles.⁹³⁻⁹⁵ Once the relaxation time is determined, it and the wave vector q can be used to determine the diffusion coefficient D by

$$\tau_r = (Dq^2)^{-1} \rightarrow D = \frac{1}{\tau_r q^2} = \frac{\Gamma}{q^2} \quad (2.3)$$

for wave vector

$$q = \left(\frac{4\pi n_0}{\lambda_0}\right) \sin\left(\frac{\theta}{2}\right) \quad (2.4)$$

where n_0 , λ_0 and θ are index of refraction (of the dispersant), wavelength of the light source (laser) and scattering angle (in radians), respectively. The Stokes-Einstein equation then allows for determination of hydrodynamic radius

$$R_h = \frac{k_b T}{6\pi\eta D} \quad (2.5)$$

where k_B is the Boltzmann constant, T is temperature and η is viscosity (of the dispersant).⁹⁰

The above methods result in a single average particle size. Other techniques can be used to estimate the width of particle size distributions including the cumulant analysis (based on the sum of exponentials)^{96,97} or alternatively, the CONTIN algorithm (technique more suitable for very polydisperse systems due to need for an inverse Laplace transform of the measured autocorrelation function).^{98,99} An example of a particle size distribution of EGaIn using dodecanethiol and determined using a CONTIN method (via DLS Malvern software) is shown by Figure 2-19. The narrow single peak indicates a relatively monodisperse solution.

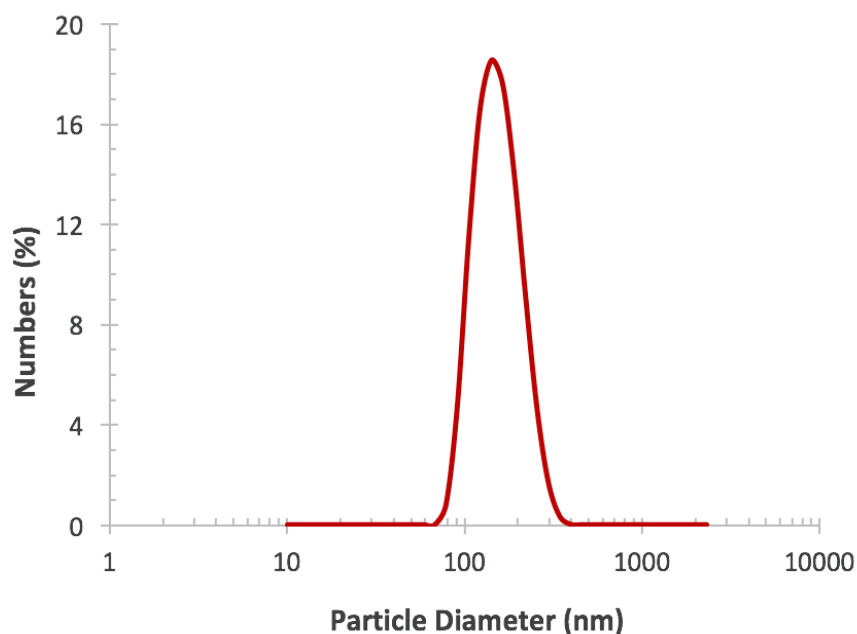


Figure 2-19. Number percent size distribution obtained from Malvern software CONTIN analysis for representative sample of EGaIn in 1 mM EtOH and dodecanethiol.

The distribution given by Figure 2-19 is a number distribution. Size data from dynamic light scattering can be represented as a number, volume or intensity distribution which show the number of particles, the total volume of particles, and the amount of scattered light scattered by differently sized particles. While all three represent the same information, intensity and volume distributions tend to highlight larger particles since from Rayleigh scattering (or scattering due to particles much smaller than the wavelength of light), intensity is proportional to particle size d^6 .¹⁰⁰ The number distribution tends to emphasize the smaller particles present, and also allows for direct comparison with other size characterization techniques (such as electron microscopy). Hence, all calculations and sizes obtained from light scattering derived from a number weighted size distribution.

2.5.2. UV/Vis spectroscopy

UV/Vis spectroscopy, short for ultraviolet-visible spectroscopy, is spectroscopy done in the ultraviolet-visible light spectrum (i.e. wavelengths approximately 200 – 800 nm). Thus, for UV/Vis there are two separate light sources, for visible and UV range, and a monochromator to separate the beam into component wavelengths.¹⁰¹ The intensity of light after having passed through a sample is measured across the range of wavelengths, which will fluctuate according to which frequencies of light cause excitation or absorption by the material.¹⁰¹ This measured intensity is often presented as compared to a reference intensity (i.e. 100% light source transmission) according to the Beer-Lambert law: $A = -\log_{10} \left(\frac{I}{I_0} \right) = \epsilon lc$ (where l = path length, c = concentration, and ϵ can represent either molar absorbance coefficient or extinction coefficient depending on the units selected).^{101,102} Application of the Beer-Lambert law can be found in section 5.3.4.

2.5.3. Mie scattering theory

Mie theory is the solution to Maxwell's equations for the scattering (and absorption) of light by a sphere. The theory was first proposed by Gustave Mie in his famous 1908 paper entitled "Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen" (translation: Contributions to the optics of turbid media, particularly of colloidal metal solutions) in which he endeavored to understand colloidal gold particles in water.¹⁰³ In contrast to Rayleigh scattering, Mie theory examines the case for when the refractive index of the scatterers is significantly different from that of the medium in which they are dispersed, for which there are both "fixed spatial relations" between scatterers and also "a strong dependence of the electric field amplitude" on position.⁹⁰ For this type of scattering, complete analytical solutions exist only in the case of spherical particles,⁹⁰ as in Figure 2-20.

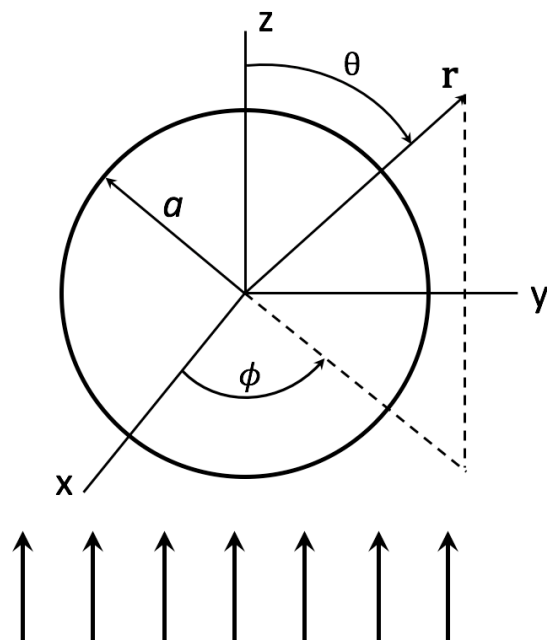


Figure 2-20. Spherical polar coordinate system used to analyze the interaction of an incident electromagnetic wave (parallel arrows) on a spherical particle of radius "a." Imaged based on diagram presented by Bohren and Huffman.

Bohren and Huffman provide a rigorous and thorough mathematical treatment of Mie theory and of finding the internal and scattered electromagnetic fields from the vector wave equations.¹⁰⁴ The most useful quantities to come from Mie theory are the scattering coefficients,

specifically those for the external scattering by a sphere (known in the literature as a_n and b_n).¹⁰⁴ From these scattering coefficients come the exact expressions for cross sections (in unit area) both for scattering (C_{sca}) and extinction (C_{ext}).¹⁰⁴ The absorption cross section (C_{abs}) can be easily recovered from $C_{ext} - C_{sca}$, which can then be used to calculate the scattering and extinction cross sections

$$C_{sca} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \quad (2.6)$$

$$C_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)\text{Re}\{a_n + b_n\} \quad (2.7)$$

for which k is a wave vector.¹⁰⁴ The extinction cross section is representative of the total attenuation of the transmitted light source due to the interaction with the suspended particles. Thus, the scattering and extinction coefficients are solved by plugging in the expressions for a_n and b_n , provided by both Bohren and Huffman¹⁰⁴ and H.C. Hulst¹⁰⁵ in terms of Riccati-Bessel functions

$$a_n = \frac{\psi'_n(y)\psi_n(x) - m\psi_n(y)\psi'_n(x)}{\psi'_n(y)\zeta_n(x) - m\psi_n(y)\zeta'_n(x)} \quad (2.8)$$

$$b_n = \frac{m\psi'_n(y)\psi_n(x) - \psi_n(y)\psi'_n(x)}{m\psi'_n(y)\zeta_n(x) - \psi_n(y)\zeta'_n(x)}. \quad (2.9)$$

In the notation of Hulst, m is theratio of the refractive index of the particle to the medium or N_1/N (N is assumed to be 1), x is wave vector k multiplied by radius of the sphere a or equivalently $x = ka = 2\pi Na/\lambda$, and lastly $y = mka = 2\pi N_1 a/\lambda$.¹⁰⁵ Hulst also defined the Riccati-Bessel functions (which differ from spherical Bessel functions by the additional factor “ z ”)

$$\psi_n(z) = \sqrt{\left(\frac{\pi z}{2}\right)} J_{n+\frac{1}{2}}(z) \quad (2.10)$$

$$\chi_n(z) = -\sqrt{\left(\frac{\pi z}{2}\right)} \mathcal{N}_{n+\frac{1}{2}}(z) \quad (2.11)$$

$$\zeta_n(z) = \sqrt{\left(\frac{\pi z}{2}\right)} \mathcal{H}_{n+\frac{1}{2}}^{(2)}(z) \quad (2.12)$$

where $\mathcal{J}$, $\mathcal{N}$ and $\mathcal{H}^{(2)}$ are spherical Bessel functions of the first and second kind and a Hankel function of the second kind, respectively.^{104,105} As is apparent from equations (3) and (4), only the solutions to (5) and (7) and their derivatives with respect to z are needed for the two scattering coefficients. However, in order to solve (7), the relationship of the two Bessel functions is defined as

$$\mathcal{H}_n^{(2)}(z) = \mathcal{J}_n(z) - i\mathcal{N}_n(z) \quad (2.13)$$

and so

$$\zeta_n(z) = \psi_n(z) - i\chi_n(z). \quad (2.14)$$

Thus, for spherical particles of known size and index of refraction (both real and imaginary) in a matrix with known index of refraction, the extinction and scattering cross sections can be calculated for a certain wavelength.

3. Experimental

3.1. EGaIn synthesis

First, raw Gallium (Ga) and Indium (In) (both 99.99% pure, Gallium Source LLC) were combined to form the eutectic composition (75.5% Ga, 24.5% In by weight). The glass jar containing the metals and a magnetic stir bar was placed on a hot mixing plate at about 200°C until the alloy appeared thoroughly mixed. Direct scanning calorimetry (DSC) (Q20, TA Instruments) was then used to verify that the alloy was indeed the eutectic of Ga-In. Figure 3-1 shows the plot obtained from this test. The melting temperature (the minimum value, labeled T_m on the graph) was determined as 16.35°C, which is just over a 1°C deviation from the literature cited T_m of EGaIn

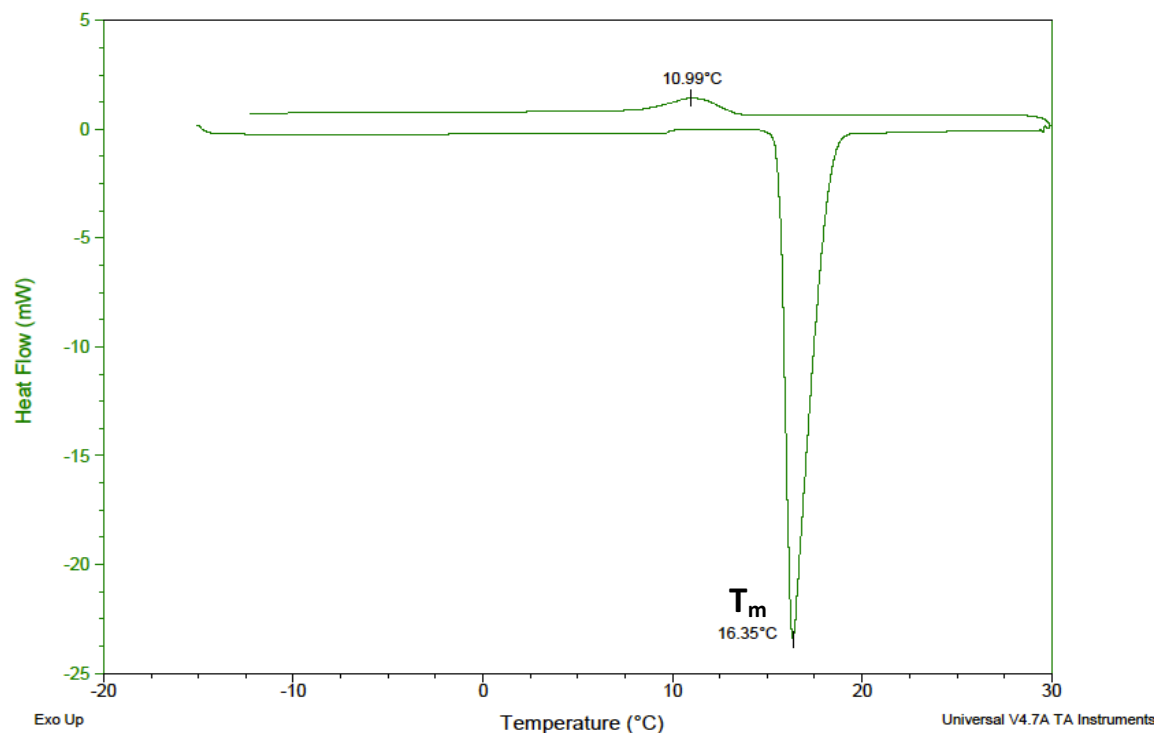


Figure 3-1. Plot of heat flow versus temperature from direct scanning calorimetry of 5.8 mg sample of EGaIn. Melting temperature is shown as 16.35oC, which is in excellent agreement with the literature value of 15.3oC [19].

(15.3°C). Once confirmed as the eutectic, approximately 1.5 mL of EGaIn was pulled into a syringe that was first repeatedly drawn with nitrogen. The liquid metal was then injected (22 Gauge, Becton Dickinson) into a 2 mL capped borosilicate glass vial (Screw-thread vial, VWR) through the red PTFE/white silicone septa. The vial was flushed with nitrogen for 5 minutes prior to the addition of EGaIn, which in addition to first purging the syringe, greatly reduced initial oxide formation (as evidenced by the resultant shiny metallic surface of the EGaIn within the vial). As a final precaution against oxygen “contamination,” the caps were tightly wrapped with a layer of Parafilm M (Bemis Company, Inc.).

3.2. Fabrication of EGaIn + polymer composite transducer

Gallium-Indium alloys (and EGaIn specifically) have already been used to make soft and stretchable resistive strain sensors^{2-5,45} via photolithography and replica molding⁴ and manual injection filling of patterned elastomer channels.^{2,5,45} While successful as a “liquid wire” for sensing applications, utilizing EGaIn as an electrode proves a more challenging endeavor. In contrast to existing applications, DEAs require a thin film of liquid EGaIn to be sealed over a large area. The electrode should be as thin as possible to minimize added mechanical impedance to dielectric deformation. As demonstrated in Figure 3-2(a), a 100 μm layer of the silicone-based elastomer PDMS was applied on a flat metal sheet using a 5 μm resolution thin film applicator (ZUA 2000 Universal Applicator, Zehntner GmbH) after treatment of the substrate with mold release (Ease Release® 200, Mann). After fully curing on a hot plate for approximately 20 minutes at 95°C, the first set (for making multiple DEAs) of EGaIn electrodes were “painted on” using an elastomer-tipped 3D printed pen in conjunction with laser-cut (VLS3.50, Universal Laser Systems) stencils of plain white printer paper.¹⁰⁶

Due to the surface oxidation of EGaIn in air, it selectively wets only to the surface of the PDMS dielectric layer and not the paper mask as it is brushed and dabbed along the stencil electrode.¹⁹ After applying a layer of EGaIn to fully cover the electrode geometry, the paper mask was carefully removed, and a 250 μm thick layer of PDMS is applied over the exposed liquid electrodes. Before this sealing step, however, a thin strip of adhesive-backed conductive paper (3M™ Fabric Tape CN-3490) that was approximately 1.5 mm $\times$ 20 mm was placed in contact with each patterned liquid metal electrode (see Figure 3-2(b)) for eventual interfacing with external electronics. After curing this encapsulating layer on a hot plate, the composite PDMS – EGaIn –

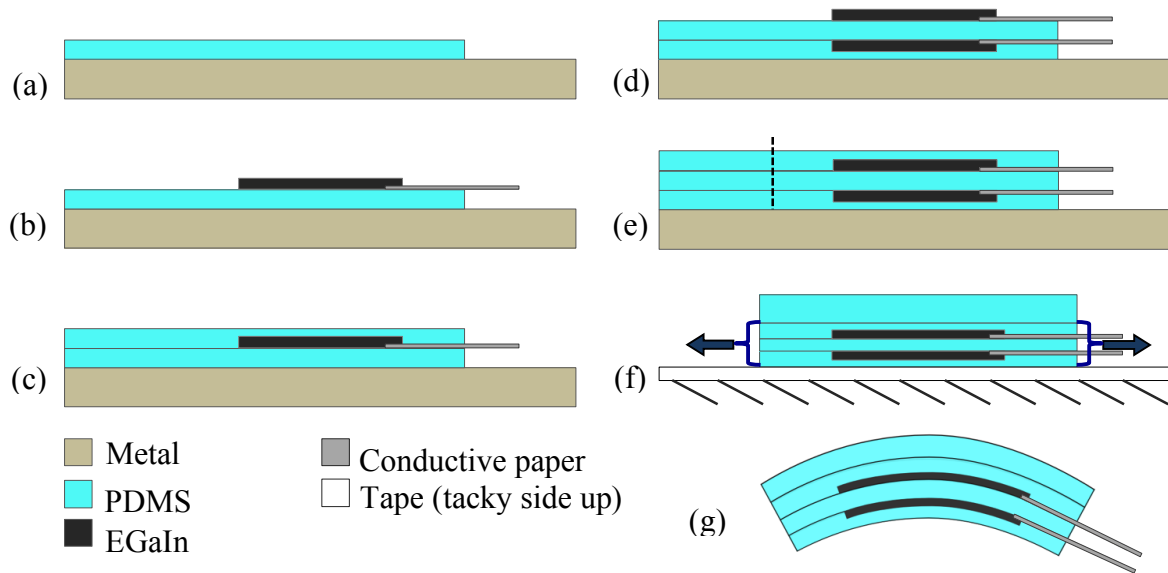


Figure 3-2. Curved DEA fabrication process showing (a) application of 100 μm dielectric layer, (b) depositing first set of EGaIn electrodes and placement of paper leads, (c) encapsulation with 250 μm PDMS layer, (d) flipping of composite and placement of second EGaIn electrode set, (e) final 250 μm sealing layer and removal of excess elastomer, (f) stretching of composite DEA and application of 600 μm PDMS “cantilever” layer and (g) final curved DEA configuration.

PDMS film was carefully peeled from the disk and flipped so that the other side of the dielectric layer was exposed.

Care was taken to minimize trapped air beneath the flipped layer when replacing it on the substrate, which could result in a non-planar surface for the second half of fabrication. A second set of electrodes was applied and encased in a similar fashion using the same stencil orientation, thus ensuring the leads of the two electrodes would be spread apart, as seen in Figure 3-2(d-e). The last step required for creating the pre-curved DEA involved pre-straining the layers of encased liquid metal electrodes and bonding with a thicker, unstrained PDMS backing layer. Because this last PDMS strip was bonded to the composite DEA while strained, the stresses from the released contracting layer forced the final equilibrium position of the DEA to be curved, as shown in Figure 3-2(g). This straining and bonding step, shown in Figure 3-2(f), was achieved by securing a strip of clear shipping tape (1.89” Heavy Duty, Office Depot®), tacky side up, to a rigid metal substrate, marking the electrode placement endpoints for 10% strain (in this case a distance of 22 mm), and

placing the stretched composite to align with the marks. Lastly, a 600 μm thick layer of PDMS was applied over the stretched DEA and placed for a final bake on the hot plate at 95°C.

3.3. EGaIn nanoparticle preparation

The following procedure for the synthesis of EGaIn nanoparticles was initially largely inspired by the work of Hohman et al.¹³ Solutions of various selected surfactants were prepared in ethanol (200 proof, Anhydrous, PHARMCO-AAPER) at 1 mM concentrations (see 5.3.1 for information on surfactants) and filtered three times (0.45 μm pore, PTFE membrane, PALL Acrodisk). From the given surfactant solution of interest, 1.5 mL was extracted and pipetted (FINNPIPETTE F₁, Thermo Scientific) into a clean (x3 solvent wash) 2 mL borosilicate vial (Screw-thread vial, VWR). Nitrogen was bubbled through the solution for 5 minutes to remove much of the dissolved oxygen. A syringe (1.0 mL TB, Becton Dickinson) was then used to extract approximately 0.2 mg of EGaIn (22 Gauge, Becton Dickinson) and inject it into the vial of surfactant solution. The vial was then capped, wrapped with Parafilm M (Bemis Company, Inc.), and placed in a secondary containment jar (120 mL Polypropylene, Qorpak) which was half filled with deionized water (Barnstead D3750, Barnstead Nanopure, Thermo Scientific). A Branson 1510 bath ultrasonicator was filled with the same deionized water, and the jar was suspended in the center of the bath with the aid of a custom cut acrylic sheet (1/8" Optically Clear Cast Acrylic Sheet, McMaster-Carr). The acrylic sheet was cut using a bench-top CO₂ laser (VLS3.50, Universal Laser Systems) to fit directly atop the sonicator with a centered hole to accommodate the polypropylene jar.

The jar was sonicated at a continuous 40 kHz for 60 minutes (water initially at $\sim 25^{\circ}\text{C}$, with no additional temperature control). After sonication, the vial was removed from within the jar and allowed to decant for 24 hours in an upright position. Exactly 1.0 mL of supernatant was then pipetted away and introduced to a clean (x3 solvent wash) disposable semi-micro cuvette (Brand UV-Cuvette, Brandtech Scientific Inc.) and used directly for testing. Figure 3-3 illustrates this basic fabrication process.

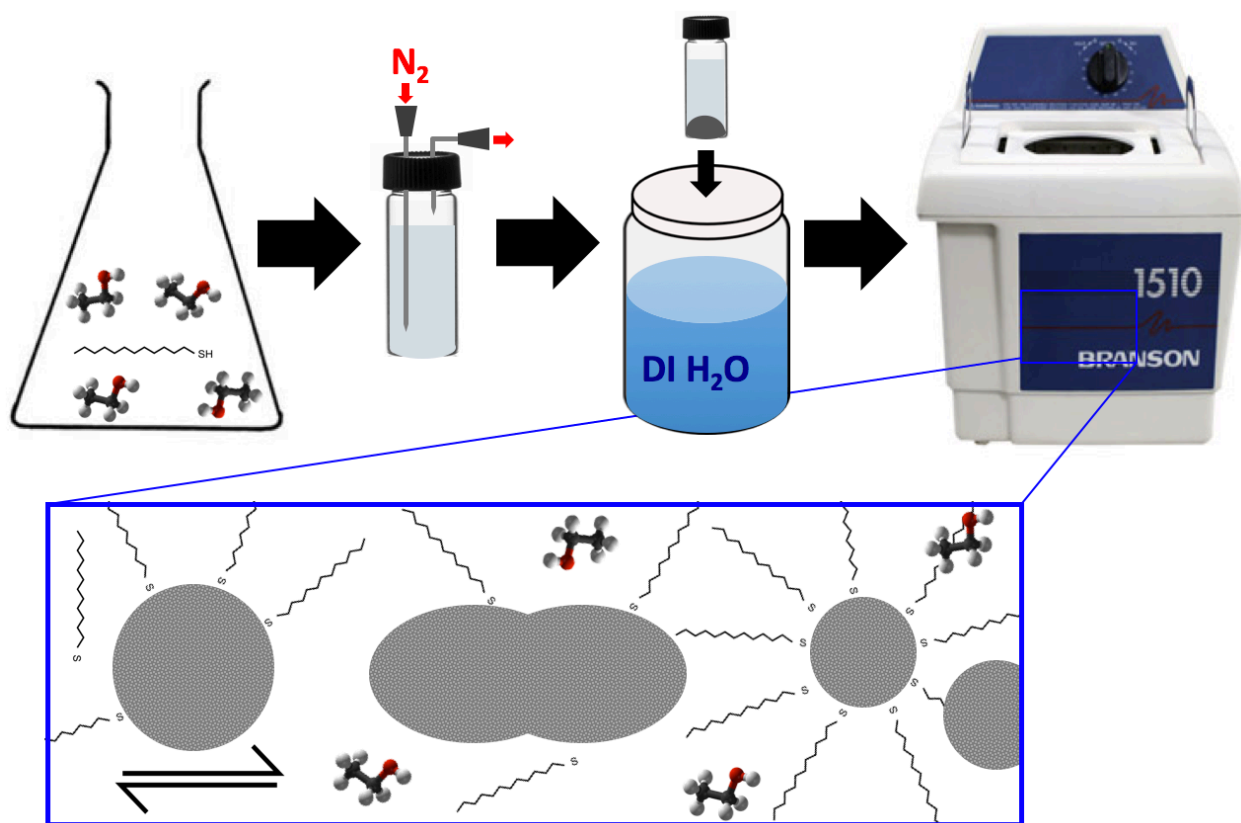


Figure 3-3. Schematic of EGaIn nanoparticle fabrication process. From (top) left to right, solution of EtOH and some surfactant was mixed to appropriate concentration and filtered x3, then 1.5 mL was pipetted into a vial and bubbled with N_2 . An EGaIn droplet (~ 0.2 g) was injected into the closed vial, which was then placed into a jar of DI water and suspended in the bath sonicator. The zoomed in view (bottom) shows the shearing and cleaving of EGaIn particles due to cavitation effects and surfactants.

3.4. Issues encountered during LMP synthesis

3.4.1. Sonicator location dependence

During early stages of developing the nanoparticle synthesis procedure, samples were initially made in batches of four. This was accomplished using an acrylic sheet with four evenly spaced laser-cut holes specifically sized for the secondary containment polypropylene jars (see

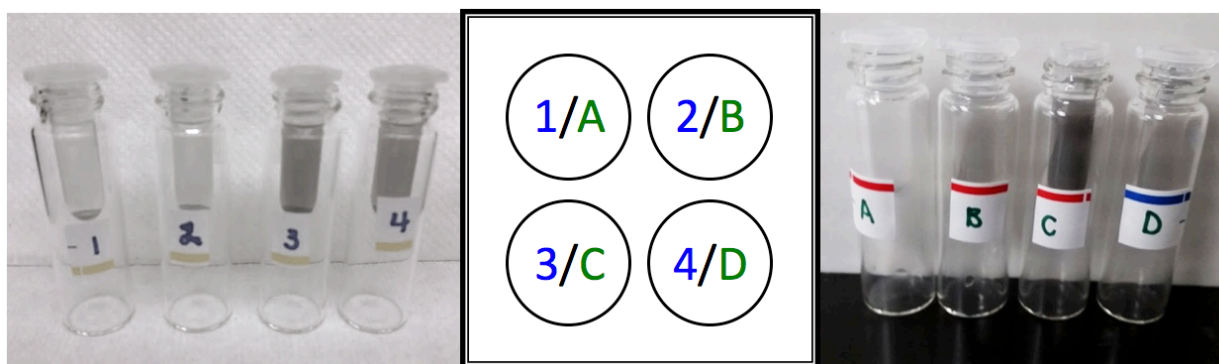


Figure 3-4. Noticeable difference in sample dispersity based on location in sonicator (center), as well as difference in results when using identical sonicator models in Bockstaller lab (left) and Majidi lab (right).

schematic in Figure 3-4, *center*). However, it was apparent that the samples were not symmetrically sonicated (indicative by color after removal) and thus effectiveness of the sonication was strongly dependent on placement in the bath. Testing using two identical Branson 1510 bath sonicators displayed the same trend of inconsistency within the bath, as well as inconsistency across equipment (Figure 3-4 *left* and *right*). Thus, all subsequent samples were sonicated one at a time, centered in the bath and using the same sonicator (in the Bockstaller lab).

3.4.2. Repeatability of EGaIn addition

The method explained in 3.3 for extracting and adding EGaIn into the sample vials is inherently prone to repeatability errors. EGaIn behaves as a non-Newtonian fluid due to its oxide formation, and inconsistently fills a pipette tip or syringe needle (even after attempted

minimization of oxide presence through nitrogen bubbling). Care was taken to fill the syringe to the same line for every sample (0.05 mL), although gravimetric measurements show a variation of added EGaIn across samples. However, this deviation in initial added EGaIn mass was not correlated to the resulting yield. Figure 3-5 below shows the spread of added masses and corresponding final concentrations (at 72 hours) over 8 samples of the same surfactant (octylamine).

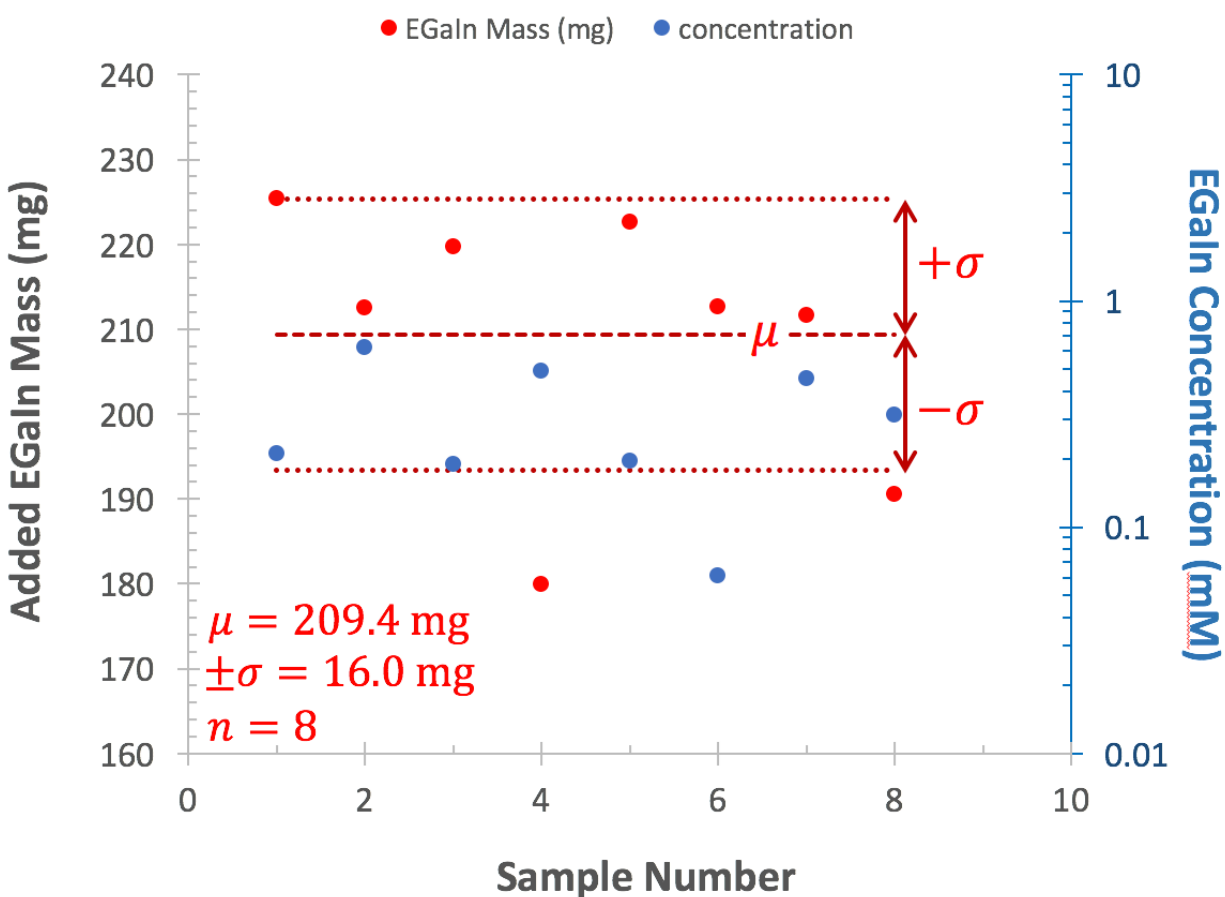


Figure 3-5. Plot of EGaIn mass added for $n = 8$ samples to highlight difficulty of high precision repeatability. Average EGaIn mass and standard deviation are listed as μ and σ , respectively. All samples were made with 1 mM octylamine in EtOH. EGaIn concentrations are at 72 hours.

3.5. Characterization of EGaIn nanoparticles

3.5.1. Dynamic light scattering

Dynamic light scattering (DLS) testing was done using a Malvern Zetasizer Nano ZS. The run settings of the Malvern were kept at the default single backscatter angle of 173°, the number of measurements per sample was set to five, and equilibrate time prior to beginning measurements was specified as 60 seconds.

Samples were measured at 24, 48 and 72 hours following their initial decanting process (i.e. the 24-hour time point was 24 hours from the time of sample vial removal from the bath sonicator). A time period of 3 days (72-hour mark) was considered long enough to judge sample stability, as solutions of suspended particles are typically used within the first 12 to 24 hours of formation. After completion of all measurements, the raw correlation data (expressed as a normalized intensity autocorrelation function, $g^{(2)}$) as well as the size based number distribution (based on software provided CONTIN fits of the measured intensity data) of each sample were exported for particle size analysis.

3.5.2. UV/Vis spectroscopy

In conjunction with DLS measurements, UV/Vis spectroscopy (Cary UV/Vis 300 spectrophotometer, Agilent Technologies) was performed on each sample to measure percent absorbance by suspended EGaIn nanoparticles. An initial measurement of neat ethanol was taken to provide a baseline for all subsequent measurements (this same baseline correction was applied to each measurement and for every sample). All readings were performed over the wavelength range of 800 – 200 nm, with an interval of 1.0 nm and a scan rate of 600 nm/min. Additionally, the Cary was always run in double beam mode with the spectral band width (SBW) set at 2.0 nm.

3.5.3. Electron microscopy

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed on a JEOL 2000EX operated at 200 kEV and Quanta 600 Environmental SEM or ESEM (operated in low vacuum mode, ~ 0.98 Torr), respectively. For TEM, particles were drop cast onto a carbon or formavar backed Cu grid (300 mesh, Ted Pella) whereas for ESEM, a droplet of particles in solution was placed directly in the sample chamber on a steel mount. It was observed that while operating both instruments, continued focus of the beam on the liquid particles could cause spreading and in rare cases, coalescence with neighboring droplets.

3.5.4. Micrograph processing and analysis

ImageJ (a free Java-based image processing program: <https://imagej.nih.gov/ij/>) was used to process and analyze all electron microscopy micrographs for comparison against DLS number weighted size distribution results. As demonstrated in Figure 3-6, images were first adjusted for

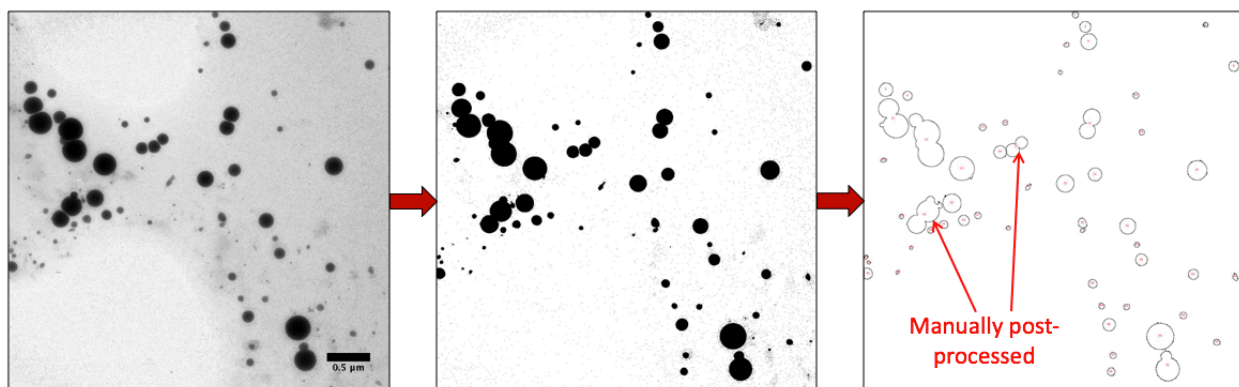


Figure 3-6. (*Left*) Original TEM micrograph; (*center*) image after threshold adjustment; (*right*) sketch of detected particles from threshold image after applying “particle analysis” feature. For the cases of multiple particles grouped together, manual measurements were taken of constituent particles. Example is for 1 mM tannic acid in ethanol. Scale bar is 500 nm.

greater contrast (using image “threshold” tool as well as sometimes applying filters), and then evaluated for particles. Individual detected particles were automatically numbered after running the “particle analysis” feature. For cases where multiple particles were grouped as a single larger

particle by the software (often due to inadequate spacing and therefore contrast between LMPs), manual measurements were made of constituent particles. As all particles were spherical, fitting circles to particles using the software was straightforward. However, micrographs with fewer of these features were preferred for analysis in order to reduce the possibility of human measurement error. The number of particles counted for creating size distributions creation ranged from approximately 150 – 200. Total particle count was based on subset of usable images from a total of 50 taken at between 10000 – 20000x magnification. Locations for imaging were spaced in a grid-like fashion to cover the inner radius of the circular 300-mesh TEM Cu grid (~2 mm).

3.6. Other experimental procedures

3.6.1. Cryogenic milling

One approach explored for the manufacturing EGaIn nanoparticles before sonication was fully adopted was the use of a cryogenic mill. A SPEX SamplePrep 6870 Large Freezer/Mill[®], shown schematically below in Figure 3-8 (*left*), was used to pulverize frozen droplets of EGaIn by rapidly shaking a vial containing EGaIn and a metal rod while immersed in a 4 – 6 L bath of liquid nitrogen. Numerous combinations of adjustable settings were investigated, such as total number of cycles, precooling time, run time per cycle, cool time between cycles, and cycle rate (number of cycles per second). A typical measurement setting is presented in Figure 3-8 (*top right*), along with results from using those settings.

The milled EGaIn presented highly variable sizes, shapes and even phases (some of the particles appeared melted). Investigation of the smallest of the particles or “powder” with SEM (Quanta 600 ESEM) resulted in similar findings (i.e. rough, non-uniform particles), as shown in Figure 3-7.

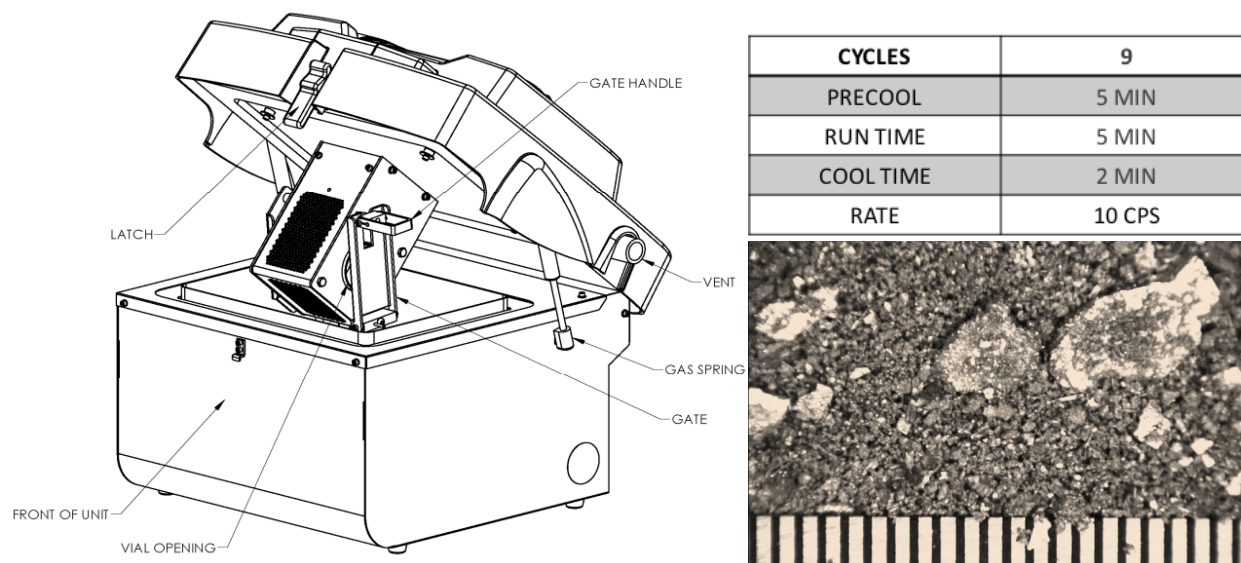


Figure 3-8. (Left) Schematic of SPEX SamplePrep 6870 Large Freezer/Mill[®] from manual; (top right) representative settings typical machine run; (bottom right) result of cryomilling with above settings shows non-uniform EGaIn platelets over a range of length scales. Ruler scale shows 1 mm ticks.

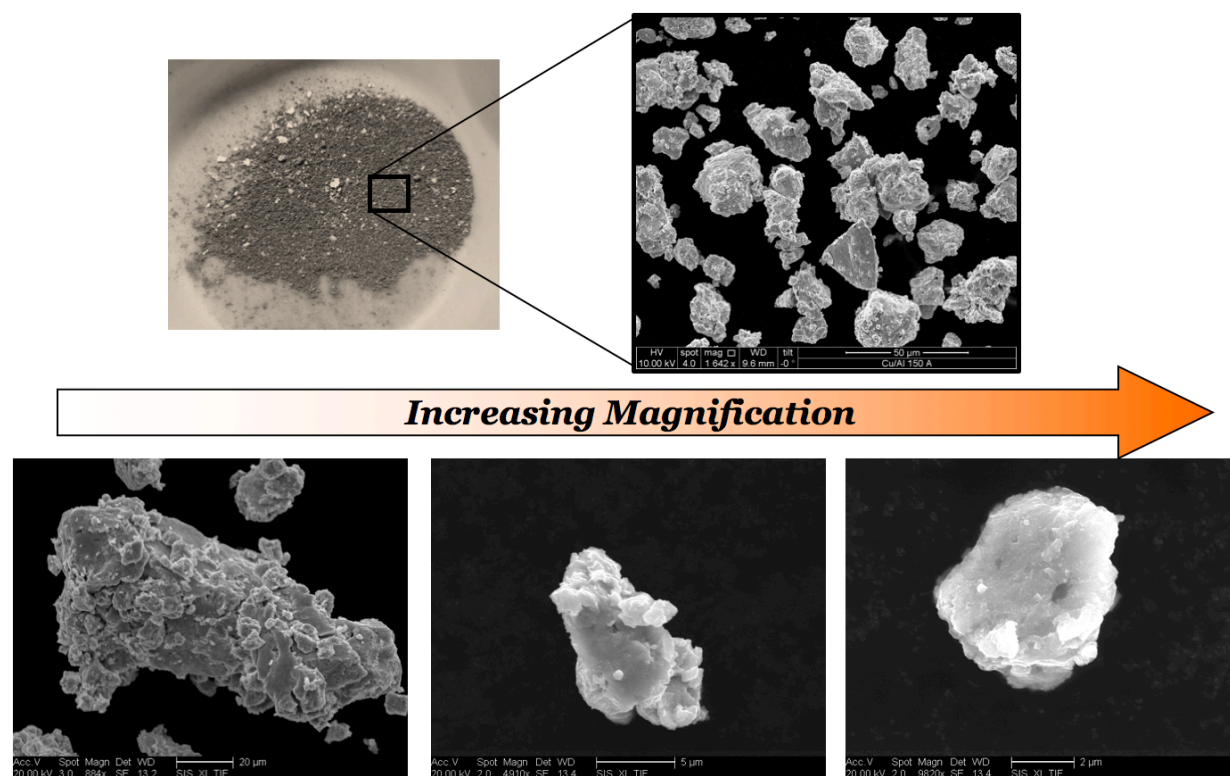


Figure 3-7. ESEM images of pulverized EGaIn "powder" obtained from cryogenic milling using SPEX SamplePrep 6870 Large Freezer/Mill[®].

4. Compliant Liquid Metal Electrodes for Dielectric Elastomer Actuators

References: The work presented in this chapter was published in:

SPIE Electroactive Polymer Actuators and Devices conference proceedings: Finkenauer, L. R., Majidi, C. Compliant Liquid Metal Electrodes for Dielectric Elastomer Actuators; Bar-Cohen, Y., Ed.; 2014; p 90563I.

Wissman, J*.; Finkenauer, L*.; Deseri, L.; Majidi, C. Saddle-like Deformation in a Dielectric Elastomer Actuator Embedded with Liquid-Phase Gallium-Indium Electrodes. *Journal of Applied Physics* **2014**, *116* (14), 144905.

*Co-first authors.

4.1. Background and motivation

The areas of soft multifunctional materials and stretchable electronics require new classes of soft and elastically deformable electronics. Unlike traditional rigid electronic components, soft-matter electronics must be flexible and/or stretchable in order to accommodate the large motions and deformations involved in applications ranging from wearable sensors^{2–5,107} and artificial skins^{45,108} to artificial muscles and biologically inspired robots.^{109–112} Progress also depends on the reliable integration of soft electronics with external circuitry. DEAs represent a promising alternative to conventional actuator technologies for powering soft bio-inspired robots, assistive wearable technologies, and other systems that depend on mechanical “impedance matching” with soft biological tissue. In contrast to electrical motors and hydraulics, DEAs can be made entirely out of soft elastic materials and fluids and remain functional under extreme bending and stretching. Moreover, they operate with very little electrical power and can exhibit as much as 90% efficiency of electrical energy input to mechanical work output. While there have been significant improvements since early studies in the late 1990s, progress in DEA performance and robotics

implementation continues to depend on advancements in materials selection, design, and predictive theoretical modeling of the underlying elasticity and electromechanical coupling.

We introduce a DEA composed of liquid-phase Gallium-Indium (GaIn) alloy electrodes embedded between layers of poly(dimethylsiloxane) (PDMS).⁶ In contrast to existing DEA designs, which contain inextensible (but flexible) frames,¹¹³ springs,¹¹⁴ or solid electrodes,¹¹⁵ the mechanics of the GaIn-embedded composite is governed entirely by the elasticity of the surrounding PDMS elastomer. Moreover, we observe that the composite forms a saddle-shape and exhibits a relationship between longitudinal bending curvature and voltage that cannot be predicted with a classical bending beam model (see e.g. Sect. 4.2.2 of Ref.¹¹⁶). Instead, we use a kinematically parameterized shell theory and use the Rayleigh-Ritz technique for minimum potential energy to estimate the shape of the DEA at static equilibrium. We find that the theoretical predictions are in strong agreement with experimental measurements (without the aid of data fitting) so long as we allow for negative Gaussian curvature ($\mathcal{K} < 0$). In addition to furnishing an accurate prediction for the GaIn-PDMS composite, we are confident that this modeling approach can be extended to other DEA materials and designs.

DEAs are composed of a soft insulating elastomer film coated with conductive fluid or rubber electrodes. Applying a potential difference Φ to the electrodes induces an electrostatic pressure (Maxwell stress) on the embedded dielectric layer. As with a capacitor, nearly no current is drawn by the DEA, and thus very little power is expended. The dielectric is frequently created with a soft elastomer, such as acrylic-based VHB tape (3MTM) or PDMS. DEA designs include diaphragms,¹¹⁷ bimorphs,^{118,119} rolls,^{118,120} and reinforced planar stacks^{121,122} and exhibit a variety of motions, load capacities, and electromechanical coupling.

A central challenge in DEA development is the selection of “stretchable” electrodes that do not constrain the elastic deformation of the embedded dielectric layer.¹²³ Typically, the surfaces of the dielectric are coated with metallic particles,¹²⁴ graphite powder,¹¹⁸ carbon fibers,¹¹⁸ carbon black,¹²² or carbon grease.^{120,125} Alternatively, DEAs may comprise conductive electrode materials such as electrolytic elastomers (hydrogels)¹²⁶ or electrodes made conductive by direct filling with conductive particles¹¹⁹ or through low-energy ion implantation.¹¹⁷ Fabrication methods include spraying, stamping, printing, laser-cutting and spin-coating, or creating thin-film metal trace electrodes of copper, silver or gold using electroplating, sputtering, evaporation and patterning with photolithography.¹²³ While carbon based electrodes are relatively cheap and easy to fabricate, they have inherently high electrical resistivity and are often grainy and inconsistent at thinner layer thicknesses. In contrast, thin film metallic electrodes are highly conductive and easily patterned, but add to the stiffness of the DEA and require clever fabrication to undergo stretching (e.g. pre-buckling and wavy electronics¹²⁷).

Liquid-phase GaIn alloys represent a promising alternative to existing carbon based and solid electrode materials.^{29,44} Like carbon grease, it does not interfere with the mechanics of the surrounding elastomer and remains conductive during stretching. However, it exhibits 3 – 6 orders of magnitude less electrical resistance, with a conductivity only 1/20th that of conventional copper wiring (see Table 4-1 for a comparison). Liquid GaIn has already been used for soft and stretchable wiring,¹²⁸ sensors,² and electronics.¹²⁹ Microfluidic channels of liquid alloy are typically produced with replica molding and needle injection using techniques adapted from “soft” lithography and microfluidics.¹⁹ However, DEAs require a thin film coating of liquid alloy that cannot be produced using needle injection. Instead, they must be produced with techniques like laser machining,⁵³ masked deposition,⁵⁰ or stencil lithography.^{106,130}

The dielectric in a DEA is typically modeled as an incompressible elastic solid subject to a Maxwell stress $\sigma_M = \epsilon_r \epsilon_0 \mathbf{E}^2$, where ϵ_0 is the permittivity of free space, ϵ_r is a dielectric constant, and $\mathbf{E}$ is the electric field strength.^{118,131–133} Recently, researchers have examined dynamics,¹³⁴ resonance,^{135,136} and failure of thin film dielectrics^{137,138} and the effect of viscoelasticity on electric instabilities and fracture.¹³⁹ In most cases, the elastomer in a DEA undergoes elastic strains and bending curvatures that are beyond the scope of linearized theories for elastic plates and shells. Instead, we must use a non-classical shell theory that treats the elastomer as an incompressible hyperelastic solid. For moderate stretch, we can model the PDMS layers with a NeoHookean constitutive law that only requires a single coefficient of elasticity.¹⁴⁰ For larger strains, we must use a Mooney-Rivlin,^{141,142} Ogden,¹⁴³ or any other model that allows for nonlinear elasticity with two or more coefficients.

This research aims to demonstrate a straightforward, effective, scalable, and repeatable method for producing highly conductive and deformable DEA electrodes, specifically through the use of the liquid metal alloy EGaln. The paragraphs that follow explain the evolving fabrication process for EGaln electrodes, demonstrate their integration as part of a curved cantilever DEA for switching, and validate their use by showing agreement to modeled actuation behavior.

Table 4-1. Comparison of EGaln conductivity²⁹ to well-established values of common metals, acetylene carbon black¹⁴⁴ and measured values of cPDMS (first number was determined along the length of cPDMS sample, while number in brackets is through the thickness).

Material	Conductivity σ ($\times 10^4$ S-cm ⁻¹)
cPDMS	1.4×10^{-6} [3.8×10^{-10}]
Carbon black	3.8×10^{-5}
EGaln	3.4
Aluminum	35.0
Gold	41.0
Copper	59.6
Silver	63.0

4.2. Sample preparation

4.2.1. Materials

Eutectic Gallium Indium (EGaIn) was purchased from Sigma Aldrich, and poly(dimethylsiloxane) (PDMS) was purchased from Dow Corning as SYLGARD® 184.

4.2.2. Device fabrication

The GaIn-PDMS composite is produced using the steps presented in Figure 4-1⁶ The PDMS dielectric layer (SYLGARD® 184; Dow Corning) is first applied on a flat substrate using a 5 μm resolution thin film applicator (ZUA 2000 Universal Applicator, Zehntner GmbH). After curing on a hot plate, eutectic GaIn (EGaIn, $\geq 99.99\%$; Sigma-Aldrich) electrodes are manually deposited using an elastomeric blotter and laser-patterned (VLS3.50, Universal Laser Systems) stencil.¹⁰⁶ After deposition, the mask is carefully removed and an encapsulating layer of PDMS is applied over the exposed liquid electrodes. Before this sealing step, a thin strip of adhesive-backed conductive paper (3M™ Fabric Tape CN-3490) is placed in contact with each patterned liquid metal electrode for eventual interfacing with external electronics. Following another cure on the hot plate, the composite PDMS-EGaIn-PDMS film is carefully peeled and flipped in order to expose the other side of the dielectric layer, and a second set of electrodes is applied in the same way. The pre-strain required for inducing curvature is achieved by manually stretching the DEA by 6% and allowing it to naturally adhere to a substrate. Lastly, a thicker layer of PDMS elastomer is applied over the stretched DEA. The sealing layer, dielectric layer (separating the embedded electrodes), and substrate layer have thicknesses of $H_1 = 163 \mu\text{m}$, $H_2 = 85 \mu\text{m}$, and $H_3 = 490 \mu\text{m}$, respectively.

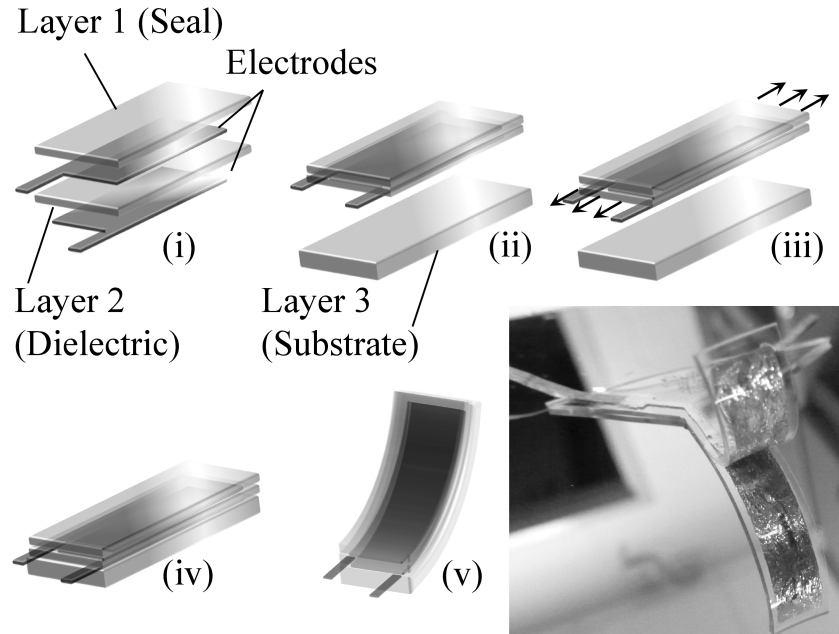


Figure 4-1. Illustration of DEA layer components during fabrication showing (i) encapsulated electrodes and compliant electrode layers, (ii) – (iv) straining of DEA composite and bonding to an initially unstrained substrate polymer layer and (v) curved configuration of released actuator with picture of actual device.

4.3. Testing setup

The resulting curved cantilever DEA was then wired to a high voltage transformer (Q50-5C, EMCO High Voltage Corporation) for testing, as demonstrated by Figure 4-2 below. Several pre-strains were explored, including 10%, 15% and 20%, though this work presents results only from devices having undergone 10% strain. This is mainly due to ongoing attempts at developing consistent and repeatable results using the given fabrication and testing setup.

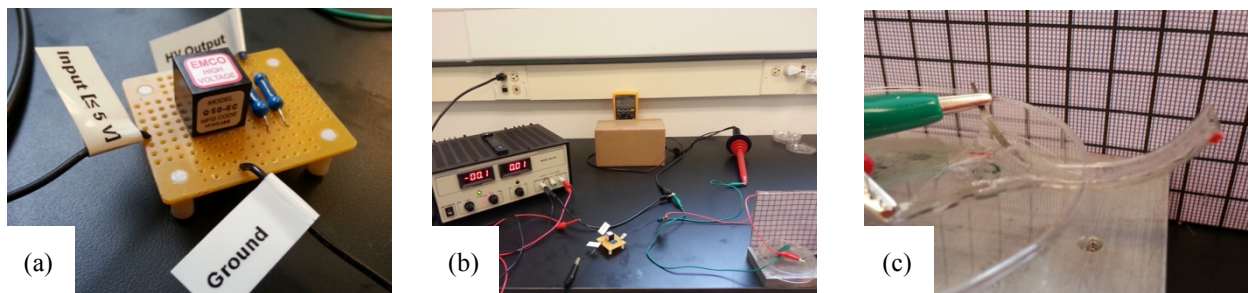


Figure 4-2. Testing setup showing (a) EMCO Q50-5C proportional high voltage (5 kV) transformer, (b) complete layout of actuator with voltage source and (c) close up of curved DEA on testing substrate.

Each completed DEA to be tested was placed on a nonconductive substrate that was sufficiently isolated from high voltage electronics, seen in Figure 4-2(c) as a polystyrene dish. Alligator clips attached the paper leads of the DEA to the high voltage setup. This particular EMCO proportional transformer had a maximum output of 5 kV, and is shown (Figure 4-2(a)) mounted on a custom fabricated board in series with two 25 M Ω resistors ($R_{\text{total}} = 50 \text{ M}\Omega$). In this configuration, the device was considered fully loaded and therefore was expected to exhibit a linear response of percentage input to output voltage. In order to observe the applied actuation voltage (typically in the kilovolt range), a high voltage probe with $\times 1000$ attenuation (PR 28A HV DMM Probe, B&K Precision) was connected to the transformer output. Thus, a typical handheld digital multimeter that was rated for an input of several hundred volts could be used to monitor the actuation voltage in real time (e.g. 5 kV displays as 5.000 V).

For each sample, the actuation voltage was slowly ($\approx 0.02 \text{ Hz}$) ramped up and down from 0.0 – 5.0 kV and logged real-time via an Arduino UNO R3 microcontroller with a custom MATLAB GUI interface while the deflection of each DEA in response to voltage is recorded. Footage of the device actuating is evaluated using a video analysis and modeling software (Tracker; <https://www.cabrillo.edu/~dbrown/tracker/>). We extract data on deformation (bending) as a function of time by monitoring the changing beam tip deflection with the aid of the automated object tracking tool. The voltage can then be interpolated and correlated with the Tracker output based on time stamps for a complete description of actuation in response to voltage.

Figure 4-3 shows a screenshot of the tool in use. As seen in the figure, a red “flag” (plastic VHB tape backing) was present to mark the tip of the curved actuator for ease of tracking during data collection. The Tracker tool measured changes in deflection (recorded as the angle between

the horizontal axis and the highest point of the “flag”), with the user-specified vertex located at the base of the curving DEA.

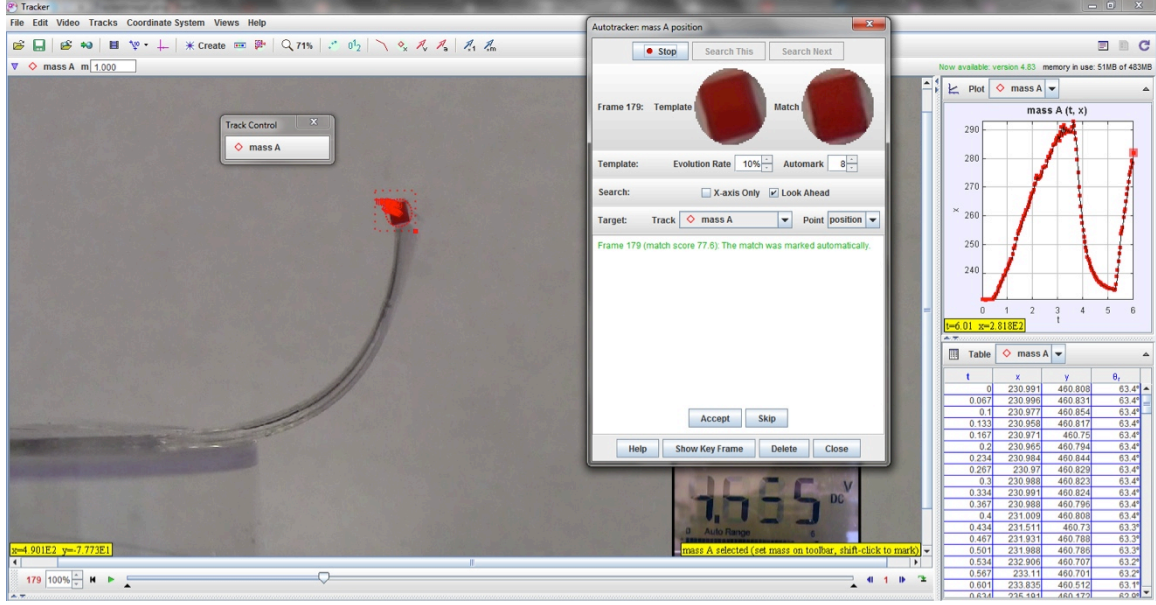


Figure 4-3. Screenshot of Tracker video analysis software with a protractor tool to determine deflection angle.

4.4. Theory

In its *natural* (i.e. isolated, stress-free) state, each PDMS layer of the DEA is a right rectangular prism with length L_i , width W_i , and thickness H_i as shown in Figure 4-4 (*right*). As illustrated in Figure 4-1, the index $i \in \{1,2,3\}$ identifies the layer (*layer 1* – sealing layer; *layer 2* – dielectric layer coated with electrodes on the top and bottom surfaces; *layer 3* – thick elastomer substrate). In order to induce residual bending curvature in the DEA, layers 1 and 2 have dimensions $L_1 = L_2 < L_3$ and $W_1 = W_2 \geq W_3$. To assemble the DEA, layers 1 and 2 are bonded together and then stretched so that they share the same length and width as layer 3. When the third layer is bonded, the composite deforms in order to relieve the residual strains in the pre-stretched layers. In general, this deformation involves changes in the width, length, and bending curvature(s)

of the composite. Moreover, the shape of the DEA at static equilibrium changes when electrical voltage Φ is applied to the electrodes. Figure 4-4 (*left*) shows the direction of beam deflection with applied voltage Φ , which results in a changing ϑ (defined as half of the arc angle $\bar{\theta}$ shown in Figure 4-4). We observe that in addition to bending about its intermediate (width-wise) axis, the GaIn-PDMS composite also bends in the opposite direction about its major (length-wise) axis to form a saddle-like shape. Saddle-like deformation ($\mathcal{K} < 0$) is examined in the following subsection. The bending curvature of the device about the intermediate axis decreases as the applied voltage Φ increases.

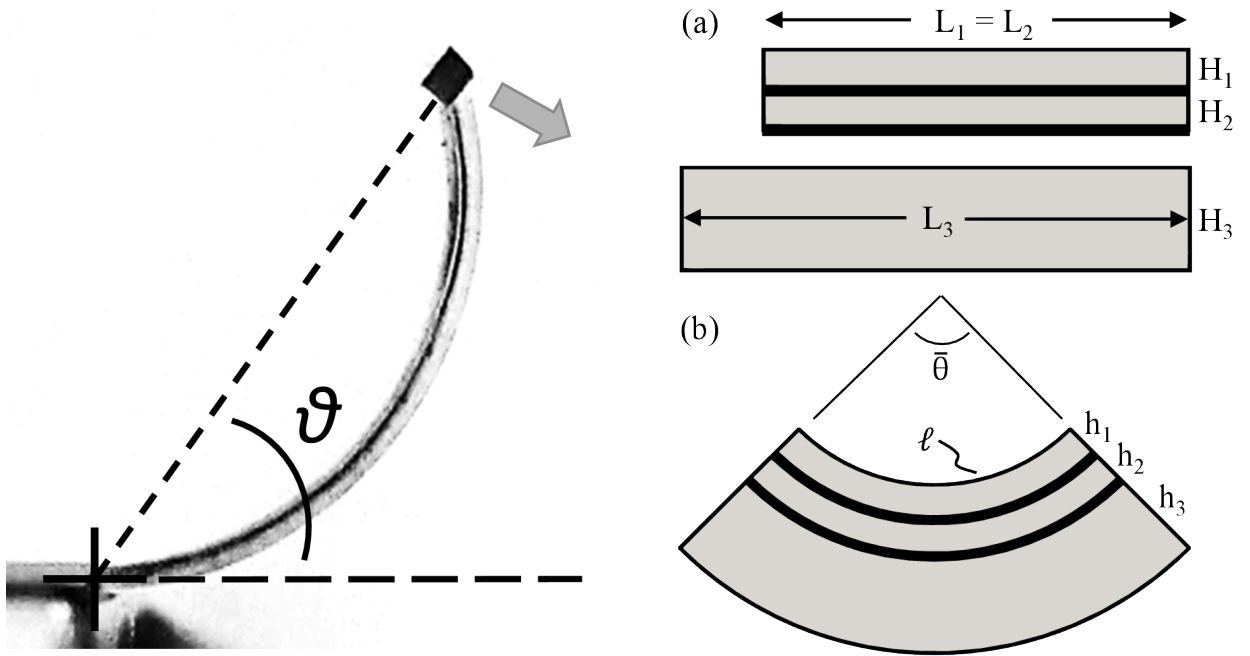


Figure 4-4. (*left*) Side view of soft-matter PDMS-GaIn DEA composite during testing. (*right*) (a) Actuator cross-section with dimensions before assembly (electrodes marked by black lines shown only for illustrative purposes and are not included in the thickness dimensions). (b) Actuator cross-section after assembly.

4.4.1. Saddle-like deformation

In practice, we observe that the DEA deforms into a saddle-like shape with negative Gaussian curvature $\mathcal{K} = -\kappa_\theta \kappa_\phi$, where κ_θ and κ_ϕ are the principal curvatures along the length ($\mathbf{e}_\theta$) and width ($\mathbf{e}_\phi$), respectively. In order to examine the dependency of $\{\kappa_\theta, \kappa_\phi\}$ on Φ , we consider three representations (placements) of the elastic layers. In the *natural* placement, each layer is isolated and has dimensions $\{L_i, W_i, H_i\}$. In the *reference* placement, the pre-stretched layers (1 and 2) are bonded to the thick substrate (layer 3) and the composite relaxes into a rectangular prism of length ℓ and width w . Here, each point has Euclidean coordinates $\{X, Y, Z\}$ where the tangent bases $\{\mathbf{e}_X, \mathbf{e}_Y, \mathbf{e}_Z\}$ are oriented along the composite length, width, and thickness, respectively. Lastly, in the *current* placement, the composite deforms such that the top of layer 1 (sealing layer) forms a *saddle surface* $\mathcal{S}_1$ with dimensions $\{\ell, w\}$ and principal curvatures $\{\kappa_\theta, \kappa_\phi\}$ as defined below. Here, each point has “inverted” spherical coordinates $\{\theta, \phi, z\}$ and the coordinate lines have tangent (covariant) vectors $\{\mathbf{e}_\theta, \mathbf{e}_\phi, \mathbf{e}_z\}$. The coordinates $\{\theta, \phi, z\}$ along with the arcangles $\{\bar{\theta}, \bar{\phi}\}$ and radii of curvature $\rho_\theta = \kappa_\theta^{-1}$ and $\rho_\phi = \kappa_\phi^{-1}$ for the $\mathcal{S}_1$ centerlines are defined in Figure 4-5.

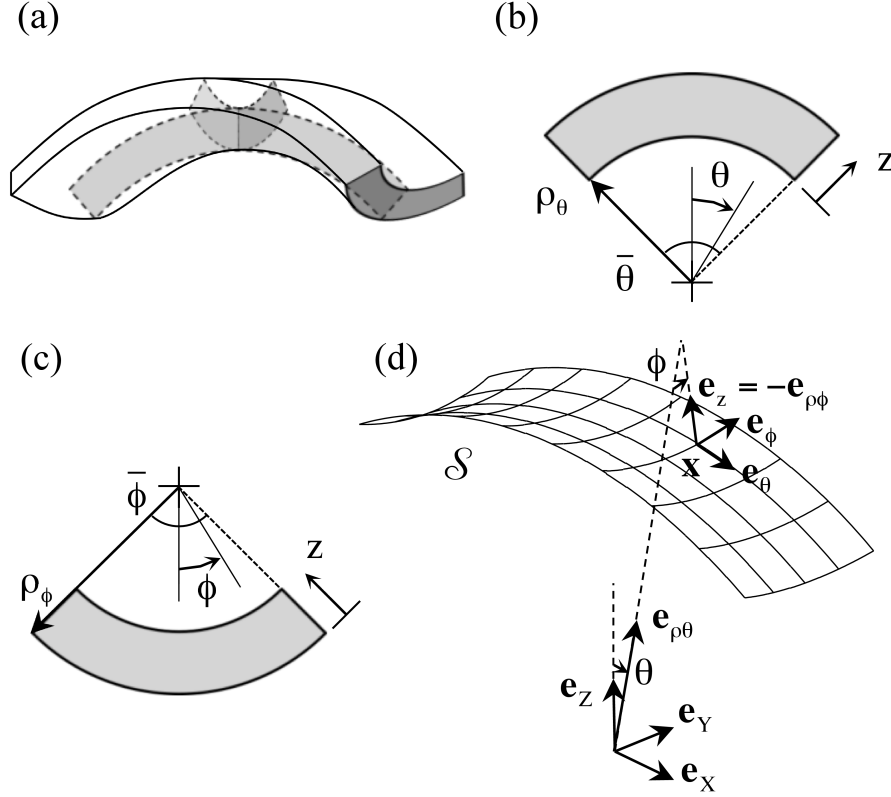


Figure 4-5. (a) DEA composite deforms to form a saddle-like geometry. (b) Deformation in the $\mathbf{e}_\theta - \mathbf{e}_z$ plane shows bending with radius $\rho_\theta = \kappa_\theta^{-1}$ in the longitudinal direction. (c) Deformation in the $\mathbf{e}_\phi - \mathbf{e}_z$ plane shows bending with radius $\rho_\phi = \kappa_\phi^{-1}$ in the width-wise direction. (d) Position of a point $\mathbf{x}$ within a saddle surface $\mathcal{S}$.

Assuming that points in the $\mathbf{e}_X - \mathbf{e}_Z$ and $\mathbf{e}_Y - \mathbf{e}_Z$ planes of the reference placement remain plane, the $\mathbf{e}_\theta - \mathbf{e}_\phi$ surfaces form saddles $\mathcal{S}$. For each z , $\mathcal{S}$ has centerlines with arcangles $\bar{\theta} = \kappa_\theta \ell$ and $\bar{\phi} = \kappa_\phi w$ and radii of curvature $\rho_\theta + z$ and $\rho_\phi - z$. The coordinate lines along the $\mathbf{e}_\theta$ and $\mathbf{e}_\phi$ directions have total lengths of $\ell_\theta = \{(\rho_\theta + z) + (1 - \cos \phi)(\rho_\phi - z)\} \bar{\theta}$ and $w_\phi = (\rho_\phi - z)\phi$, respectively. Referring to Figure 4-5, a point in $\mathcal{S}$ has a position

$$\mathbf{x} = \mathbf{x}(\theta, \phi, z) = (\rho_\theta + \rho_\phi) \mathbf{e}_{\rho\theta}(\theta) + (\rho_\phi - z) \mathbf{e}_{\rho\phi}(\theta, \phi) \quad (5.14)$$

where $\mathbf{e}_{\rho\theta} = \sin \theta \mathbf{e}_X + \cos \theta \mathbf{e}_Z$ and $\mathbf{e}_{\rho\phi} = \sin \phi \mathbf{e}_Y - \cos \phi \mathbf{e}_{\rho\theta}$. For each z , the saddle surface $\mathcal{S}$ has an area of

$$a(z) = \left\{ [\rho_\theta + \rho_\phi] \bar{\phi} - 2(\rho_\phi - z) \sin \left(\frac{\bar{\phi}}{2} \right) \right\} \bar{\theta} (\rho_\phi - z). \quad (5.15)$$

Each layer of the composite is assumed to be incompressible and so the final thicknesses h_i can be estimated by dividing the initial volume by the final area of its top surface: $h_i \approx W_i L_i H_i / a_i$, where $a_1 = a(0)$, $a_2 = a(h_1)$, and $a_3 = a(h_1 + h_2)$. The final layer thicknesses h_i are only approximations because they are calculated using the area of the top surface rather than mid-plane of each layer. Moreover, the exact layer thickness will be non-uniform since the principal stretch λ_θ in the $\mathbf{e}_\theta$ direction increases with $|\phi|$. Nonetheless, the above approximations are used since it allows the thickness to be estimated *explicitly* by calculating $a_1, h_1, a_2, \dots, h_3$ in sequence.

Each layer is treated as a *hyperelastic* solid with principal stretches $\{\lambda_\theta, \lambda_\phi, \lambda_z\}$ in the $\{\mathbf{e}_\theta, \mathbf{e}_\phi, \mathbf{e}_z\}$ directions and a strain energy density $\psi = \psi(\lambda_\theta, \lambda_\phi, \lambda_z)$. The stretches λ_θ and λ_ϕ are calculated by dividing the arclength of each convecting coordinate line by its original length in the natural placement: $\lambda_\theta(\phi, z) = \ell_\theta / L_i$ and $\lambda_\phi(z) = w_\phi / W_i$, where $i = 1, 2$, and 3 for $z \in [0, h_1), [h_1, h_1 + h_2)$, and $[h_1 + h_2, h_1 + h_2 + h_3]$, respectively. Incompressibility implies $\lambda_z = 1/\lambda_\theta \lambda_\phi$ and that the total elastic strain energy $\Omega = \sum_{i=1}^3 \Omega_i$ can be calculated by integrating ψ in the current placement where now Ω_i are evaluated as follows:

$$\Omega_1 = \int_0^{h_1} \int_{-\phi/2}^{\phi/2} \psi \ell_\theta (\rho_\phi - z) d\phi dz, \quad (5.16)$$

$$\Omega_2 = \int_{h_1}^{h_1+h_2} \int_{-\phi/2}^{\phi/2} \psi \ell_\theta (\rho_\phi - z) d\phi dz, \quad (5.17)$$

$$\Omega_3 = \int_{h_1+h_2}^{h_1+h_2+h_3} \int_{-\phi/2}^{\phi/2} \psi \ell_\theta (\rho_\phi - z) d\phi dz. \quad (5.18)$$

For a pre-strain of <10% in layers 1 and 2, we expect only moderate stretches at static equilibrium.

Therefore, we again treat the composite as a NeoHookean solid and let

$$\psi = 2C_1 \left(\lambda_\theta^2 + \lambda_\phi^2 + \frac{1}{\lambda_\theta^2 \lambda_\phi^2} - 3 \right), \quad (5.19)$$

where $C_1 = Y/6$ is the coefficient of elasticity as before.

When voltage Φ is applied, the DEA has a total potential energy $\Pi = \Omega + U_\phi$, where U_ϕ is the electrical enthalpy. Since the electrodes are surrounded by a border that is $b = 0.75$ mm wide, the final area is approximately χa_2 , where $\chi = (W_2 - 2b)(L_2 - 2b)/W_2 L_2$. In the current placement (i.e. saddle-shape configuration), the capacitance between the two electrodes is estimated as $C \approx \chi \epsilon_r \epsilon_0 a_2 / h_2$ and the electrical enthalpy is

$$U_\phi = -\frac{1}{2} C \Phi^2 = -\chi \frac{\epsilon_r \epsilon_0 a_2 \Phi^2}{2 h_2}. \quad (5.20)$$

Lastly, the unknown kinematic parameters $\{w, \ell, \kappa_\theta, \kappa_\phi\}$ are determined by minimizing the total potential energy Π . This may be accomplished either by performing a multivariable optimization or finding the solution to the stationary conditions $\partial \Pi / \partial w = \partial \Pi / \partial \ell = \partial \Pi / \partial \kappa_\theta = \partial \Pi / \partial \kappa_\phi = 0$. While both approaches are valid, numerical minimization is more convenient since it eliminates the additional step of calculating the partial derivatives of Π .

4.5. Results and discussion

Results from the experiments and theory are presented in Figure 4-6. The grey dots correspond to experimental measurements collected from a single DEA sample and the solid curve with circular markers is the general saddling theory. These predictions correspond to a uniaxial pre-stretch of layers 1 and 2 during the DEA assembly. As discussed above, the two layers are first bonded together and stretched so that they share the same width and length of layer 3. For pure uniaxial loading, the two layers stretch by an amount $\hat{\lambda}_X = L_3 / L_1 = L_3 / L_2$ in the $\mathbf{e}_X$ direction and $\hat{\lambda}_Y = \hat{\lambda}_Z = \hat{\lambda}_X^{-1/2}$ in the $\mathbf{e}_Y$ and $\mathbf{e}_Z$ directions. This requires an initial width $W_1 = W_2 = W_3 / \hat{\lambda}_Y =$

$W_3\sqrt{L_3/L_1}$. We use the term “uniaxial” since the elastomer is under uniaxial stress during pre-stretch with the condition $\sigma_Y = \sigma_Z = 0$ implying $\hat{\lambda}_Y = \hat{\lambda}_Z$.

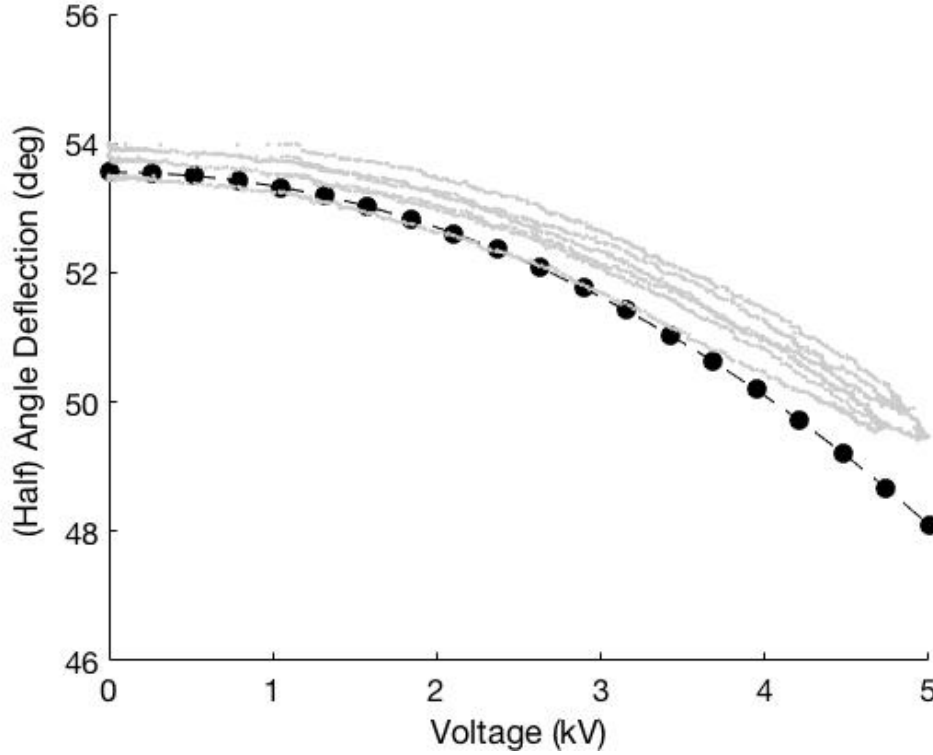


Figure 4-6. Comparison of experimental measurements and theoretical predictions for the arcangle $\vartheta = \bar{\theta}/2$ as a function of applied voltage Φ : (gray dots) experimental data collected from repeated measurements on a single DEA sample; (circles) prediction from the generalized theory with "uniaxial" pre-stretch.

The theoretical prediction appears to be in strong agreement with the experimental measurements (without the aid of data fitting). While the resulting observed change in bending curvature is less than has been demonstrated by other unimorph type DEAs,¹²⁴ our device both takes into account saddling due to pre-stretch and also displays no obvious degradation of the electrode material throughout testing (though a much more extensive study is necessary to verify this claim).

The theoretical predictions presented in Figure 4-6 were obtained for geometries and materials constants based on the experimental DEA sample: $L_1 = L_2 = 20$ mm, $L_3 = 1.06L_1 = 21.2$ mm, $W_3 = 6.5$ mm, $b = 0.75$ mm, $H_1 = 163$ μ m, $H_2 = 85$ μ m, and $H_3 = 490$ μ m. The

Young's modulus, $E = 1$ MPa, was determined through tensile tests with an Instron[®] materials testing system (Model #4467; Instron) and was similar to values found in the literature.^{2,145–148} A dielectric constant $\epsilon_r = 2.72$ was reported in the product data sheet of the materials supplier (Dow Corning, Inc.). The double integrals for computing Ω_i were performed in MATLAB R2011b and R2013a using an adaptive Simpson quadrature (*dblquad*) and Π was minimized for $\{w, \ell, \kappa_\theta, \kappa_\phi\}$ using a direct simplex search method (*fminsearch*).

Figure 4-7 demonstrates the versatility and usefulness of EGaIn through the integration of a working flexible circuit with a curved cantilever DEA as presented in this paper. Here, EGaIn was utilized as flexible electrodes in the DEA as well as for the “liquid wire” used to create the LED circuit. In the same manner mentioned in section 4.2.2, the circuit shape was patterned onto a regular piece of white printer paper using a laser engraver (VLS3.50, Universal Laser Systems). More complex features such as the serpentine resistor element included in Figure 4-7 were simple to incorporate, as numerous geometries could be quickly sketched in any CAD or vector drawing software and then produced with the laser engraver. In the same fashion that DEA electrodes were deposited, the negative mask of the circuit was traced with the novel 3D printed pen to deposit the liquid metal in the shape shown below. Removal of the paper mask left only the completed circuit outline. Next, strips of the 3M conductive paper, which functioned as electrical leads, were placed at the circuit terminals. Lastly, the liquid Gallium-Indium circuit was sealed with a layer of PDMS using the thin film applicator. The resulting soft circuit was then paired with a curved cantilever DEA, which completed the connection when actuated. This was demonstrated by reversibly turning the LED inside the circuit on and off. Electrical contact between the DEA and LED circuit occurred along the bottom of DEA, where an exposed film of EGaIn made reversible contact with two parallel paper leads attached to circuit terminals.

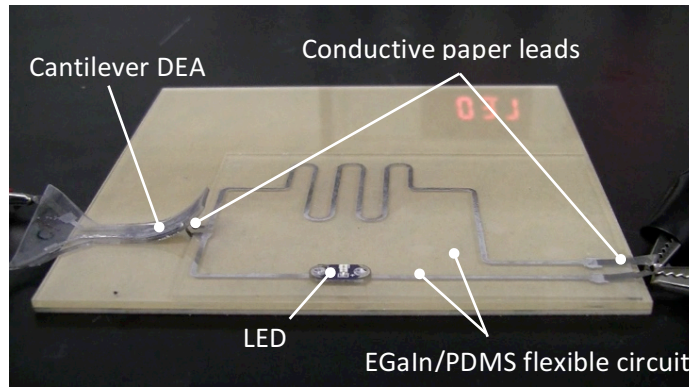


Figure 4-7. Circuit implementing liquid metal electrode DEA to activate LED.

4.6. Conclusions

An entirely soft DEA that contains no rigid or inextensible materials has been introduced. It is composed of PDMS embedded with a liquid-phase GaIn alloy. After assembly, the GaIn-PDMS spontaneously deforms into a saddle-shape that changes curvature when voltage is applied to the liquid electrodes. This shape is accurately predicted with an elastic shell theory based on the principle of minimum potential energy and hyperelastic constitutive model. Since the materials undergo only moderate strains ($<10\%$), good agreement between theory and experiment can be achieved with a NeoHookean constitutive law, which only requires a single coefficient of elasticity. In general, DEAs with large pre-stretch and bending curvature should be modeled with a more accurate nonlinear constitutive law. However, even in these cases, the proposed 4-parameter kinematic representation for a saddle-shaped shell with negative Gaussian curvature is sufficient for predicting the shape at static equilibrium for prescribed pre-stretches and voltage. While the focus was on two types of pre-stretch (so-called uniaxial and plane strain loading), the theory is sufficiently general for any biaxial loading condition on the dielectric layer prior to bonding and release.

The liquid metal alloy eutectic Gallium-Indium was primarily chosen as the compliant electrode material for these devices due to its relatively high conductivity (less than an order of magnitude different from traditionally utilized metallic conductors). Since EGaIn is liquid at room temperature, it also does not provide any mechanical resistance to compression and expansion of the device during actuation. The oxide skin formed by EGaIn in the presence of air is another property that makes it advantageous as DEA electrodes, as this layer coats the inside of the encapsulating elastomer membrane and ensures uniform conductivity. The unique wetting properties of EGaIn, again due to its oxide skin, allowed for deposition via stencil lithography onto elastomer substrates for use as flexible circuitry (as explained in section 4.2.2 regarding the patterning of the cantilever DEA electrodes). Using EGaIn, this process was straightforward, repeatable and relatively fast. We have verified that liquid metal behaves as expected and can be used as electrodes in soft actuators as it does not alter the mechanics of the host material. However, future work should aim to replace these “pools” of liquid metal with more stable nanodroplets to avoid the possibility of leaking, spillage, contamination, risk of film non-uniformity, etc.

5. Analysis of the Efficiency of Surfactant-Mediated Stabilization Reactions of EGaIn Nanodroplets

Reference: The work presented in this chapter has been submitted for publication in Langmuir: Finkenauer, Lauren R.; Lu, Qingyun; Hakem, Ilhem F.; Majidi, Carmel; Bockstaller, Michael R. “Analysis of the efficiency of surfactant-mediated stabilization reactions of EGaIn nanodroplets.”

5.1. Background and motivation

When dispersed in a soft carrier medium, nanoscale droplets of low temperature metals or alloys can be used to tailor the electronic, optical or thermal properties of the host material without significantly altering its elasticity or rheology. These liquid metal (LM) dispersions represent an intriguing platform for developing functional nanocomposite materials that manage electricity, electric field, and heat in biomechanically compatible machines and polymer electronics. To match the mechanical properties of natural human tissue, such composites must exhibit low-modulus (~ 0.1 - 1 MPa) elastic deformation up to large strains ($>100\%$) and accommodate large bending and torsional deformations. This combination of mechanical, electrical, and thermal properties is difficult to accomplish with dispersions of rigid particle filler in a soft polymer due to internal mechanical mismatches that lead to mechanical hysteresis, stiffening, and embrittlement of the polymer matrix.¹⁴⁹ Recent advances in the development of low temperature eutectic alloy compositions have rendered liquid metal filler inclusions an attractive alternative to solid particle fillers.¹⁵⁰ Of particular interest has been eutectic gallium/indium alloys that exhibit a eutectic melting temperature (at 1 bar) of $T = 15.3^\circ\text{C}$. For example, Ga-based LM alloys embedded in polymers have been used to create numerous types of devices such as a variety of antennas to include patch,³² coil^{1,33} and reconfigurable^{3,34,35} structures, or tunable split-ring resonator,³⁶ compliant electrodes^{37,38,32,39-42} for circuits and actuators^{6,7,43}; a multitude of compliant and robust pressure^{2,4} and strain sensors.^{1,2,45,46} Self-healing capabilities have been demonstrated for

extensible wires⁵⁵ and electrodes,⁴⁴ as well as soft composites.⁵⁶ Dispersion of liquid metal microdroplets in elastomeric matrices has led to elastic composites with LM inclusions and tunable electronic properties.^{8,9}

While the applications listed above illustrate the potential of polymer-LM composites as a platform for material innovations, current fabrication processes also present constraints that limit the application of this new class of hybrid materials. In particular, current fabrication methods depend on the direct dispersion of liquid metal inclusions by mechanical (and/or sonic) mixing methods. This results in poor control of the dispersion morphology and leads to irregularly shaped micron sized ‘droplet’ inclusions that give rise to pronounced optical scattering and hence opaque materials.¹⁵¹ To reduce scattering losses and to enable the integration of liquid-metal based nanocomposites into optically transparent coatings (e.g. for use in polymer photovoltaics), research has focused on the development of surfactant-stabilization methods. Tethering of surfactants to the surface of inorganic (or organic) nanoparticles is ubiquitously being used in nanomaterial synthesis.¹⁵² The approach rests on surfactant binding to inhibit mass transport across the liquid/particle interface (thereby preventing particle growth) as well as to induce interactions that prevent particle aggregation and coagulation. Several previous studies have reported the use of surfactants to synthesize stabilized EGaIn (as well as other liquid metal) nanodroplets.^{10,12,13,15–18} For example, Hohman et al. evaluated the sonochemical formation of EGaIn nanodroplet formation in the presence of 1-dodecanethiol (C12) and 3-mercaptop-N-nonylpropionamide (1ATC9).¹³ The authors observed nanoparticles down to tens of nanometers formed in the surfactant solutions. Without surfactants present, rapid agglomeration was reported. The stabilization of EGaIn nanodroplets was interpreted as a consequence of chemisorption of sulfur atoms with gallium and/or indium at the surface. This might indeed be expected given the strong

bond dissociation energy of Ga-S and In-S bonds which are on the order of 300 kJ/mol.¹⁵³ The authors also noted that minor amounts of oxygen supported particle stabilization as the wrinkles and instabilities of the skin helped to further cleave particles during sonication. A yield of 50 – 150 µg/mL for particles capped with 1-dodecanethiol was reported. More recently, Sudo et al. sonicated gallium in chloroform with both dodecanoic acid and dodecanamine as a surfactant, resulting in TEM observed particles of approximately 20 nm.¹⁵ Consistent with observations by Hohman et al., no surfactant resulted in aggregated structures. Kramer and coworkers sonicated EGaIn particles in neat ethanol with and without the presence of SAM forming 1ATC9.¹⁰ Drop casted particles subjected to “mechanical sintering” tests revealed that thiol capped particles ruptured more easily than oxide covered particles (no thiol), suggesting a lower surface tension of thiol capped compared to gallium oxide coated particles. The results highlight that the mechanism of surfactant stabilization remains an outstanding question. Harnessing surfactant-based synthesis for the fabrication of LM-based nanocomposite materials depends on a better understanding of the role of surfactants on the particle stabilization process. Here it is important to note that while previous studies have focused on the effect of surfactant on the size of nanodroplets, no systematic evaluation of the *efficiency* of nanodroplet formation (that is the yield of surfactant-mediated synthesis) has been reported. We attribute the lack of data on reaction efficiency to the difficulty of evaluating nanodroplet concentrations using established methods such as gravimetry that arise from the typically small amounts of material (see below).

The purpose of the present contribution was to systematically evaluate the role of surfactant composition on the size *and* yield of surfactant-mediated EGaIn nanodroplet formation. Concurrent UV/Vis absorption spectrophotometry and dynamic light scattering was applied to quantitatively determine size and size distribution of nanodroplets as well as EGaIn mass

concentration. In agreement with previous reports, thiol-based surfactants were found to be most effective in stabilizing nanosized EGaIn droplets. The efficiency was found to increase with the fraction of unpolar (aliphatic) groups, hence the yield of nanodroplet formation increased by 37% for 1-octadecanethiol as compared to the 1-dodecanethiol analog. Interestingly, the quantitative comparison of the effectiveness of nanodroplet formation in the presence/absence of surfactants revealed a ‘threshold’ chain length of the aliphatic moiety to enhance nanodroplet formation. A second interesting finding is that while the yield of nanodroplet formation increased by 340% (in the case of the most efficient surfactant system 1-octadecanethiol), the overall efficiency of the process is found to be rather modest. This, in conjunction with the poor solubility of surfactant-stabilized nanodroplets, suggests that the mechanism of surfactant stabilization is more complex as previously noted and distinct from stabilization by ‘self-assembled monolayer formation’ process that has been proposed for other metal particle metal particle systems.^{10,13,15,17,61}

5.2. Experimental methods

5.2.1. EGaIn synthesis

Raw gallium (Ga) and indium (In) (99.99% pure, Gallium Source LLC) were combined to form the eutectic composition (75.5% Ga, 24.5% In by weight). The glass jar containing the metals and a magnetic stir bar was placed on a hot mixing plate at about 200°C until the alloy appeared thoroughly mixed. Direct scanning calorimetry was then used to verify that the alloy was indeed the eutectic of Ga-In. The melting temperature was determined as 16.35°C, which is within a 1°C range from the literature cited T_m of EGaIn (15.3°C). Once confirmed as the eutectic, approximately 1.5 mL of EGaIn was pulled into a syringe that was first repeatedly drawn with nitrogen. The liquid metal was then injected into a capped borosilicate glass vial through the septa. The vial was flushed with nitrogen for 5 minutes prior to the addition of EGaIn, which in additional

to first purging the syringe, greatly reduced initial oxide formation (as evidenced by the resultant shiny metallic surface of the EGaIn within the vial). As a final precaution against oxygen “contamination,” the caps were tightly wrapped with a layer of Parafilm M.

5.2.2. EGaIn nanoparticle synthesis

Solutions of various selected surfactants were prepared in ethanol (200 proof, Anhydrous) at 1 mM concentrations and filtered three times (0.45 μm pore, PTFE membrane, PALL Acrodisk). From the given surfactant solution of interest, 1.5 mL was extracted and pipetted into a 2 mL borosilicate vial. Nitrogen was bubbled through the solution for 5 minutes to remove much of the dissolved oxygen. A syringe was then used to extract approximately 0.2 mg of EGaIn and inject it into the vial of surfactant solution. The vial was then capped, wrapped with Parafilm M, and placed in a secondary 120 mL polypropylene containment jar which was half filled with deionized water. A Branson 1510 bath ultrasonicator was filled with the same deionized water, and the jar was suspended in the center of the bath with the aid of a custom cut acrylic plate. The jar was sonicated at a continuous 40 kHz for 60 minutes (water initially at $\sim 25^\circ\text{C}$, with no additional temperature control). After sonication, the vial was removed from within the jar and allowed to decant for 24 hours in an upright position. Exactly 1.0 mL of supernatant was then pipetted away and introduced to a disposable semi-micro cuvette and used directly for testing. See section 3.3 for process diagram.

5.2.3. Characterization

Dynamic light scattering (DLS) was performed on samples after 24, 48 and 72 hours following their initial decanting process. A Malvern Zetasizer Nano ZS was used to record the scattering intensity autocorrelation function $g_2(q, t)$ at a scattering vector $q = 4\pi n \lambda^{-1} \sin(\theta/2) = 2.72$

$\times 10^7 \text{ m}^{-1}$ where n is the medium refractive index, $\lambda = 633 \text{ nm}$ is the vacuum wavelength of the incident light, corresponding to a scattering angle of $\theta = 173^\circ$ (converted to radians for q).

$$g_2(q, t) = \frac{\langle I(q, 0) I(q, t) \rangle}{\langle I(q, 0) \rangle^2} \quad (6.1)$$

$I(q)$ is the scattering intensity at a scattering vector q . The Siegert relation is used to compute the normalized autocorrelation function of the scattered electric field $g_1(q, t)$

$$g_2(q, t) = 1 + f^* |\alpha g_1(q, t)|^2 \quad (6.2)$$

where f^* is an experimental instrument factor (determined by calibration), and α is the fraction of total scattered intensity stemming from fluctuations with correlation times longer than 10^{-7} s. The experimental $C(q, t) = \alpha g_1(q, t)$ describes the dynamics of the concentration fluctuations. A number size distribution representing the polydispersity of the sample was determined by the Malvern software, which was converted from the intensity size distribution using Mie theory.

UV/Vis spectroscopy was performed using a Cary UV/Vis 300 spectrophotometer (Agilent Technologies) on each sample to measure percent absorbance by suspended EGaIn nanoparticles. Experiments were performed over a wavelength range of 800 – 200 nm, with an interval of 1.0 nm and a scan rate of 600 nm/min in double beam mode with the spectral band width (SBW) set at 2.0 nm. The experimental extinction A was determined using Beer-Lambert's law as $A = -\log_{10}(I/I_0)$ where I and I_0 represent the intensity of the transmitted and incident light, respectively.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed on a JEOL 2000EX operated at 200 keV and a Quanta 600 Environmental SEM (operated in low vacuum mode, ~ 0.98 Torr), respectively. All analysis of TEM micrographs was done using processing software ImageJ (see section 3.5.4).

5.2.4. Calculation of the extinction cross section of nanoparticles

The scattering and extinction cross section of EGaIn nanoparticles was determined using Mie theory for homogenous spheres, as explained in section 2.5.3. Calculations were performed using a following the procedure detailed by Bohren and Huffman.¹⁰⁴ Specifically, the expression for the extinction cross section (C_{ext}) is given by

$$C_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}\{a_n + b_n\} \quad (6.3)$$

for which k is a wave vector¹⁰⁴ and a_n and b_n are the Mie scattering coefficients that are defined in terms of Riccati-Bessel functions of order n $\Psi_n(z)$, $\chi_n(z)$, $\zeta_n(z)$ as

$$a_n = \frac{\psi'_n(y)\psi_n(x) - m\psi_n(y)\psi'_n(x)}{\psi'_n(y)\zeta_n(x) - m\psi_n(y)\zeta'_n(x)} \quad (6.4)$$

$$b_n = \frac{m\psi'_n(y)\psi_n(x) - \psi_n(y)\psi'_n(x)}{m\psi'_n(y)\zeta_n(x) - \psi_n(y)\zeta'_n(x)} \quad (6.5)$$

Here, m is the ratio of the (complex) refractive index of the particle to the medium or N^*/N_m , where $N^* = N + iK$ is the complex refractive index of the EGaIn particle, x is wave vector k multiplied by radius of the sphere a or equivalently $x = ka = 2\pi N_m a / \lambda$, and $y = mka = 2\pi N^* a / \lambda$ (where λ is wavelength). For numerical evaluation the sum was truncated at n_{max} iterations defined by Bohren and Huffman¹⁰⁴ to as $n_{max} = x + 4x^{1/3} + 2$.

5.3. Results and discussion

5.3.1. Systematic surfactant variation

To evaluate the role of surfactant composition on the formation of EGaIn nanodroplets a library of aliphatic surfactant systems with varying chemistry of head group and amphiphilicity were

considered. Thiol-surfactants were considered because of the strong affinity of sulphur to a wide range of transition metals.^{13,78} Amine and carboxyl-surfactants were considered because of their expected affinity to oxides since partial oxidation was hypothesized to play a role in EGaIn nanodroplet formation in the literature.^{15,16,78} Aliphatic groups were considered because of the reported effectiveness of aliphatic surfactants in stabilizing EGaIn nanodroplets as well as to enable the select evaluation of the role of amphilocity at otherwise constant chemical constitution. Table 5-1 summarizes the distinct surfactant systems that were considered in this study. An example of surfactant-dependent differences seen in the samples is shown by Figure 5-1.

Table 5-1. List of surfactants selection for variation study, along with ligand identifier, chemistry (functional group) and molecular weight. All surfactants used at 1.0 mM in ethanol.

Surfactant	Identifier	Functionality	M _w (g/mol)
C ₁₈ H ₃₇ – SH	C18	thiol	286.56
C ₁₂ H ₂₅ – SH	C12	thiol	202.40
C ₈ H ₁₇ – SH	C8	thiol	146.29
C ₄ H ₉ – SH	C4	thiol	90.19
C ₁₀ H ₂₁ – NH ₂	N10	amine	157.30
C ₈ H ₁₇ – NH ₂	N8	amine	129.24
C ₁₇ H ₃₅ – COOH	SA	carboxylic acid	284.48
C ₁₁ H ₂₃ – COOH	DA	carboxylic acid	200.32

All tests were conducted at a concentration of 1mM surfactant in ethanol (EtOH) solution at 293 K. This corresponds to reaction conditions that were previously reported as being ‘most effective’ for the stabilization of EGaIn nanodroplets. To validate the conclusion of previous reports, solvent variation tests were performed in which the formation of EGaIn nanodroplets was evaluated in polar protic solvents (water, methanol, ethanol, isopropyl alcohol) as well as polar aprotic (dimethylformamide, dimethylsulfoxide) and unpolar solvents (toluene). Results of these tests are discussion in the next section (5.3.2). Among all solvents, the analysis of nanodroplet formation (using the experimental procedures described below) was observed to be most effective

in ethanol. While the origin for the particular efficiency of ethanol is not currently known, we hypothesize that it might be related to the solvation capability of ethanol that suppresses the formation of micellar aggregate structures of surfactants in solution (the latter was confirmed by dynamic light scattering on surfactant solutions). Similarly, the variation of the concentration of mercaptododecane in ethanol within the range 0.1 – 20 mM revealed maximum nanodroplet formation at 1 mM $C_{12}H_{25}SH$ concentration (results not shown). This confirms prior reports by Hohman and coworkers who identified a surfactant concentration of 1 mM as ‘optimum’ for nanodroplet synthesis.¹³

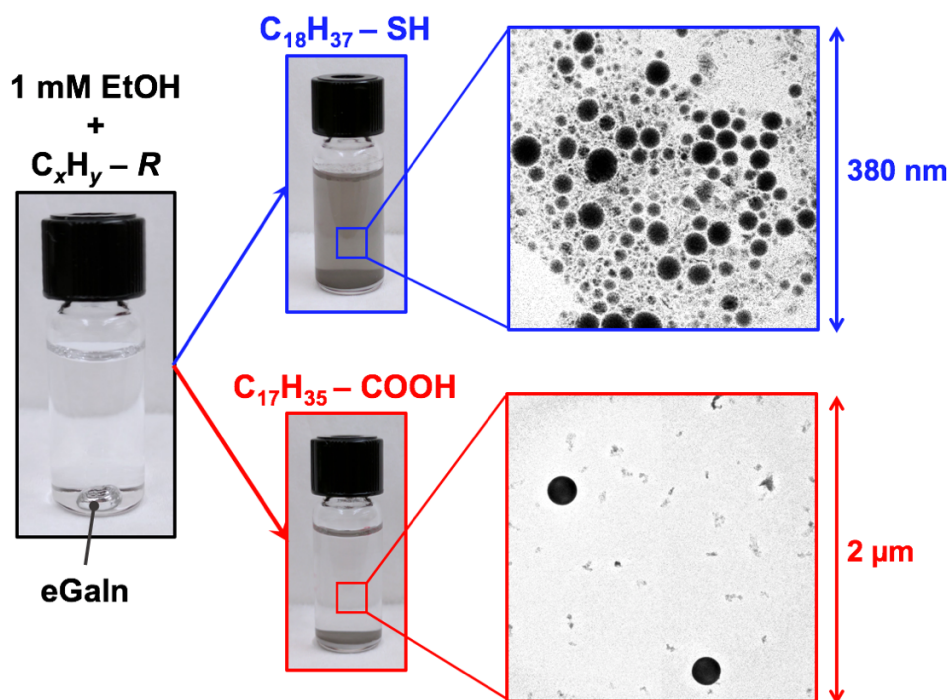


Figure 5-1. Illustration of differences in nanoparticle size and density in suspension as a function of aliphatic surfactant in 1 mM ethanol (EtOH). In this example, octadecanethiol (blue) and stearic acid (red) are compared.

5.3.2. Justification of experimental conditions

As mentioned in the previous section, multiple solvents besides ethanol were investigated for dispersing EGaIn in 1 mM $C_{12}H_{25}SH$ or C12 solutions. The unpolar solvent (toluene) as well as two of the polar solvents tested – water (protic) and dimethylformamide or DMF (aprotic) –

were not effective for creating nanodroplets. Of the solvents that demonstrated successful LMP stabilization, ethanol (EtOH) displayed on average the highest concentration of EGaIn suspension, as shown in Figure 5-2. (Note that only one of the three DMSO samples resulted in a dispersed

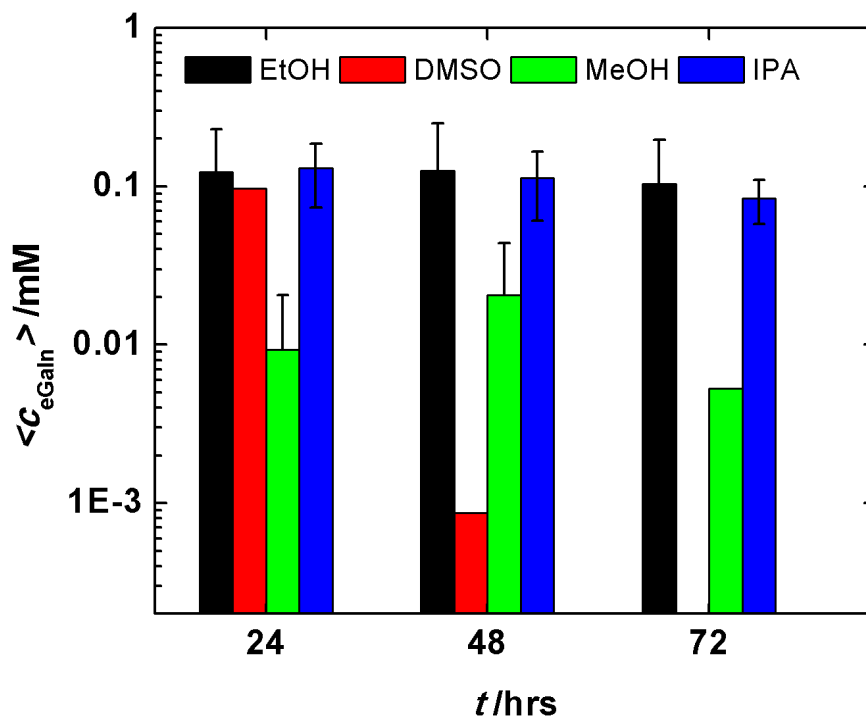


Figure 5-2. EGaIn concentration evolution over three days for 1 mM C12 in various solvents. EtOH = ethanol; DMSO = dimethyl sulfoxide; MeOH = methanol; IPA = isopropanol. Error bars represent standard deviation of $n = 3$ samples.

solution which could be tested, hence the lack of an error bar.) From the graph, isopropanol (IPA) appears to perform nearly as well as EtOH. However, particle analysis from dynamic light scattering (DLS) revealed consistently bimodal number size distributions when using IPA (unlike the narrow unimodal distributions characteristic of ethanolic solutions). A typical observed distribution is given by Figure 5-3.

As an additional check, DLS was performed for all surfactants in EtOH to ensure correlation and size data came from only dispersed LMPs in solution. Concentrations of 1.0, 5.0, 10, 15 and 20 mM were tested (the latter are an order of magnitude more concentrated than the solution used thus far for LMP synthesis). Figure 5-4 displays raw correlation for 1.0 mM and 20

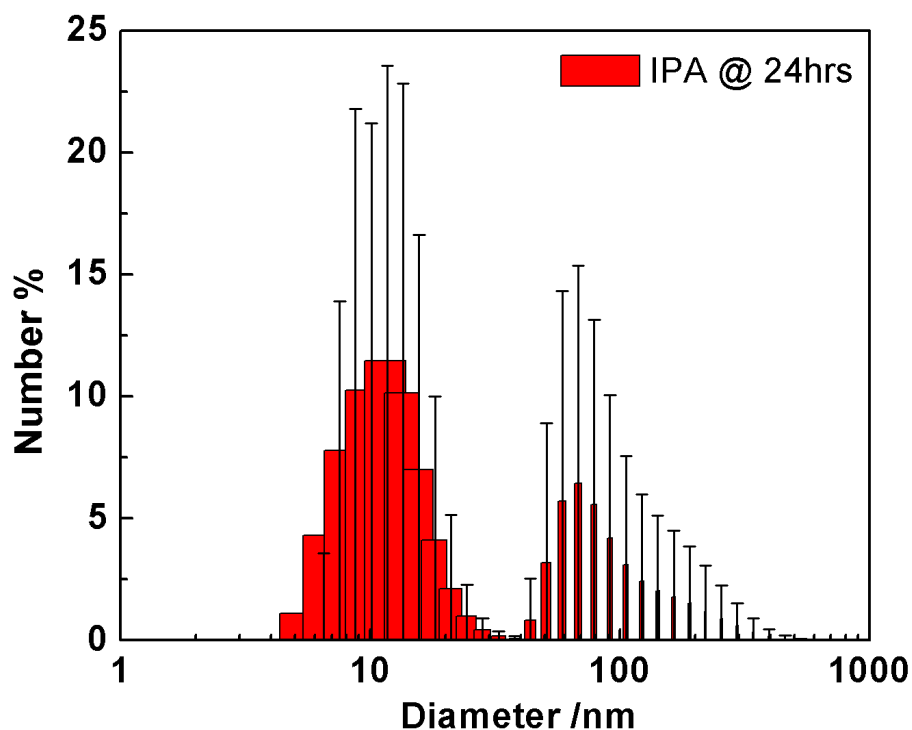


Figure 5-3. Representative number weighted size distribution obtained from dynamic light scattering software using CONTIN analysis of EGaIn LMPs in 1 mM C12 + IPA.

mM C12 solutions as an example, which show no correlation. Thus, the experimental concentrations are still in the dilute regime (much below the critical micelle concentration or CMC of C12 in EtOH) and the size results are more readily trusted. Conversely, the same surfactant in toluene showed correlation at just 1.0 mM, as evidenced by the correlation function in Figure 5-5. Therefore, toluene (and other polar solvents) are not suitable alternatives for synthesizing EGaIn LMPs using C12 since micelles readily form. Attempts to sonicate EGaIn in 1.0 mM C12 and toluene were unsuccessful (EGaIn did not disperse at all), as was also the case for water and DMF as mentioned before.

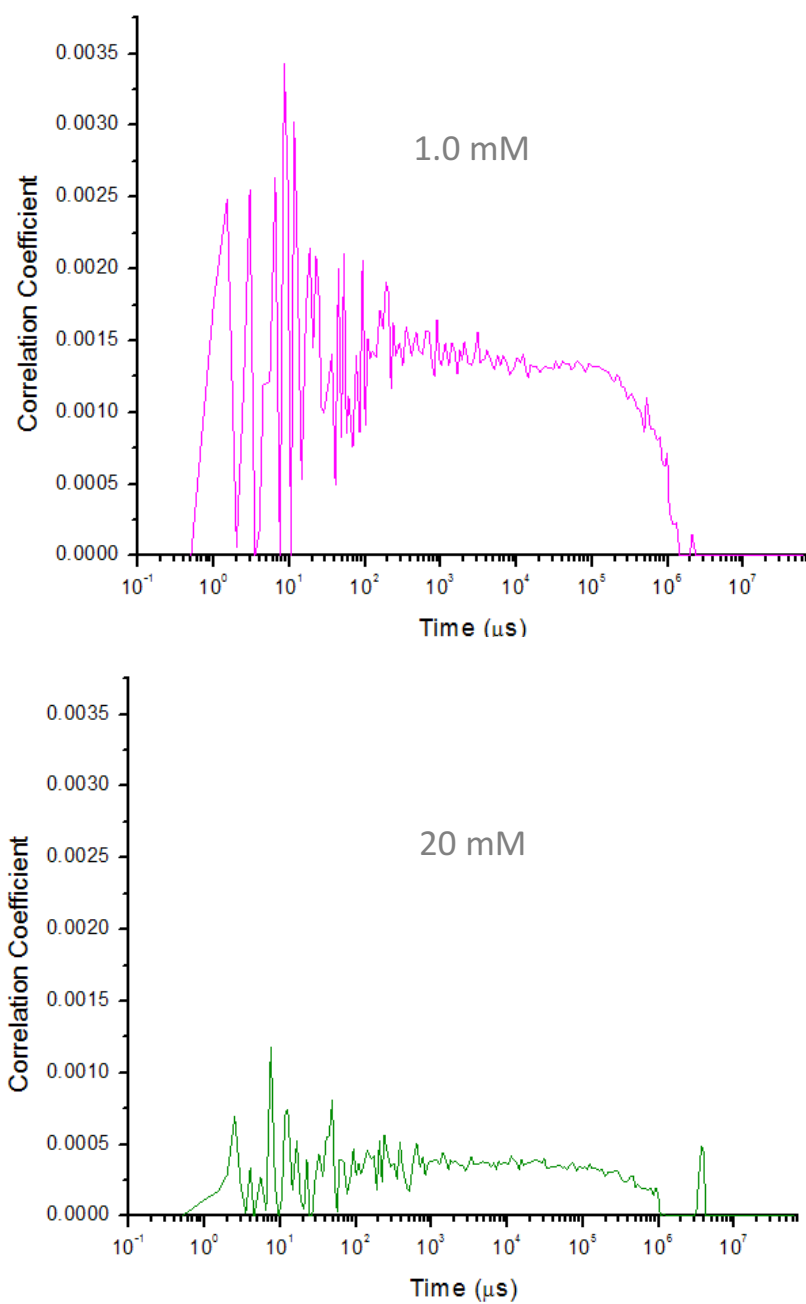


Figure 5-4. Representative DLS correlation data of 3x filtered dodecanethiol in ethanol at (top) 1.0 mM and (bottom) 20 mM concentrations showing no correlation (no micelle formation).

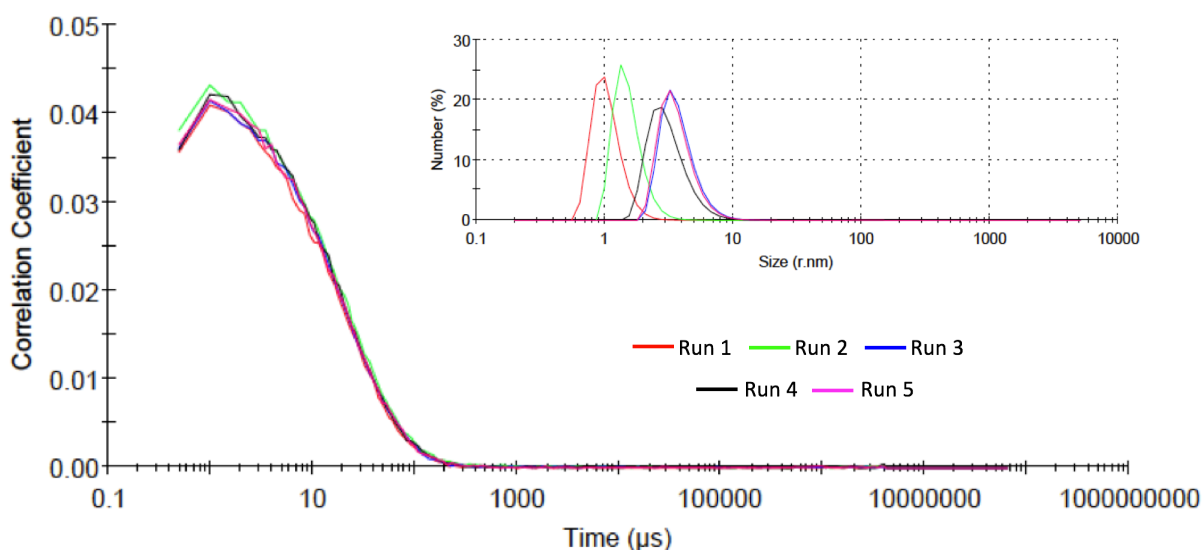


Figure 5-5. Correlation data of 1.0 mM dodecanethiol in toluene showing clear correlation and (inset) Malvern determined particle radii (< 10 nm). The very short decay time (corresponding to smaller size) and relatively low concentration at which this is observed is suggestive of surfactant micelles.

Part of the experimental procedure for the synthesis of LMPs is the partial deoxygenation of the solution prior to EGaIn addition, explained in 5.2.2 as bubbling of nitrogen through the solution. The role of oxygen was briefly investigated for the suspension of EGaIn droplets. As seen in Figure 5-6, some amount of dissolved O₂ appears necessary for any sustained particle dispersion, which is in agreement with literature findings.¹³ The complete removal of oxygen or lack of any degassing resulted in completely sedimented samples (usually within hours after removal from the sonicator).

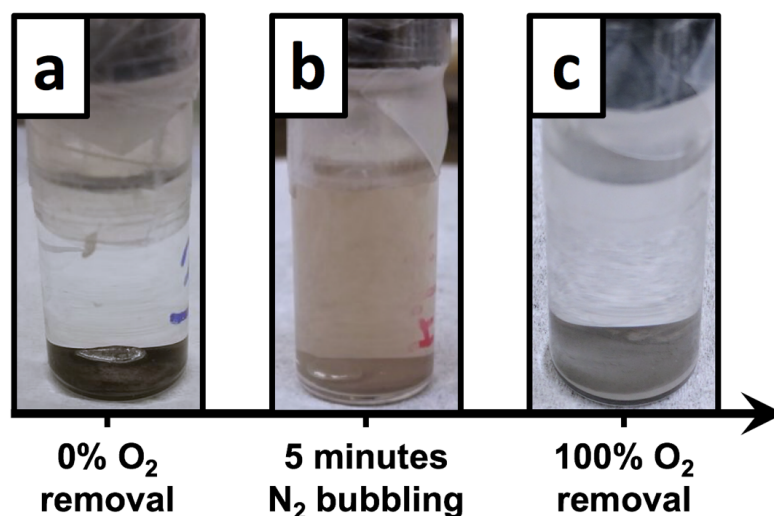


Figure 5-6. Comparison of samples after 24 hours decanting with (a) no attempted deoxygenation, (b) 5 minutes of nitrogen bubbling through solution prior to EGaIn addition and (c) degassing from freeze-pump-thaw method. Samples (a) and (c) show transparent solutions due to complete sedimentation of EGaIn, whereas the slight tint of sample (b) is indicative of suspended particles.

5.3.3. Evaluation of nanoparticle dispersions

To induce nanodroplet formation, ~ 0.2 mg of EGaIn was mixed with 1.5 mL of surfactant solution. The mixtures were subsequently sonicated for 60 minutes at 40 kHz. To evaluate the role of surfactants on nanodroplet formation all reactions were carried out multiple times under identical conditions to ascertain the reproducibility of reactions. Values reported for efficiency and particle size thus represent average values calculated on the basis of three experiments. Because gravimetric methods were found to be impractical for determining the yield of nanodroplet formation, an optical characterization process based on the quantitative analysis of the scattering strength of nanodroplet solutions was employed instead. The process is composed of three steps: First, the determination of particle size distributions using dynamic light scattering (DLS). Second, the measurement of the extinction coefficient of nanodroplet solutions using UV/Vis spectrophotometry. Finally, the yield was deduced by analysis of the total scattering strength of nanodroplet solutions with a Mie model for disperse EGaIn spheres with corresponding size distribution. Figure 5-7 depicts the experimental field autocorrelation function $C(q, t)$ measured at

$q = 2.72 \times 10^7 \text{ m}^{-1}$ 24 hrs after sonication of EGaIn dispersion in EtOH/C₁₂H₂₅SH. CONTIN analysis of $C(q, t)$ was used to determine the number-weighted particle size distribution $P_n(D_H)$ where D_H denotes the hydrodynamic diameter of particles (the fit as well as residuals is shown in Figure 5-7).

Since hydrodynamic interactions in suspensions of spheres are expected to be negligible in

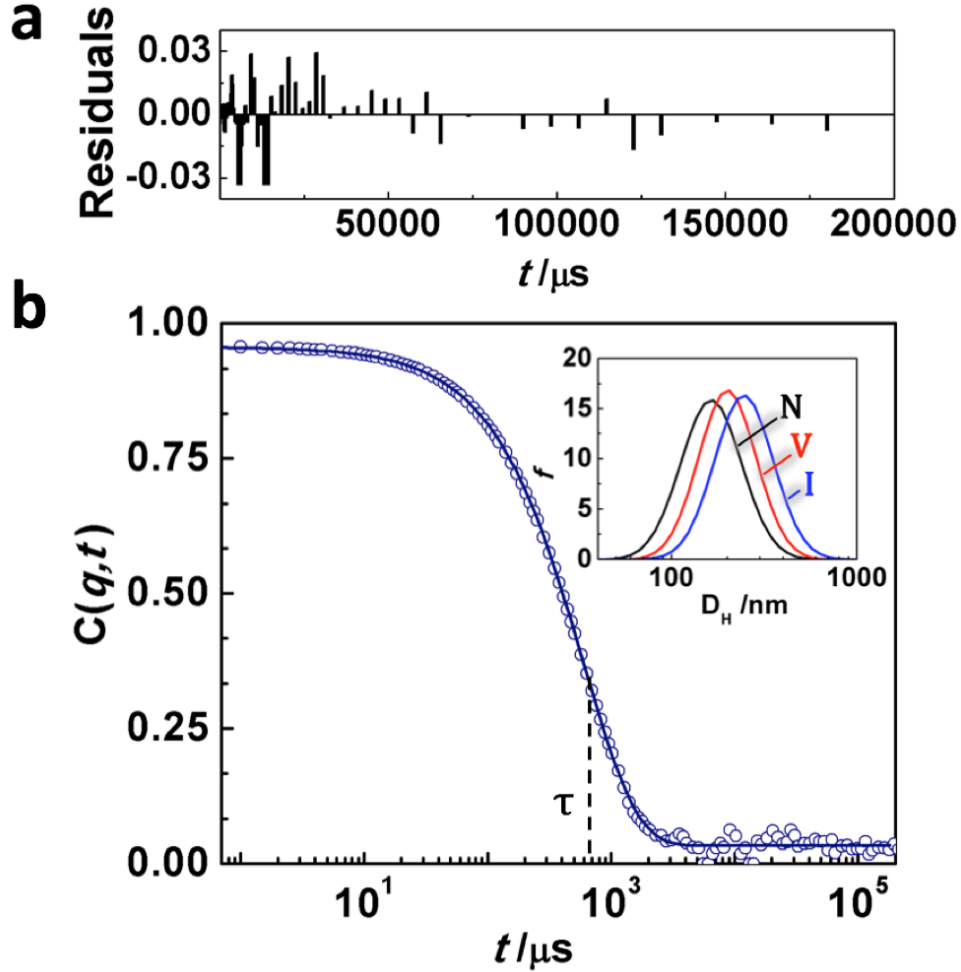


Figure 5-7. Representative light scattering results of EGaIn nanodroplets in EtOH/C₁₂H₂₅SH at $q = 2.72 \times 10^7 \text{ m}^{-1}$ (see text for more details). Figure shows experimental autocorrelation function of the electric field $g_1(t)$ 24 hrs after sonication along with CONTIN fit. Inset in main figure shows number (black), volume (red), and intensity (blue) weighted distributions of hydrodynamic diameters that were determined through CONTIN analysis. Top panel shows random variation of residuals thus confirming high quality of fit.

the limit of $(V/N)^{1/3} \gg D$ (where $(V/N)^{1/3}$ denotes the average distance between spheres in the suspension and R denotes the sphere diameter) the hydrodynamic size is in the following assumed

to be equal to the geometric diameter of EGaIn particles. The proximity of number, weight and intensity weighted distributions (shown in the inset of Figure 5-7) confirms the narrow size distribution of nanodroplets. To validate the results from DLS analysis, the particle size of select systems was concurrently evaluated using transmission electron microscopy (TEM).

Figure 5-8 depicts the corresponding number weighted size distribution $P_n(D)$ along with the corresponding size distribution determined by TEM analysis for the EGaIn/C₁₂H₂₅SH system, in which the image processing software ImageJ was used to determine the size of 200 particles from TEM micrographs (see section 3.5.4). The excellent agreement between the respective average values $\langle D \rangle_{\text{DLS}} = 176 \text{ nm}$ and $\langle D \rangle_{\text{TEM}} = 150 \text{ nm}$ confirms the DLS analysis. Because light scattering is a bulk characterization method that allows the rapid evaluation of macroscopic material volumes, DLS analysis was used to determine size distributions of EGaIn nanodroplets in suspension.

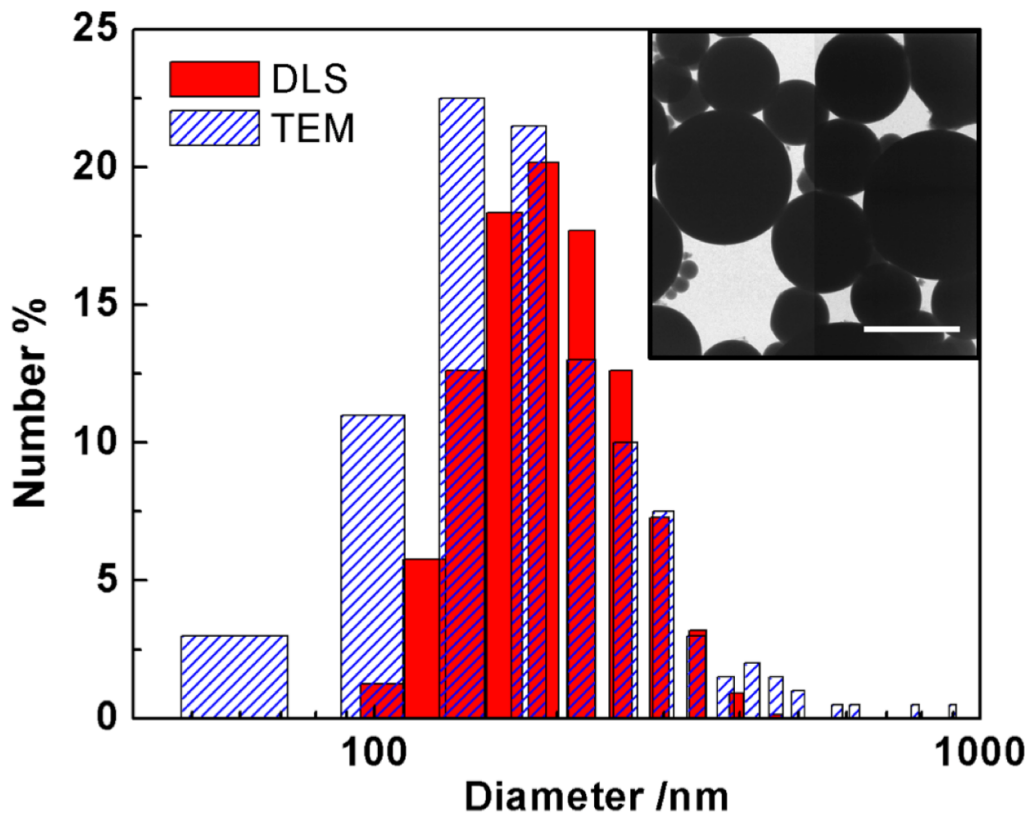


Figure 5-8. Comparison of DLS software provided number size distribution with $\langle D_{\text{TEM}} \rangle \approx 150$ nm for dodecanethiol thiol sample at 24 hours with particle size distribution for dodecanethiol sample determined from 200 particles using electron microscopy where $\langle D_{\text{DLS}} \rangle \approx 176$ nm. Inset is TEM micrograph of sample showing range of particles consistent with distributions. Scale bar 500 nm.

5.3.4. Calculation of extinction and particle yield

To quantitatively relate the size distribution of EGaIn nanodroplets to the extinction coefficient of nanodroplet suspensions, calculations of the average extinction cross section of disperse spherical nanodroplets using Mie theory were performed. A prerequisite for performing these calculations was knowledge of the optical constants N and K that represent the real and imaginary part of the refractive index of EGaIn nanodroplets, respectively. Optical constants were determined from tabulated values of indium and gallium using an effective medium method (see Appendix section 9.2 for listed EGaIn values as a function of wavelength).^{154,155} The latter has been shown to provide adequate representation of the optical and dielectric properties of uniform

atomic solutions of components that are expected for EGaIn above the eutectic temperature. Thus the effective dielectric constant was calculated using Newton's formula which represents a simple volume weighted average of the dielectric properties of the constituents, *i.e.* $\epsilon_{\text{eff}} = \phi\epsilon_1 + (1-\phi)\epsilon_2$, where ϕ denotes the volume fraction and ϵ_i the dielectric constant of component i . Optical constants were subsequently calculated based on the relations $\epsilon_{\text{eff}}' = N^2 - K^2$ and $\epsilon_{\text{eff}}'' = 2NK$ where ϵ_{eff}' and ϵ_{eff}'' represent the real and imaginary part of the effective dielectric constant, respectively. Figure 5-9 illustrates the trend of N and K of EGaIn nanodroplets that was determined based on an effective medium theory along with the respective optical constants of the constituent components.

It is noted that the process for calculating the optical constants that is outlined above neglects any effect due to the finite size on the optical constants of EGaIn nanodroplets. Size effects on the optical properties of metal nanoparticles have been shown to primarily result from classical surface scattering of electrons that arises if the size of particles decreases below the

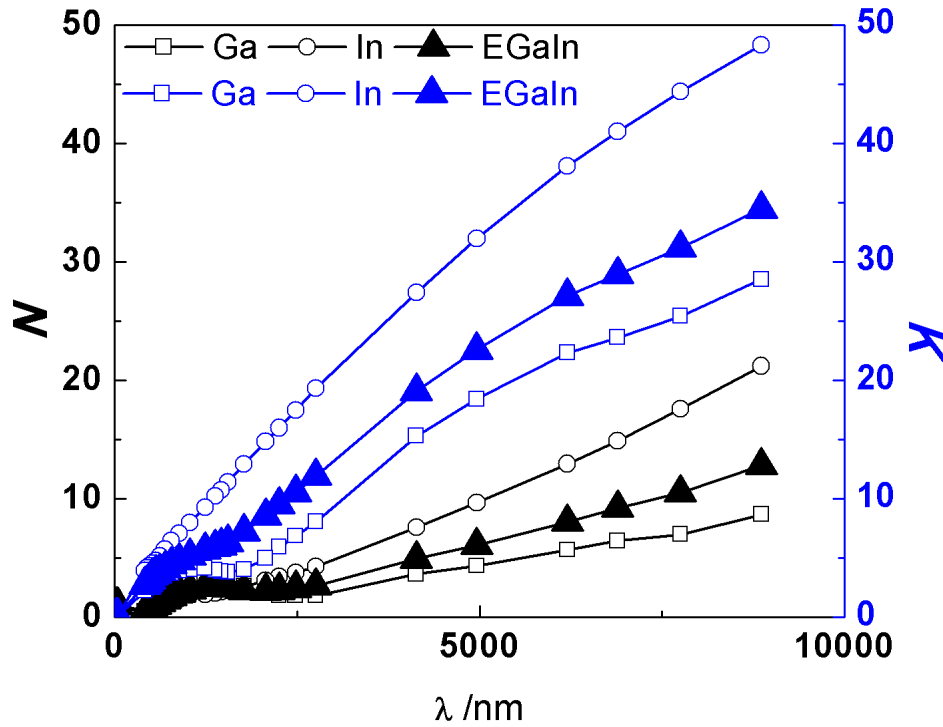


Figure 5-9. Real (N) and imaginary (K) components of the refractive index for EGaIn as determined from effective medium approximations compared with known values for Gallium and Indium as a function of wavelength.

electron mean free path (except for the limit of very small particle size where quantization effects can occur).¹⁵⁶ Since the electron mean free path in metals is typically of the order of 20 nm, *i.e.* much less than the average size of EGaIn nanodroplets, bulk properties can safely be assumed in the present case.

The extinction cross section of disperse nanodroplets was subsequently determined as

$$\langle C^{ext}(\lambda) \rangle = \int C^{ext}(D, \lambda) P_n(D) dD / \int P_n(D) dD \quad (6.6)$$

using Mie theory (see eqs. 6.3 – 6.5) where the denominator in eq. 6.6 equals to one if $P(D)$ is normalized.¹⁵⁷ From the experimental extinction A (see section 5.2.3), the number of EGaIn nanodroplets was then determined via substitution in Beer-Lambert equation, given in section 3.5.2 with the general form¹⁵⁸

$$I = I_0 \exp(-C^{ext}lc) \quad (6.7)$$

where C^{ext} is the extinction cross section for a single particle size, l is the pathlength of light through the medium (in this case, the width of the sample cuvette) and c was defined as the number concentration of particle (units of volume⁻¹). From the relationship in of A to the log of the intensities (see 5.2.3), the equation can be rewritten after a change of base as

$$A = \frac{1}{2.303} C^{ext} l \left(\frac{N}{V} \right) \quad (6.8)$$

and rearranged to solve for total number of particles $N_{tot} = 2.303AV\langle C^{ext}(\lambda^*) \rangle^{-1}l^{-1}$, where substituted for C^{ext} is $\langle C^{ext}(\lambda^*) \rangle$ or the average extinction cross section for the corresponding particle distribution $P_n(D)$ at a test wavelength λ^* , $l = 1$ cm and V is the sample volume. The test wavelength was chosen to be $\lambda^* = 505$ nm for reasons of practicality (*i.e.* good signal-to-noise ratio with no interference by solvent or surfactant components). We note that the choice of λ^* introduces some ambiguity with regards to the uniqueness of the result; however, based on the good agreement

between experimental and calculated A (see below) the error associated with any particular choice of λ^* (in the range of $450 \text{ nm} < \lambda^* < 600 \text{ nm}$) is expected to be less than 5%. We further note that for calculation of the extinction cross section, the refractive index of the solvent medium was assumed to be equal to the value of pristine EtOH ($n_{\text{EtOH}} = 1.3616$). The neglect of surfactant contributions to the refractive index is not expected to result in relevant errors due to the small surfactant concentration of 1 mM. Figure 5-10 displays the experimental extinction of EGaIn nanodroplets in EtOH/C₁₂H₂₅SH solution along with the calculated extinction (for $N_{\text{tot}} = 5.7 \times 10^8$). The figure reveals excellent agreement between calculated and experimental values across most of the visible wavelength range. Note that good agreement is only achieved by accounting for particle size dispersity. This is illustrated in the inset of Figure 5-10 that depicts the respective scattering and absorption cross sections of EGaIn nanodroplets assuming a uniform size equal to

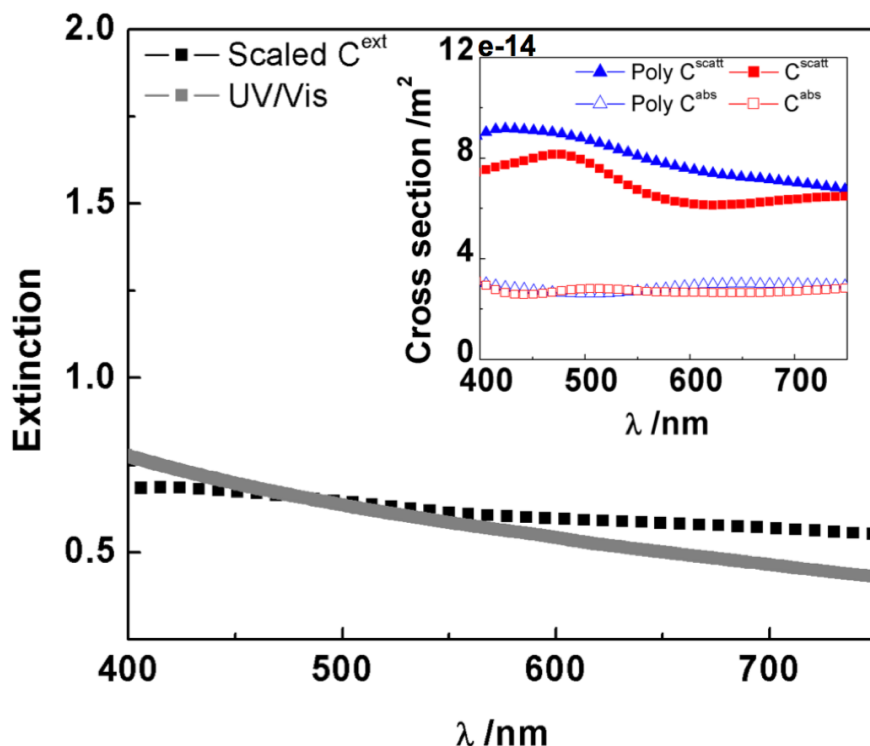


Figure 5-10. Extinction as a function of wavelength for the visible spectrum from raw UV/Vis data and scaled extinction coefficient data as determined from the efficiency code. Inset shows the scattering and absorption cross sections for the case of a uniform particle size compared to a disperse distribution.

the average droplet diameter (*i.e.* $D = \langle D \rangle$) (red symbols) as well as a size distribution corresponding to $P_n(D)$.

Comparison of the scattering (filled symbols) and absorption (open symbols) cross sections also reveals that the optical extinction of EGaIn nanodroplet solutions is dominated by the scattering of nanodroplets. This supports previous reports on the optical properties of metal nanoparticles that have shown that the scattering cross section typically exceeds the absorption cross section for particle diameter exceeding 20 nm (the latter can be rationalized as a consequence of the distinct dependences of the cross sections on the particle volume, *i.e.* $C^{\text{scatt}} \sim V_p^2$ and $C^{\text{abs}} \sim V_p$).^{151,155,159,160}

5.3.5. Computational approach

The MATLAB program *Poly_Mie.m* (given in Appendix section 9.1.1) was coded to solve for a weighted average extinction cross section for a polydisperse solution based on the equations described in section 2.5.3 and above in 5.2.4. The Riccati-Bessel functions were defined as function handles and were scripted using MATLAB's built in Bessel functions (namely “besselj”). The script is provided in the Appendix under Mie scattering from polydisperse solution. Prior to running the program, DLS measurements must have been made. Additionally, the user must initially provide the real and imaginary optical constants (as a function of wavelength) as a separate file as mentioned in 5.3.4, and also the index of refraction for the matrix material (in this case, ethanol). Once started, the program asks the user to select the storage location of the size output files (number size distribution). For each existing particle size in a sample determined by the DLS software CONTIN analysis, *Poly_Mie.m* uses nested “for” loops to calculate the extinction cross section over the wavelength range 100 – 1000 nm. Since equation 6.3 for the extinction cross

section contains an infinite sum, a value of $n_{\max}$ iterations was defined by Bohren and Huffman¹⁰⁴ to truncate the series: $n_{\max} = x + 4x^{\frac{1}{3}} + 2$, where again $x = ka = 2\pi a/\lambda$. The resulting array of C^{ext} values (over the range of wavelengths and also sizes) is then multiplied by the frequency or number fraction of the corresponding particle size to give a column of values equaling $C_{eff} = \langle C^{ext}(\lambda^*) \rangle$. It should be noted that the number size distribution is normalized.

Once the effective extinction cross section has been determined, the program *efficiency_calc_poly.m* (see Appendix 9.1.2) calculates the mass of EGaIn in the sample, as well as a weighted size average of EGaIn droplets for a specified wavelength (in this case $\lambda = 505$ nm). The absorbance $A_{\lambda=505}$ must be input by the user based on UV/Vis testing, though the extinction cross section is automatically pulled from the array output of *Poly_Mie.m*. As mentioned before, there were several reasons for selecting a seemingly arbitrary wavelength of 505 nm. First, initial UV/Vis data showed good signal (measurable absorbance) at this value. Second, the value of the calculated C_{eff} was provided for this wavelength, requiring no further interpolation. Thus, the program solves the rearranged Beer-Lambert equation for number of particles at each size, and then computes $\sum_{i=1}^n N_i m_i$ where n is the total number of particle sizes, N_i is the number of particles at size i , and m_i is the mass of particle size i . Additionally, the program calculates a weighted average particle size (in nm) based on the frequency of the different particle sizes and the total number of determined particles N_{tot} .

A third MATLAB program, *DLS_Correlation.m* (found in the Appendix, section 9.1.3), imports the raw correlation data .txt files saved from DLS measurements and fits measurements with single exponential decay. The user is asked to select the correlation range to analyze (using MATLAB's "ginput" function) to discount any non-representative artifacts (e.g. static at larger

decay times due to dust). The average particle size is then solved for using the Stokes-Einstein equation following the method described in 2.5.1.

5.3.6. Process summary for yield determination

Calculation of yield is a multi-step procedure that requires experimental data input from both light scattering (particle number size distribution) and UV/Vis spectroscopy (particle absorbance or “extinction”). As discussed above, MATLAB is then used to calculate an effective extinction cross section from the number size distribution (Mie theory), and then total number of EGaIn particles from the absorbance (extinction) measured by UV/Vis. Consequently, the total EGaIn mass in suspension is calculated. Figure 5-11 below summarizes this process.

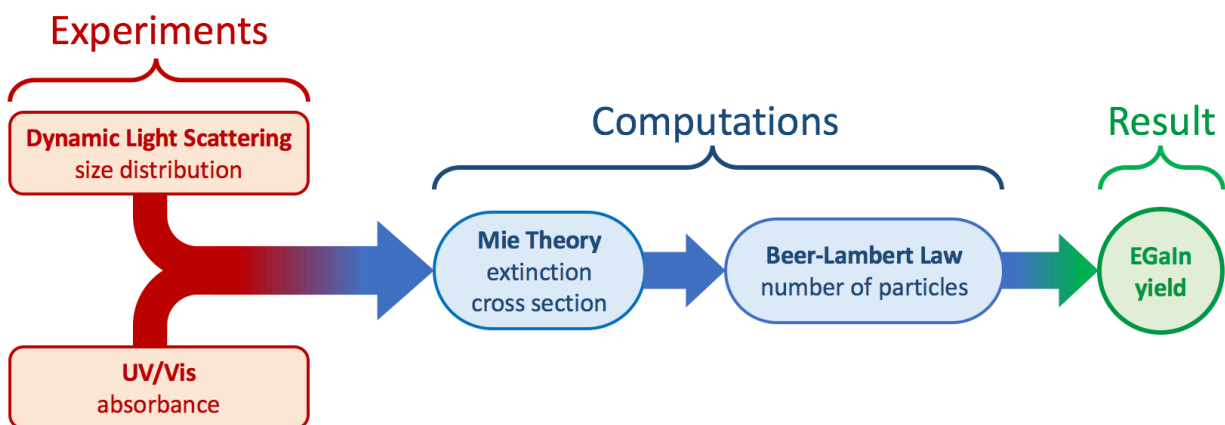


Figure 5-11. Flow chart summarizing experimental and computational process to determine EGaIn yield. Size distribution obtained through DLS is percent number distribution from CONTIN analysis.

5.3.7. Size and efficiency results

Figure 5-12 depicts the number average particle diameter $\langle D \rangle$ of EGaIn nanodroplets using each surfactant for $n = 3$ samples that was determined from the particle size distributions (via $\langle D \rangle = \int DP_n(D)dD$). Average particle diameter ranged from $\langle D \rangle = 80$ nm for $C_{18}H_{37}SH$ to $\langle D \rangle = 250$ nm for stearic acid solutions. Note that the result for mercaptododecane $\langle D \rangle = 170$ nm closely matches the results reported by Hohman et al. who first reported the surfactant mediated synthesis of EGaIn nanodroplets.¹³ A pertinent feature that is revealed by Figure 5-12 is that nanodroplet formation also occurs in pristine EtOH solution, *i.e.* in the absence of surfactant additives. For all solution systems nanodroplet size was found to be stable for 72 hours (the exception being stearic acid which showed a decreasing particle size). It is important to note that, because nanodroplet

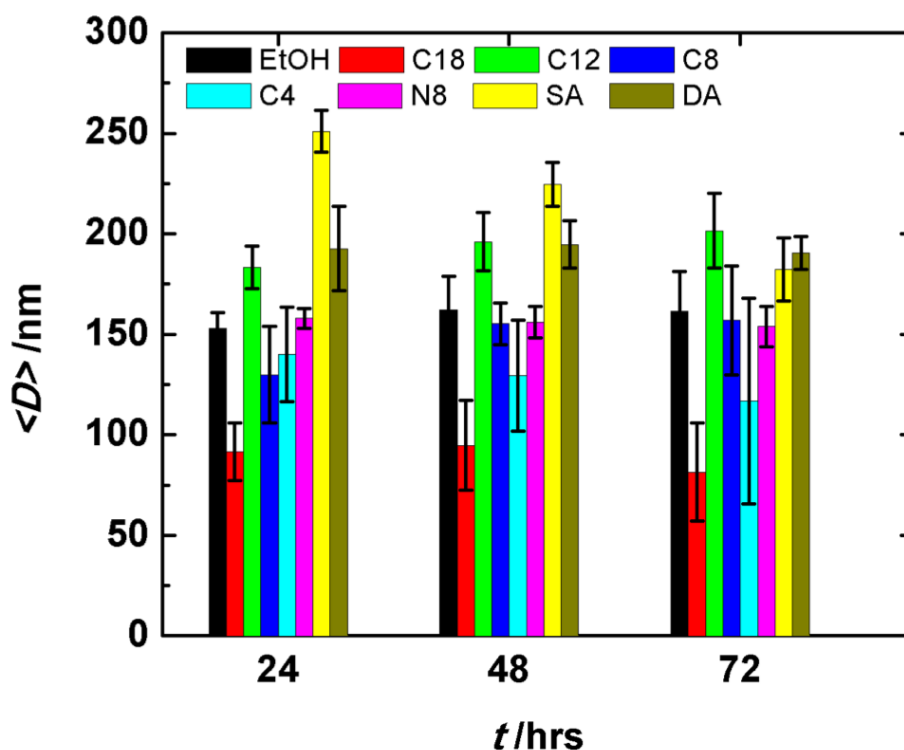


Figure 5-12. EGaIn particle size evolution over three days for various surfactants in 1 mM ethanol solutions compared against neat ethanol (EtOH). C8 = octadecanethiol, C12 = dodecanethiol, C18 = octanethiol, C4 = butanethiol, N8 = octylamine, SA = “stearic acid” or octadecanoic acid, DA = dodecanoic acid. Error bar is standard deviation for $n=3$ samples.

formation is also observed in pristine EtOH, the evaluation of droplet size is not sufficient to assess the benefit of surfactant addition but rather the yield of droplet formation has to be determined.

The average particle diameter of the y-axis on Figure 5-12 refers to the weighted size (calculated in MATLAB) based on the number weighted size distribution obtained from light scattering. As discussed in 5.3.5, both this weighted size and a fitted size (exponential decay fit to raw correlation data) were determined for each sample. For situations with a near monodisperse solution, one would expect these values to be quite similar. While this was the case for some samples, more often a discrepancy was found where usually the weighted size was less than the fitted size. Figure 5-13 illustrates this case for dodecanethiol (C12) samples, where although both averages were similar, the fitted size was usually larger with more deviation between measurements (larger standard deviation). This may have been due to scattering of larger particles

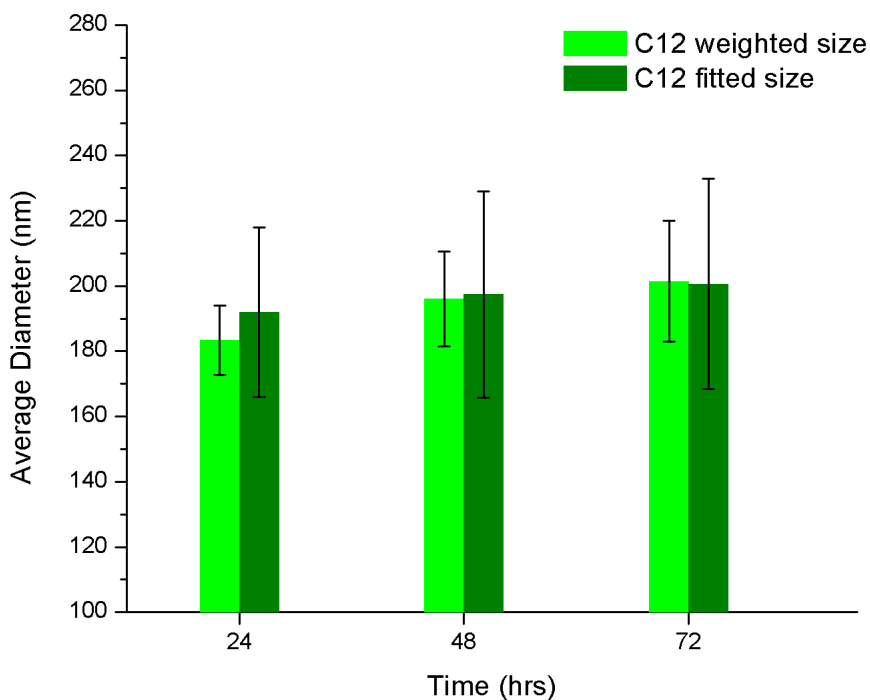


Figure 5-13. Comparison of weighted size (determined from DLS number distribution) to fitted size (from fitting of exponential decay) evolve results for the example of 1 mM dodecanethiol (C12) in EtOH. Error bar is standard deviation for n = 3 samples.

skewing the correlation data, which is a measurement of average intensity fluctuation and is highly sensitive to larger dispersants. Transmission electron microscopy confirmed the presence of both larger and smaller particles. Thus, weighted sizes were used for all sample comparisons as they were considered more representative of the actual dispersions.

The total mass of EGaIn nanodroplets dispersed in surfactant solutions was determined from the experimental number density of EGaIn droplets as $m_{\text{EGaIn}} = N_{\text{tot}}(4\pi/3)\rho_{\text{EGaIn}} \int (D/2)^3 P_n(D) dD$ where $\rho_{\text{EGaIn}} = 6.25 \text{ g/mL}$ is the density of EGaIn and normalization of $P_n(D)$ has been assumed. Figure 5-14 displays the resulting EGaIn concentrations as molarity ($c_{\text{EGaIn}} = \text{mmol}_{\text{EGaIn}}/L_{\text{solvent}}$) at 24 hrs, 48 hrs, and 72 hrs after sonication. Figure 5-14 reveals several pertinent features: First, mercapto-based surfactants display higher yields for nanodroplet formation as compared to alternative solvent systems. Second, of the different aliphatic surfactant systems tested in the present study, mercapto-octadecane exhibits the highest yield of nanodroplet formation (0.15 mM or 15.7 $\mu\text{g/mL}$), exceeding the yield of mercapto-dodecane (0.12 mM or 10 $\mu\text{g/mL}$) – the previously mentioned most efficient aliphatic surfactant – by approximately 200%. The higher yield of $\text{C}_{18}\text{H}_{37}\text{SH}$ (as compared to $\text{C}_{12}\text{H}_{25}\text{SH}$) is associated with smaller droplet size ($\langle D \rangle = 80 \text{ nm}$ vs 170 nm). The latter should be of interest from an application perspective. In both $\text{C}_{18}\text{H}_{37}\text{SH}$ and $\text{C}_{12}\text{H}_{25}\text{SH}$, the concentration and size of droplets was found to be stable within the 72-hour time interval tested in the present study. Interestingly, the quantification of nanodroplet yield also reveals that most surfactant systems do not improve nanodroplet formation in statistically relevant amounts. Even for $\text{C}_{12}\text{H}_{25}\text{SH}$, the more significant experimental uncertainty renders a determination difficult. Only for $\text{C}_{18}\text{H}_{37}\text{SH}$ is the benefit of surfactant addition unequivocal, raising the yield of nanodroplet formation by over 300% as compared to pristine EtOH.

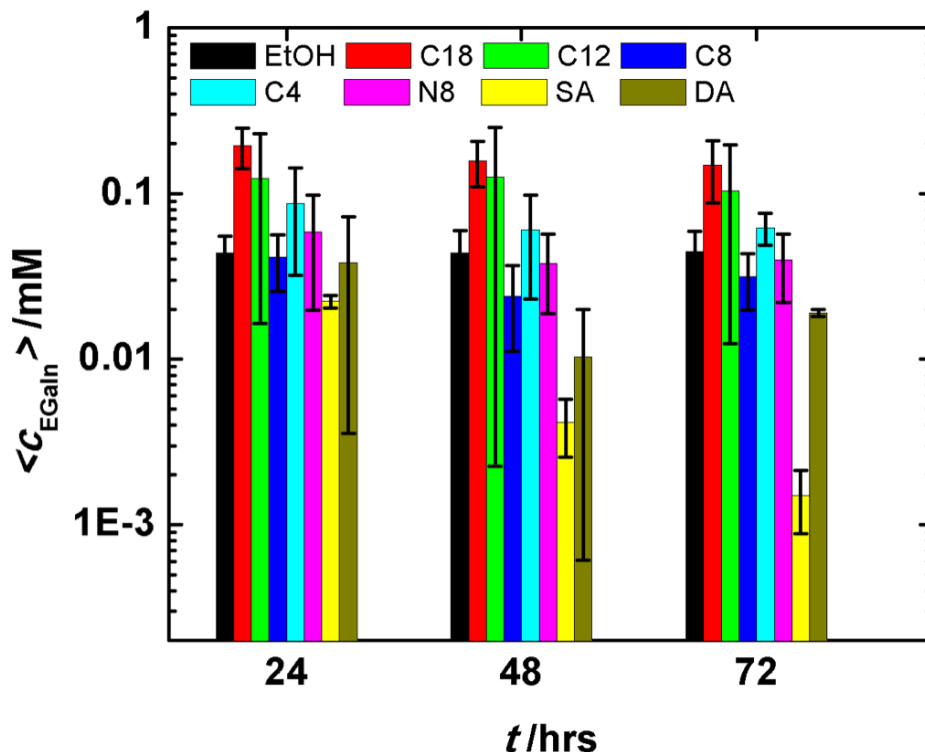


Figure 5-14. EGaIn concentration evolution over three days for various surfactants in 1 mM ethanol solutions compared against neat ethanol (EtOH). C8 = octadecanethiol, C12 = dodecanethiol, C18 = octanethiol, C4 = butanethiol, N8 = octylamine, SA = “stearic acid” or octadecanoic acid, DA = dodecanoic acid. 0.1 mM $\approx$ 8.1E-3 mg/mL. Error bar is standard deviation for n = 3 samples.

To further elucidate the mechanism of surfactant addition on EGaIn nanodroplet formation, dispersed nanodroplets were transferred to a variety of organic solvents, as discussed in section 5.3.2. Even in the case of $C_{18}H_{37}SH$, stabilized nanodroplet precipitation was observed in unpolar media such as toluene. This suggests that the stabilization mechanism is not related to the formation of dense self-assembled monolayers that have been commonly observed in metal particle systems.^{161,162} Additionally, hypoeutectic and hypereutectic mixtures of Ga-In alloy were created to investigate compositional effect on LMP formation. As demonstrated by Figure 5-15, the hypo- and hypereutectic compositions – Ga-rich and In-rich regions, respectively – were selected along the 25°C isotherm and thus remained in the liquid regime. Results of total particle suspension using these alloys compared to that of EGaIn (in 1 mM EtOH and $C_{12}H_{25}SH$) is shown in Figure 5-16. Although the change in composition from the eutectic point to the hypereutectic

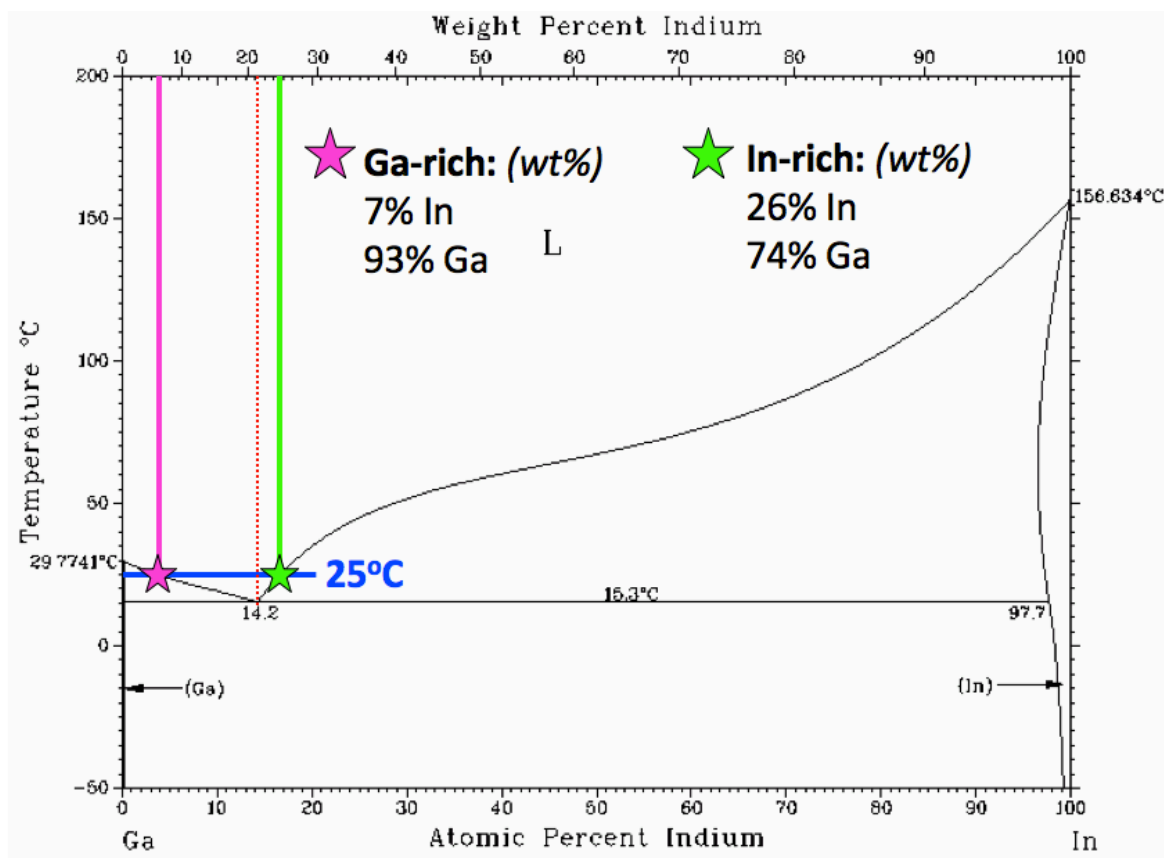


Figure 5-15. EGaIn phase diagram showing composition lines for the eutectic point (dotted red), a gallium rich or Ga-rich alloy (magenta) and an indium rich or In-rich formulation (green). Corresponding colored stars are intersections of the hypo- and hypereutectic compositions with isothermal line at 25°C (compositions according to weight % of Ga and In shown inside graph).

point (green star in Figure 5-15) is relatively minimal (especially compared to the difference between Ga-rich and EGaIn), the nanodroplet yield is clearly lower when more indium is present, by more than a factor of 2 compared to EGaIn. This is potentially due to that fact that alloys in the hypereutectic region are more sensitive to β -phase transformations, and thus small errors in composition could result in partial crystallization and reduce the effectiveness of sonication. However, it is not simply a trend of increased yield with increasing gallium. From Figure 5-16, the Ga-rich hypoeutectic composition behaves similarly to EGaIn and within experimental error may be considered roughly the same. This behavior suggests that LMP formation and stabilization are largely determined by the presence of gallium. Yamaguchi et al. maintained that $C_{12}H_{25}SH$ (as well native oxide formation) are important for regulating nanoparticle size and preventing

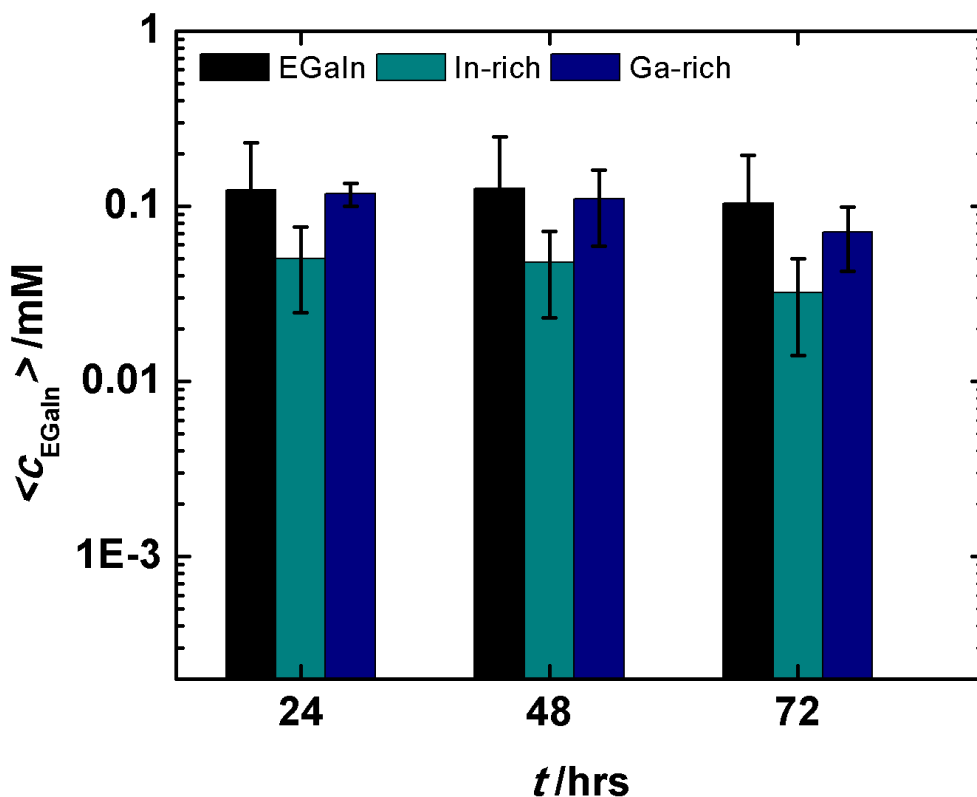


Figure 5-16. LMP concentration evolution over three days for various compositions of Ga-In in 1 mM EtOH and C12: eutectic (EGaIn), hypoeutectic (Ga-rich) and hypereutectic (In-rich). Error bar is standard deviation for $n = 3$ samples.

coalescence for the case of gallium nanodroplets.¹⁷ Such reasoning can be extended to this similar system and intimates that the mechanism of surfactant-enhanced synthesis involves manipulation of the solvent surface tension which might promote breakup of EGaIn during sonication. Clearly, more research will be needed to better understand the role of surfactant addition on the stabilization of EGaIn nanodroplet formation.

5.4. Conclusions

An optical characterization approach based on concurrent dynamic light scattering and photospectrometry was applied to evaluate the efficiency of aliphatic surfactant systems to stabilize EGaIn nanodroplets during the sonication of dispersions. Nanodroplet formation was

most significant in the presence of thiol-based surfactants, and mercapto-octadecane was found to be the most effective surfactant system. The analytical process reveals that quantification of particle size alone is insufficient to determine the efficiency of surfactant based EGaIn nanodroplet synthesis since significant nanodroplet formation also occurs in the pristine solvent. Only in the case of two surfactant systems (mercapto-dodecane and -octadecane) was the yield of nanodroplet formation found to exceed the one of the solvent beyond the error margin. The results suggest that surfactants play a fundamentally different role in nanodroplet stabilization as in other metal particle systems where the formation of dense self-assembled monolayers has been widely observed.

The behavior of stabilized droplets in nonpolar solvents as well as the sensitivity of the process to the presence of oxygen could mean that instead of the classical picture of SAMs forming on noble metals, droplet formation is instead driven by mechanical effects. In this depiction, sonication of EGaIn disrupts the surface of the metal and forms droplets (making the liquid phase a requirement for creating nanodroplets). Stabilization could then be explained as a result of the formation of oxide (most likely gallium oxide) on the exposed droplet surfaces. Certain surfactants which have shown to improve solubility (such as long chain mercapto-based molecules) may aid in this stabilization process by slowing oxidation or preventing its excess, which perhaps is why there exists a “sweet spot” level oxygenation for successful LMP suspension. Future research should focus on the elucidation of the surface chemical composition of EGaIn nanodroplets and its relation to the reaction yield to better understand the mechanism of surfactant-induced stabilization. It is hoped that the process presented in this contribution will assist in the development of facile synthesis processes towards EGaIn (and other low temperature and liquid metal) nanomaterials.

6. Plant Derived Surfactant Systems for Benign Synthesis of EGaIn Nanomaterials

Reference: Work presented in this chapter is *in preparation* for submission to Green Chemistry: Finkenauer, Lauren R.; Lu, Qingyun; Kim, Christine; Majidi, Carmel; Bockstaller, Michael R. “Plant derived surfactant systems for benign synthesis of EGaIn nanomaterials.”

6.1. Background and motivation

The biosynthesis of metallic nanoparticles has garnered much attention in recent years due to the need for more eco-friendly fabrication approaches. This has been especially true of plant-mediated synthesis techniques.¹⁶³ Such methods are seen as advantageous due to their simplicity, cost-effectiveness and nontoxicity.^{163–166} When compared to other biosynthetic methods such as microbial stabilization, “phytosynthesis” results in more stable nanoparticles, allows more control over morphology, is more reproducible and accelerated¹⁶⁴ and is a less tedious and time-consuming process.¹⁶³ The literature has largely focused on phytosynthesis of Ag and Au nanoparticles, but other common metals include Pt, Pd, Fe, and Cu (with particle sizes ranging anywhere from 5 – 300 nm depending on particular plant and processing conditions).^{84,167} Plant biomass is a promising substitute for microbes because plant-contained biomolecules (such as polyphenols, flavonoids, alkaloids and terpenoids) are capable of reducing metal ions to nanoparticles.¹⁶⁸ Plant-mediated synthesis is also advantageous over more familiar and proven metallic nanoparticle synthesis techniques such as laser ablation, lithography, aerosol technologies, and UV irradiation, as these approaches remain expensive and expel various levels of harmful pollutants.¹⁶⁶

Almost all shrubs, herbs or trees containing alcohols, phenols, proteins, latex, aroma and flavonoids can be used to generate metallic nanoparticles from metal salts.¹⁶⁷ Due to the extensive variety of candidates for this type of synthesis, there is vastly increased flexibility and control over the resultant particle shapes and sizes (in addition to generally more straightforward particle

creation).¹⁶⁵ As an example, facile particle size control is achieved through slight variations in process parameters such as extract concentration, temperature, pH and incubation time.¹⁶³ Given the same metallic precursor concentration, average particle size will decrease with increasing biomolecule concentration; increased reaction temperature has resulted in narrower nanoparticle size distributions.¹⁶⁴ Thus, the appeal of this process has led to numerous exploratory experiments testing the effects of different plant extract on properties of biosynthesized metallic nanoparticles.

The first demonstration of metallic nanoparticle biosynthesis using plant extract was by Gardea-Torresdey et al. in 1999.^{87,164} Biomass of *Medicago sativa* (alfalfa) was added to Au(III) solutions and used to synthesize Au nanoparticles via bio-precipitation. Using live alfalfa plants, these authors were able to produce both Au and Ag nanoparticles.¹⁶⁴ Plant-mediated synthesis approaches take advantage of multiple components: parts of their roots, leaves, seeds, stems and latex are used as part of the samples.¹⁶⁶ One example, the polyphenol caffeic acid – which is found in all plants due to its importance in lignin biosynthesis – was used both as a stabilizer and reducing agent to create Ag nanoparticles through a one-step reduction method.¹⁶⁹ Transmission electron microscopy showed that the shapes of these nanoparticles were spherical and fairly uniform with a size distribution ranging from 3 – 10 nm and an average diameter of 6.67 ± 0.35 nm. Dynamic light scattering was then used to measure the hydrodynamic diameter and zeta potential, which was found to be 8.72 ± 0.89 nm and -37.6 ± 2.24 mV, respectively.¹⁶⁹ The large negative zeta potential indicated a high negative surface charge of the caffeic acid-mediated nanoparticles, and suggested that they are stable in aqueous (or colloidal solutions).¹⁶⁹ Further investigation using these caffeic acid-capped Ag nanoparticles involved treating human hepatoma HepG2 cells to evaluate its anti-cancer activity. It was found that the amount of necrosis occurring amongst these

cells was not largely affected, suggesting the cytotoxic characteristic (or anti-tumor effect) of these plant-mediated nanoparticles could possibly assist radiotherapy when treating cancer.¹⁶⁹

Manufactured metallic nanoparticles are ubiquitously used in the field of nanotechnology. As a common example, Ag nanoparticles are widely utilized in the production of food, medicine, cosmetics and antimicrobial agents in consumer products and commercial medical materials.^{166,167} Increasingly, synthesized particles are being used in biotechnology applications which require a high degree of bio-compatibility and therefore minimized toxicity such as for drug delivery (Au), cancer therapy (Au, Fe) and as anti-cancer treatments (Se, Pt, Ag, Fe).¹⁶⁸ The use of plant-mediated synthesis for creating benign nanoparticles is a natural step in this effort. Thus, the purpose of this research is to demonstrate stabilization of liquid metal eutectic nanodroplets (extending from the work in Chapter 5) using common and readily available plant molecules (flavonoids and polyphenols).

6.2. Experimental methods

6.2.1. Material preparation

Bulk EGaIn was prepared according to the synthesis technique outlined in sections 3.1 and 5.2.1. Raw gallium (Ga) and indium (In) (99.99% pure, Gallium Source LLC) were combined to form the eutectic composition (75.5% Ga, 24.5% In by weight). The glass jar containing the metals was placed on a hot mixing plate until alloyed. Direct scanning calorimetry was then used to verify that the alloy was indeed the eutectic of Ga-In. The liquid metal was then injected into a capped borosilicate glass that had been flushed with nitrogen for 5 minutes prior, greatly reducing initial oxide formation, and finally wrapped tightly with a layer of Parafilm M. All plant derived surfactants were obtained from Sigma Aldrich and used as received: tannic acid, ACS reagent;

acetophenone, analytical standard; caffeic acid $\geq 98\%$ (HPLC); chlorogenic acid $\geq 95\%$ (titration); coumarin $\geq 99\%$ (HPLC); rutin trihydrate, analytical standard; hesperidin $\geq 80\%$; morin hydrate (powder); naringin $\geq 95\%$ (HPLC); 4-hydroxybenzoic acid $\geq 99\%$. Ethanol (200 proof, Anhydrous) was purchased from PHARMCO-AAPER.

6.2.2. EGaIn nanoparticle synthesis

EGaIn nanodroplets were dispersed in 1 mM ethanolic solutions using each of the plant derived molecules following the same procedure described in 5.2.2 (see section 3.3 for more detail). After filtration (0.45 μm pore, PTFE membrane, PALL Acrodisc), 1.5 mL was extracted and pipetted into a 2 mL borosilicate vial. Nitrogen was bubbled through the solution for 5 minutes before injecting approximately 0.2 mg of EGaIn. The vial was then capped, wrapped with Parafilm M, placed in a secondary containment jar, and then suspended in the center of a Branson 1510 bath ultrasonicator. The jar was sonicated at a continuous 40 kHz for 60 minutes and then allowed to decant for 24 hours in an upright position. Exactly 1.0 mL of supernatant was then pipetted out to be used directly for testing.

6.2.3. Characterization

As discussed in section 5.2.3, dynamic light scattering (DLS) was performed on samples after 24, 48 and 72 hours using a Malvern Zetasizer Nano. The scattering intensity autocorrelation function $g_2(q,t)$ was recorded at a scattering vector $q = 4\pi n\lambda^{-1}\sin(\theta/2) = 2.72 \times 10^7 \text{ m}^{-1}$ (n is the medium refractive index, $\lambda = 633 \text{ nm}$ is the laser vacuum wavelength) for backscattering angle $\theta = 173^\circ$ (converted to radians for q). The Siegert relation is then used to compute the normalized autocorrelation function of the scattered electric field $g_1(q,t)$. A number size distribution

representing the polydispersity of the sample was determined by the Malvern software, which was converted from the intensity size distribution using Mie theory.

UV/Vis spectroscopy of each sample was performed on a Cary UV/Vis 300 spectrophotometer (Agilent Technologies) over a wavelength range of 800 – 200 nm, with an interval of 1.0 nm, a scan rate of 600 nm/min in double beam mode, and with the spectral band width (SBW) set at 2.0 nm. The experimental extinction was then determined using Beer-Lambert's law as $A = -\log_{10}(I/I_0)$ where I and I_0 represent the intensity of the transmitted and incident light, respectively.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed on a JEOL 2000EX operated at 200 keV and a Quanta 600 Environmental SEM (operated in low vacuum mode, ~ 0.98 Torr), respectively. The processing software ImageJ was used for all analysis of TEM micrographs (see section 3.5.4).

6.2.4. Calculation of the extinction cross section of nanoparticles

Applied Mie theory for homogenous spheres was used to determine the extinction cross sections of EGaIn dispersions. Following the calculations presented by Bohren and Huffman¹⁰⁴, detailed in section 2.5.3 (as well as 5.2.4), the expression for the extinction cross section (C_{ext}) as a function of Mie scattering coefficients a_n and b_n (defined in terms of Riccati-Bessel functions) was solved numerically in MATLAB over a range of wavelengths. The sum in the extinction expression was truncated at n_{max} iterations defined by Bohren and Huffman¹⁰⁴ to as $n_{max} = x + 4x^{1/3} + 2$.

6.3. Results and discussion

6.3.1. Benign surfactant variation

Organic surfactant solutions were tested (in EtOH) and then compared against the literature benchmark system of dodecanethiol. The range of ten plant molecules selected for the study are given by Figure 6-1. As detailed in section 5.3.2, dynamic light scattering was performed on all

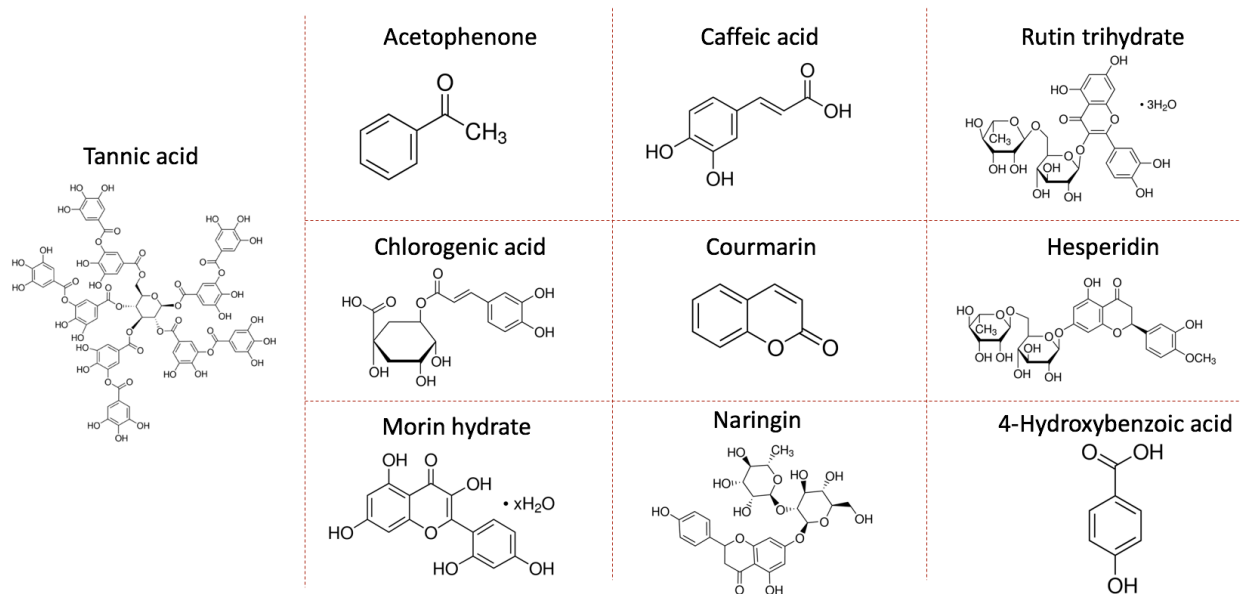


Figure 6-1. List of common plant molecules (polyphenols and flavonoids) and their associated structures used as surfactants in benign synthesis study.

plant “surfactant” solutions to verify the availability of molecules to reduce and stabilize EGaIn nanodroplets (*i.e.* confirm the absence of micelles). Only rutin trihydrate displayed micelle formation. Figure 6-2 shows that of the nine remaining solutions, all but hesperidin and naringin were soluble in ethanol (at 20 mM – 20 times the concentration of solution to be used for nanodroplet synthesis). Thus, the seven plant “surfactants” evaluated for benign EGaIn syntheses were chlorogenic acid, acetophenone, 4-hydroxybenzoic acid, coumarin, caffeic acid, morin hydrate and tannic acid.

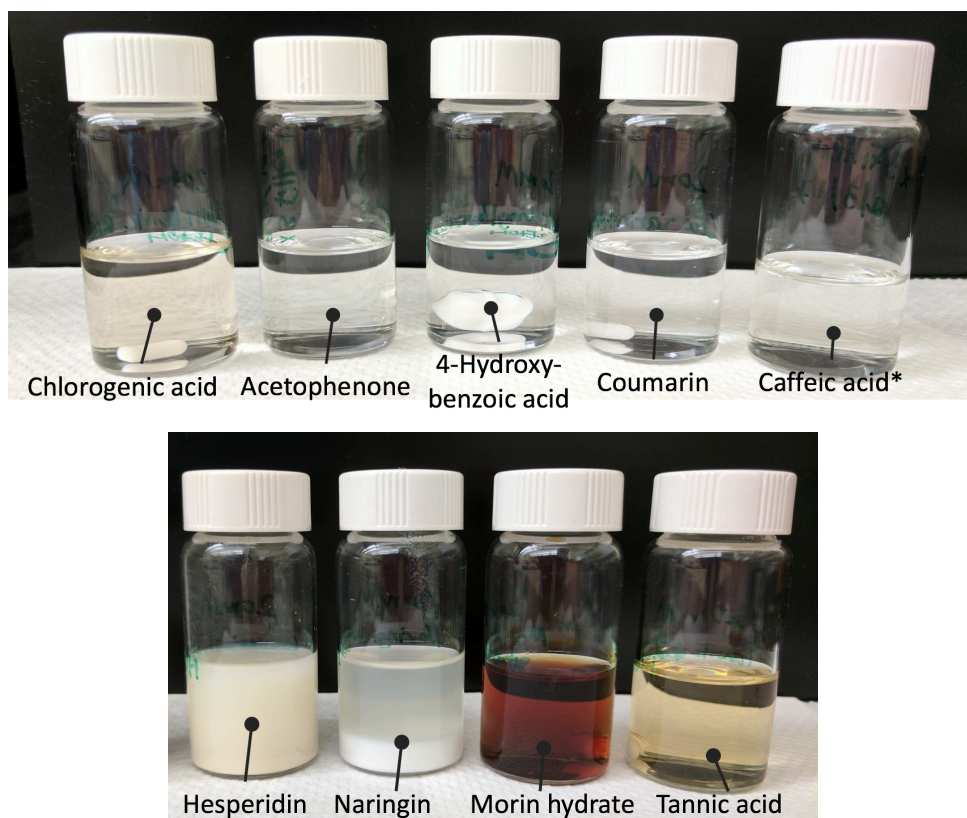


Figure 6-2. (Top) Plant-based molecules from study selection that were optically transparent and clearly soluble in ethanol; (bottom) insoluble (hesperidin, naringin) and strongly tinted solutions. All vials shown are 20 mM in ethanol (except caffeic acid* at 10 mM).

6.3.2. Evaluation of EGaIn nanoparticle dispersions

The computational approach of determining the average extinction coefficient of nanodroplet suspensions from DLS obtained size distribution data and applied Mie theory – presented thoroughly in the previous chapter (specifically section 5.3.4) – was extended to this study. In order to represent the polydispersity of the sample, an effective or average extinction cross section was determined from $\langle C^{ext}(\lambda) \rangle = \int C^{ext}(D, \lambda) P_n(D) dD / \int P_n(D) dD$ where $P_n(D)$ is the normalized number weighted size distribution from light scattering and $C^{ext}(D, \lambda)$ is the extinction cross section calculated for a given particle size (note the wavelength dependence). From the experimental extinction A (see section 6.2.3), the number of EGaIn nanodroplets was

then determined via substitution in Beer-Lambert equation, given in section 3.5.2 with the general form¹⁵⁸ $I = I_0 \exp(-C^{ext}lc)$ where C^{ext} is the extinction cross section for a single particle size, l is the pathlength of light through the medium (in this case, the width of the sample cuvette) and c was defined as the number concentration of particle (units of volume⁻¹). As first discussed in 5.3.3, the equation can be rewritten after a change of base and rearranged to solve for total number of particles $N_{tot} = 2.303AV\langle C^{ext}(\lambda^*) \rangle^{-1}l^{-1}$. The average extinction cross section $\langle C^{ext}(\lambda^*) \rangle$ for the corresponding particle distribution $P_n(D)$ at a test wavelength λ^* is substituted for single particle extinction (and $l = 1$ cm and V is the sample volume). The test wavelength was again selected as $\lambda^* = 505$ nm due to its good signal-to-noise ratio. For the calculation of $\langle C^{ext}(\lambda^*) \rangle$, the refractive index of the solvent medium was assumed to be equal to the value of pristine EtOH ($n_{EtOH} = 1.3616$).

As was the protocol previously, Figure 6-3 depicts the number weighted size distribution $P_n(D)$ from DLS along with the corresponding size distribution determined by TEM analysis for the EGaIn/tannic acid system. ImageJ was used to determine the size of 150 particles from TEM micrographs (see section 3.5.4). Although results from TEM show a stronger representation of smaller particles (on the order $D = 30$ nm), this is likely due to artifacts counted with the image processing software and does not affect the overall high match between distributions. The good agreement between the respective average values $\langle D \rangle_{DLS} = 120$ nm and $\langle D \rangle_{TEM} = 130$ nm confirms the DLS analysis. Because light scattering is a bulk characterization method that allows the rapid evaluation of macroscopic material volumes, DLS analysis was used to determine size distributions of EGaIn nanodroplets in suspension.

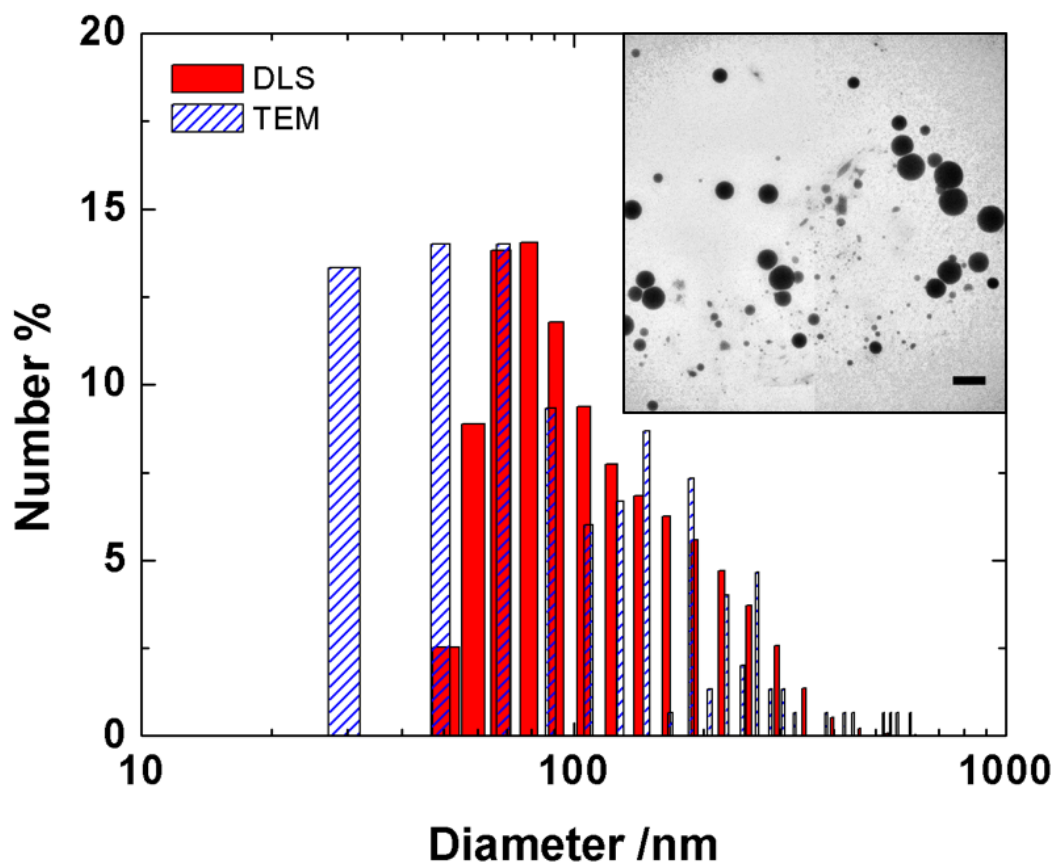


Figure 6-3. Comparison of DLS software provided number size distribution with $\langle D_{\text{TEM}} \rangle \approx 130$ nm for tannic acid sample at 24 hours with particle size distribution for sample determined from 150 particles using electron microscopy where $\langle D_{\text{DLS}} \rangle \approx 120$ nm. Inset is TEM micrograph of sample showing range of particles consistent with distributions. Scale bar 500 nm.

6.3.3. Size and efficiency results

Figure 6-4 shows the number average particle diameter $\langle D \rangle$ of EGaIn nanodroplets for each tested plant based surfactant (error bars show standard deviation for $n = 3$ total samples per surfactant) that was again determined from the particle size distributions (via $\langle D \rangle = \int D P_n(D) dD$). Average particle diameter ranged from $\langle D \rangle = 80$ nm for chlorogenic acid to just over $\langle D \rangle = 200$ nm for $\text{C}_{12}\text{H}_{25}\text{SH}$ solutions. Note that the sizes presented here fall in the (upper) range of Ag nanoparticles previous synthesized with plant extract (see Table 2-4).⁸⁴ All tested solution systems

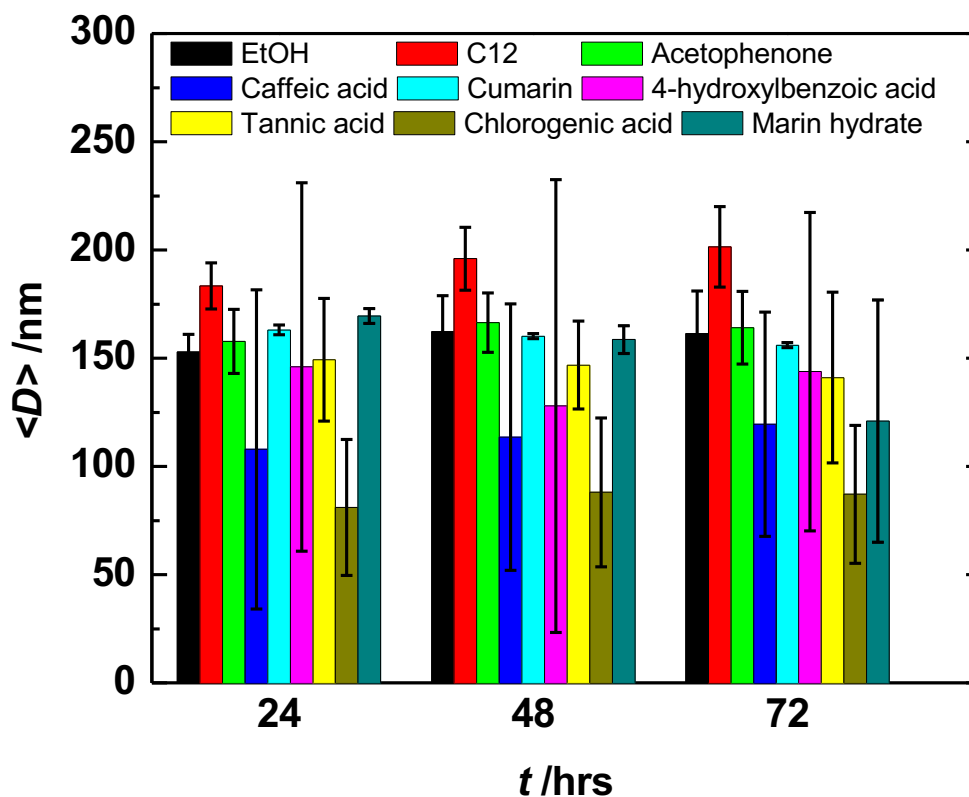


Figure 6-4. EGaIn particle size evolution over three days for various plant-based surfactants in 1 mM ethanolic solutions. EtOH = ethanol. C12 = dodecanethiol. Error bar is standard deviation for $n = 3$ samples.

(in the cases where surfactants were soluble in ethanol) displayed stable nanodroplet sizes for 72 hours (average diameter remained relatively constant).

The evolution of EGaIn nanoparticle concentration (or mass yield) over 72 hours is given by Figure 6-5. The mass of nanodroplets dispersed in solutions was determined from the experimental number density of EGaIn droplets as $m_{\text{EGaIn}} = N_{\text{tot}}(4\pi/3)\rho_{\text{EGaIn}}\int (D/2)^3 P_n(D)dD$ where $\rho_{\text{EGaIn}} = 6.25 \text{ g/mL}$ is the density of EGaIn ($P_n(D)$ is normalized). The figure reveals that of the tested bio-molecules, the large polyphenol tannic acid most effectively solubilizes EGaIn with an average concentration of 0.27 mM (22 $\mu\text{g/mL}$). Additionally, it outperforms the literature standard of $\text{C}_{12}\text{H}_{25}\text{SH}$ (considering the average concentrations). Tannic acid has proven able to stabilize various metallic nanoparticles such as Ag, Au, Pd in addition to gold chloride and iron

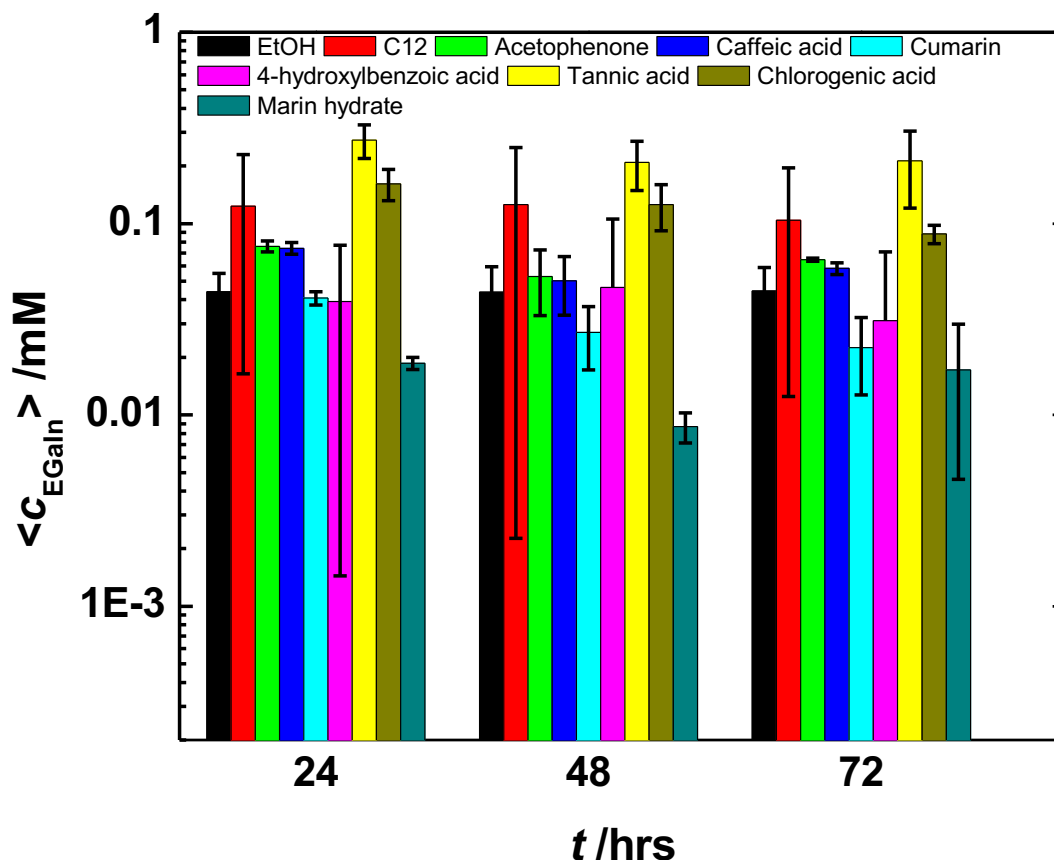


Figure 6-5. EGaIn concentration evolution over three days for various plant-based surfactants in 1 mM ethanolic solutions. EtOH = ethanol. C12 = dodecanethiol. 0.1 mM $\approx$ 8.1E-3 mg/mL. Error bar is standard deviation for n = 3 samples.

oxide.¹⁷⁰ This result suggests that the presence of excess –OH groups may interact with and help reduce the gallium oxide layer during EGaIn nanoparticle synthesis.

6.4. Conclusions

A proven optical characterization approach based on concurrent dynamic light scattering and photospectrometry was applied to evaluate the efficiency of plant-based surfactant systems to induce benign stabilization of dispersed EGaIn nanodroplets. The greatest concentration of suspended liquid metal droplets was found in the presence of tannic acid, thus proving it to be the most effective surfactant system (more-so than the benchmark system of dodecanethiol). The

results are promising for the solubilization of liquid metal nanodroplet by alternative “green chemistry” means, as well as the extension of the efficiency test approach to other systems.

7. Conclusions and future work

7.1. Conclusions

The stability of EGaIn nanodroplet suspensions in ethanol was investigated through a systematic study involving variation of coupling chemistry and chain lengths of several aliphatic type surfactants. Optical experimental techniques such as dynamic light scattering, UV/Vis spectroscopy and electron microscopy, in conjunction with principles from Mie scattering theory, allowed for the characterization and evaluation of liquid metal emulsions. In particular, a novel contribution was made to the area of LMP suspensions, namely a technique based for the determination of particle yield was developed and implemented via a computational software (MATLAB). Yield quantification allowed for objective comparison and classification of surfactant system effectiveness where previously there may have been no significant discernable differences or way of measuring results. From this method, octadecanethiol was found to be the most effective surfactant for stabilizing EGaIn. Extension of this study to plant derived surfactants for benign EGaIn nanodroplet stabilization identified tannic acid as a promising alternative.

Additionally, research done on applications of EGaIn and polymer composites has demonstrated the viability of further exploring such composites. The combined high conductivity and low mechanical resistance imparted (in some cases negligible) by EGaIn make it a promising material both for devices such as DEAs and discussed applications possible with stabilized nanodroplets. The framework for creating, testing and modeling such devices has already been established via published research on polymer-EGaIn composite instruments (specifically DEAs).

7.2. Future work

7.2.1. Development of more effective dispersion methods

The research could extend to the use of higher weight polymer ligands and possibly atom transfer radical polymerization (ATRP) initiator based surfactants that would enable the surface-initiated controlled polymerization of long chain ligands. Such systems might be more effective in stabilizing LMPs due to their higher molecular weight and longer chain length (as was revealed in Chapter 6, the higher M_w octadecanethiol molecule resulted in the greatest number of solubilized EGaIn nanodroplets).

Varying the combination of solvent-surfactant systems, as well as Pickering emulsions, may also be useful to stabilize LMPs. Specifically, dimethyl sulfoxide (DMSO) was briefly examined as an example where no additional solvent was added, and thus the solution functioned as both surfactant and solvent. Preliminary results using pure DMSO seemed promising, as sonication in the liquid appeared to have successfully dispersed EGaIn (solution remained dispersed or “tinted” for several months), as shown in Figure 7-1. Further sample testing and analysis – via the procedures for determining particle size and yield outlined in this thesis work – is necessary for further understanding of the system.

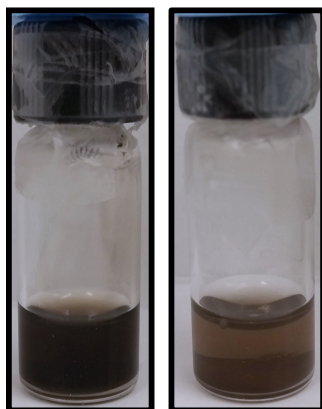


Figure 7-1. Examples of EGaIn suspended in pure DMSO (same experimental procedure from Chapter 6 used, minus addition of surfactant).

7.2.2. Understanding of surface chemistry and composition of nanodroplets

To further elucidate the structure and composition of nanodroplet surfaces, more in-depth oxygen variation studies should be performed. The necessity of some (unknown) amount of oxygen was discussed in Chapter 6, as too much or too little resulted in complete particle sedimentation. A detailed review of the solubility characteristics of EGaIn suspensions over a more finite range of deoxygenation levels could aid in the understanding of surface composition.

As mentioned in previous the section, DMSO suggests as a promising potential all-in-one system for solubilizing EGaIn. TEM of some initial samples (such as those shown in Figure 7-1) revealed numerous clusters of particles that appeared to be individually stabilized by even smaller solid particles, resembling a Pickering emulsion (see Figure 7-2). Further optical analysis should be performed on these solutions, and other “pure solvents” should be examined for their potential to form Pickering emulsions. EGaIn particles stabilized in this way could prove more robust and processible than ligand solubilized droplets.

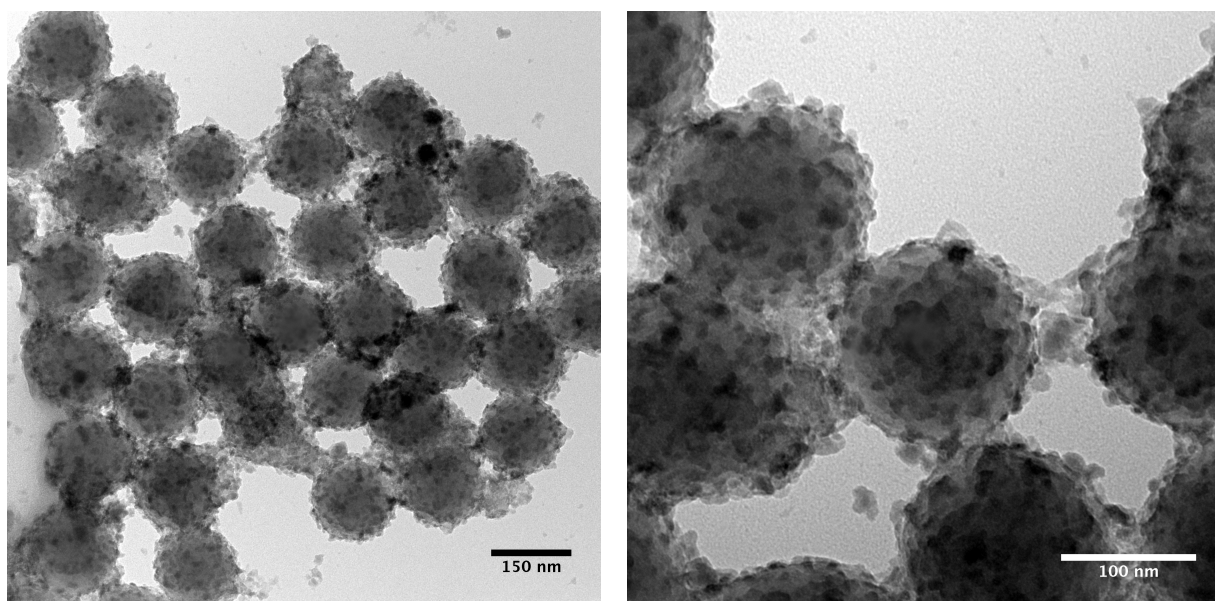


Figure 7-2. TEM micrographs of stabilized particles resembling a Pickering emulsion created from sonicating EGaIn in pure DMSO (following standard nanoparticle synthesis protocol).

7.2.3. Functional materials based on EGaIn nanodroplets

Future work includes evaluating the effect of surfactant modification on the morphology of polymer/LMP nanocomposite materials. The compatibility of LMPs in polymeric blends would be evaluated by structural characterization (using electron imaging) of solvent and bulk polymer/LMP blends after terminal annealing. Morphology would be judged to be “random dispersed” (i.e. miscible) if the particle nearest neighbor distance is approximately equal to the theoretical value $\langle d \rangle \cong (V/N)^{1/3}$. The morphology of nanocomposites would be interpreted on the basis of liquid/polymer interactions that can be elucidated, for example, via the respective Hildebrandt solubility parameters.¹⁴⁹ The solubility of the surfactant in a polymer matrix should be directly correlated to its ability to stabilize a particle in the polymer. Properties such as optical transparency and refractive index of the polymer nanocomposite should be dictated by polymer ligand length, which would control particle spacing.

Polymer ligand stabilized EGaIn nanoparticles should be dispersed in several well-studied polymer systems, such as polystyrene (PS), poly(methyl methacrylate) (PMMA) and poly(dimethylsiloxane) (PDMS) and could be extended to block copolymer systems. Optical transparency and mechanical tensile loading tests would be performed on the bulk nanocomposites, as well as measurements of dielectric permittivity and thermal and/or electrical conductivity. Electron microscopy would permit visualization of the particle dispersion characteristics and also pre- and post-testing states.

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9. Appendix

9.1. MATLAB Code

9.1.1. Mie scattering from polydisperse solution

```
%% Program Poly_Mie.m
%
% Computes WEIGHTED AVERAGE extinction cross section of arbitrary spherical
% bodies based on imported percent number size distribution
('polydispersity")
% data from DLS. Optical constants
% (n,k) have to be provided in separate file (see 80).
% Computation of Riccati-Bessel functions according to H.C. van de Hulst
% p.123 ('Light Scattering of Small Particles')
% predefined function-files (for k = z from van de Hulst)
%   psifunction(n,k)=spherical Bessel function with argument k
%   etafunction(n,k)=spherical Hankel function, k
%   psiprimefunction(n,k)=derivative of psifunction with respect to k
%   etaprimefunction(n,k)=derivative of etafunction with respect to k
%   psikfunction(n,N,k)=spherical Bessel function with argument N*k
%   psikprimefunction(n,N,k)=derivative of psikfunction with respect to N*k
%
% validation against online 'Mie Calculator'
% http://omlc.org/calc/mie\_calc.html
%
% system: N = 1.5 +i*0 , nm = 1; a = 500 nm; lambda = 632.8 (Mie
%         Calculator), 633 (Mie.m)
% result: 'Mie Calculator' - extEfficiency = 3.8962 ; Cext = 3.0601 10^-12
% m^2
%         Mie.m - extEfficiency = 3.909 ; Cext = 3.07 10^-12
% m^2
%
%% Import size distribution data
% Code to import and average 5 .txt files from Malvern output size
% distribution

path = uigetdir('/Users/lauren1/Google Drive/RESEARCH/DLS/Number_stats');
path = [path, '/'];

files = dir([path, '*.txt']);

dat = ones(70,10);

for k = 1:5

    filename = files(k).name;

    % search for first line of values under header
    h = 16;
    while(true)
        A = importdata([path,filename], '\t', h);
        if A.data(1) == 0.400000005960464
            break
        end
    end
end
```

```

    h = h-1;
end

    dat(:,2*k-1) = A.data(:,1);
    dat(:,2*k) = A.data(:,4);

end

size_avg = transpose(mean(transpose(dat(:,2:2:10))));

hist_dat = [dat(:,1),size_avg]; %2 column array of size vs number % averages

%remove rows with zero percentages
hist_dat(~all(hist_dat,2),:) = [];

%assign two columns (size and frequency) to different variables
size_dist = transpose(hist_dat(:,1)/2*(1.0E-9)); %convert diameters into
radii and from meters to nm; make into 1 x 14 array
freq = transpose(hist_dat(:,2))/100;

%%
% use long numbers
format long;

% define wavelength interval of interest (in meter)
lambdamax=0.000001;
lambdamin=0.0000001;
lambda=[lambdamin:((lambdamax-lambdamin)/100):lambdamax];

%%define optical constants of particle & matrix
%
% (1) particle:
%
% assume existence of file with optical
% constants of particle. Format (lambda, n, k)
%
% read in optical constants (lambda, n, k), form the transpose of data array
% and interpolate values on vector lambda
%
% definition of variables:
% nReal=real part refractive index interpolated at values 'lambda'
% nImag=imaginary part refractive index interpolated at values 'lambda'

data=load('OpticalConstEGaIn.dat');
wavelength=(data(:,1))';
nRealddata=(data(:,2))';
nImagdata=(data(:,3))';
nReal=interp1(wavelength,nRealddata,lambda,'pchip');
nImag=interp1(wavelength,nImagdata,lambda,'pchip');

% (2) matrix:
% refractive index (here: ethanol) @ 548 nm; neglect dispersion
nm=1.3616; %ethanol
%nm=1.479; %DMSO

```

```

%% relative (complex) refractive index
% aka 'optical contrast'; provides measure for scattering strength
N=(nReal+i*nImag)/nm;

% (1) definition of function handles to Bessel, Hankel, etc functions.
% note: program assumes function definitions are stored in same folder
p=@psifunction;
pprime=@psiprimefunction;
e=@etafunction;
eprime=@etaprimefunction;
pk=@psikfunction;
pkprime=@psikprimefunction;

% (2) Definition of coefficients an, bn (source: BOHREN & HUFFMAN p101)
%
% an=((N.*feval(pk,n,N,k).*feval(pprime,n,k)-
feval(p,n,k).*feval(pkprime,n,N,k))./(N.*feval(pk,n,N,k).*feval(eprime,n,k)-
feval(e,n,k).*feval(pkprime,n,N,k)));
%
% bn=((feval(pk,n,N,k).*feval(pprime,n,k)-
N.*feval(p,n,k).*feval(pkprime,n,N,k))./(feval(pk,n,N,k).*feval(eprime,n,k)-
N.*feval(e,n,k).*feval(pkprime,n,N,k)));

CextPoly=zeros(length(lambda),length(size_dist))';
CscattPoly=zeros(length(lambda),length(size_dist))';

for counter = 1:length(size_dist)

% define sphere radius 'a' (in meter)
a = size_dist(counter);

% define vector z (reduced geometrical dimension), k (reduced optical
% dimension), and s (wave vector)
z=2*pi*nm*a./lambda;
k=z;
s=2*pi*nm./lambda;

% define expansion range for evaluation of Mie coefficients
kMax=max(k);
x=round(kMax+4*kMax.^(1/3)+2)+1; %suggested as n_max for truncating series in
Appendix A, pg 477, Bohren & Huffman

%% Calculation of Extinction, Scattering, and Absorption Cross Section
%
%
Cext=zeros(1,101);
Cscatt=zeros(1,101);

n = 1;

for iteration=1:x

```

```

Cext=Cext+2*pi./(s.^2).*(2*n+1).*(real(((N.*feval(pk,n,N,k)).*feval(pprime,n,k)
)-
feval(p,n,k).*feval(pkprime,n,N,k))./(N.*feval(pk,n,N,k).*feval(eprime,n,k)-
feval(e,n,k).*feval(pkprime,n,N,k)))+(feval(pk,n,N,k).*feval(pprime,n,k)-
N.*feval(p,n,k).*feval(pkprime,n,N,k))./(feval(pk,n,N,k).*feval(eprime,n,k)-
N.*feval(e,n,k).*feval(pkprime,n,N,k))));

Cscatt=Cscatt+2*pi./(s.^2).*(2*n+1).*(abs(((N.*feval(pk,n,N,k)).*feval(pprime,
n,k)-
feval(p,n,k).*feval(pkprime,n,N,k))./(N.*feval(pk,n,N,k).*feval(eprime,n,k)-
feval(e,n,k).*feval(pkprime,n,N,k))).^2+abs(((feval(pk,n,N,k).*feval(pprime,
n,k)-
N.*feval(p,n,k).*feval(pkprime,n,N,k))./(feval(pk,n,N,k).*feval(eprime,n,k)-
N.*feval(e,n,k).*feval(pkprime,n,N,k)))).^2);
    n = n+1;
end

    CextPoly(counter,:)=Cext;
    CscattPoly(counter,:)=Cscatt;

    %output = sprintf('loop %d for size = %d (m) is complete. Number of
multipoles is %d',counter,a,x);
    %disp(output);

    counter=counter+1;

end

%calculation of average cross section

Cext_avg = zeros(101);
Cext_avg = freq*CextPoly(:,,:);

%% Plotting & exporting the results

yMaxCextAvg=max(Cext_avg);

figure;
plot(lambda,Cext_avg,'-or'), axis([0.0000003 0.0000008 0
2*yMaxCextAvg]),xlabel('\lambda (m)'),ylabel('<C_{ext}>
(m^2)'),legend('average C_{ext}'); %title(['Avg EGaIn sphere diameter: '

extinction_avg=[lambda' Cext_avg'];

```

9.1.2. Calculation of EGaIn quantity

```

%% Program efficiency_calc_poly.m
%
% This script determines the "efficiency" of the surfactant + sonication
% process to create spherical nanodroplets of EGaIn. THE USER MUST FIRST RUN
% THE PROGRAM *Poly_Mie.m* to determine the extinction cross section for the
% wavelength of interest, and have also performed UV/Vis to provide an %

```

```

absorbance value for the given wavelength.

%% Theory
%
% Beer-Lambert law to express intensity difference:
%  $I = I_0 \exp(-C_{\text{ext}} \cdot L_{\text{path}} \cdot \text{conc})$  "conc" = concentration =  $N/V_{\text{soln}}$ 
% Absorbance  $A = \log_{10}(I_0/I)$ 
% Conversion to natural log and substitution gives:  $A = (1/2.303) \cdot C_{\text{ext}} \cdot L_{\text{path}} \cdot (N/V_{\text{soln}})$ 

%% User defined

format long

% define absorbance (EXTINCTION) @ interested wavelength (505 nm usually)
absorbance = 0.1976007074;

%% Other variables
%
% define extinction cross section from Poly_Mie.m code results (here @ lamda
= 505 nm)
C_ext=Cext_avg(:,46);

% define EGaIn density, in g/cm^3
rho = 6.25;

% define path length of laser (equal to width of cuvette), in meters
L_path = 0.01;

% define volume of solution (here 1.0 mL) in cuvette (in m^3)
V_soln = 1.0e-6;

%% Solve for Num
% Num is total experimental particles from Beer-lambert law

Num = (absorbance*2.303*V_soln)/(C_ext*L_path);

N_dist = freq*Num; %Number of particles at each size

%% Calculate total mass in system
% Total EGaIn mass = SUM[N_i*mass_i], where  $m_i = 4/3 \cdot \pi \cdot R_i^3 \cdot \rho$ 

%Find radii (in cm)

R_dist = (size_dist/2)/(1.0E-2); %in cm

mass_dat = zeros(1,length(R_dist));

for i = 1:length(R_dist)

    mass_dat(:,i) = rho*(4/3)*pi*(R_dist(:,i)^3)*(1.0E3); %weight in mg

end

```



```

%For total mass, multiply N by each corresponding weight

mass_EGaIn_mg = mass_dat*transpose(N_dist)

weighted_size_avg_nm = 2*size_dist*transpose(freq)*(1E9)

%% Save output to .txt file

textedit_filename =
'/Users/lauren1/Desktop/Research/Bockstaller/Calculations/MATLAB_output/Efficiency_results_dispersivity2.txt';

%open file and append data, 'a'
fid = fopen(textedit_filename,'a');

string_name = A.textdata(3,:);
sample_name = string_name(:,1);

fprintf(fid,'%s\t%d\t%d\n',sample_name(15:24),weighted_size_avg_nm,
mass_EGaIn_mg);

```

9.1.3. Fitting average correlation data

```

%% Program DLS_Correlation.m
% Import DLS correlation .txt files and fit single exponential decay

path = uigetdir('/Users/lauren1/Google Drive/RESEARCH/DLS');
path = [path, '/'];

files = dir([path, '*.txt']);

%% Variables for calculating particle size
theta = 173; %degrees
n_0 = 1.375;
eta = 1.08E-3; %Pa-s
lambda = 6.33E-7; %wavelength of Malvern laser
T = 298; %Kelvin
k_B = 1.38E-23; %m^2kg/s^2K
q = ((4*pi*n_0)/lambda)*sin(deg2rad(theta)/2);

%% Read in .txt correlation files
dat = ones(192,10);
text_info = cell(1,5);

for k = 1:5

    filename = files(k).name;

    A = importdata([path,filename],'\t',10);

    dat(:,2*k-1) = A.data(:,1);
    dat(:,2*k) = A.data(:,2);

```

```

text_info(:,k) = A.textdata(3,1);

end

ft = fitttype('a*exp(-x/b)+y_0');

for i = 2:2:10

x = dat(:,1);
y = dat(:,i).^5;

figure
plot(x,y,'o'), axis([10e-2 10e8 0 1]);
set(gca,'xscale','log');

[x_plot,y_plot] = ginput;
x_short = find(x <= x_plot);

sample_name = text_info{:,i/2}(15:end);

%% Plot runs and export saved plots to folder as .pngs
f = fit(x(x_short),y(x_short),ft,'StartPoint',[.85,600,.1]);
plot(f,x,y), axis([10e-2 10e8 0 1]), xlabel('Time (\mus)'),
ylabel('g(1)'),title(sample_name,'Interpreter','none');
set(gca,'xscale','log');

f_name =
'/Users/lauren1/Desktop/Research/Bockstaller/Calculations/MATLAB_output/corre
lation_plots/';
saveas(gcf,[f_name,sample_name,'.png']);

%% Save output to .txt file

filename =
'/Users/lauren1/Desktop/Research/Bockstaller/Calculations/MATLAB_output/corre
lation_fit_results.txt';

%open file and append data, 'a'
fid = fopen(filename,'a');
a_coef = f.a;
b_coef = f.b;
y_coef = f.y_0;

%calculate diameter in nanometers
gamma = 1/(b_coef/1E6);
D = gamma/q^2;
R_h = (k_B*T)/(6*pi*eta*D);
D_h = R_h*2*1000000000; %in nanometers

fprintf(fid,'%s\t%d\t%d\t%d\t%d\n', sample_name, a_coef, b_coef, y_coef,
D_h);

end

```

9.2. Calculated EGaIn optical constants

Optical constants calculated by using Newton's effective medium model.

Note: N_{Re} and K_{Im} only calculated for wavelengths where both Ga and In values were available.

Wavelength (m)	Refractive index (Re)	Refractive index (Im)
8.8621450E-06	1.2795527E+01	3.4455071E+01
7.7543769E-06	1.0515408E+01	3.1189960E+01
6.8927794E-06	9.2091192E+00	2.8924395E+01
6.2035015E-06	8.0424485E+00	2.7100786E+01
4.9628012E-06	6.0659015E+00	2.2558813E+01
4.1356677E-06	4.9152092E+00	1.9066613E+01
2.7571118E-06	2.6450886E+00	1.1911848E+01
2.4814006E-06	2.4422460E+00	1.0543318E+01
2.2558187E-06	2.2864559E+00	9.4752626E+00
2.0678338E-06	2.2145005E+00	8.5345712E+00
1.7724290E-06	2.2409018E+00	7.2178554E+00
1.5508754E-06	2.4740647E+00	6.3222316E+00
1.4596474E-06	2.5999718E+00	6.0313201E+00
1.3785559E-06	2.6271131E+00	5.8967322E+00
1.2407003E-06	2.5335119E+00	5.6702788E+00
1.0339169E-06	2.3162498E+00	5.1666678E+00
8.8621450E-07	2.0455496E+00	4.7773568E+00
7.7543769E-07	1.7459679E+00	4.4393531E+00
6.8927794E-07	1.4725964E+00	4.0984462E+00
6.2035015E-07	1.2749174E+00	3.8635861E+00
5.6395468E-07	1.0296603E+00	3.7338270E+00
5.1695846E-07	7.6021001E-01	3.4718406E+00
4.7719242E-07	6.0483325E-01	3.1859608E+00
4.4310725E-07	5.1929237E-01	2.9253752E+00
4.1356677E-07	4.6616924E-01	2.7248473E+00
4.1356677E-08	9.7343031E-01	9.2041880E-02
4.0178118E-08	9.7719821E-01	9.2676377E-02
3.9028006E-08	9.8097760E-01	9.3861037E-02
3.7907128E-08	9.8378329E-01	9.5099297E-02
3.6816033E-08	9.8565010E-01	9.6505608E-02
3.5765359E-08	9.8694752E-01	9.7168956E-02
3.4743778E-08	9.8816066E-01	9.7510257E-02
3.3751368E-08	9.8907209E-01	9.8192453E-02
3.2779400E-08	9.8940590E-01	9.8615068E-02
3.1845490E-08	9.8916148E-01	9.8557247E-02
3.0932443E-08	9.8901403E-01	9.7959156E-02
3.0048445E-08	9.8887596E-01	9.7364992E-02
2.9186081E-08	9.8869278E-01	9.6697872E-02
2.8352383E-08	9.8818955E-01	9.6101653E-02
2.7540517E-08	9.8722359E-01	9.5229544E-02
2.6750761E-08	9.8620783E-01	9.3898284E-02
2.5983252E-08	9.8541585E-01	9.2271464E-02
2.5243139E-08	9.8457746E-01	9.0710486E-02
2.4519769E-08	9.8388651E-01	8.8904881E-02
2.3818397E-08	9.8325268E-01	8.7185796E-02
2.3134445E-08	9.8257081E-01	8.5397326E-02
2.2472384E-08	9.8185643E-01	8.3363486E-02
2.1827943E-08	9.8112998E-01	8.1583268E-02

2.1204927E-08	9.8030655E-01	7.9799747E-02
2.0595954E-08	9.7933891E-01	7.7518522E-02
2.0008068E-08	9.7875686E-01	7.5095611E-02
1.9434528E-08	9.7837923E-01	7.2869369E-02
1.8878580E-08	9.7792405E-01	7.0910223E-02
1.8337279E-08	9.7717606E-01	6.8929250E-02
1.7813357E-08	9.7665863E-01	6.6221616E-02
1.7301636E-08	9.7689099E-01	6.3869383E-02
1.6807102E-08	9.7692389E-01	6.2028097E-02
1.6327152E-08	9.7711393E-01	6.0552910E-02
1.5859648E-08	9.7660178E-01	5.9493707E-02
1.5404772E-08	9.7544505E-01	5.8126116E-02
1.4964423E-08	9.7435177E-01	5.6102616E-02
1.4534914E-08	9.7289071E-01	5.3853063E-02
1.4119726E-08	9.7205018E-01	5.0896261E-02
1.3715458E-08	9.7170057E-01	4.8015579E-02
1.3322241E-08	9.7153628E-01	4.5387989E-02
1.2941486E-08	9.7123023E-01	4.2480757E-02
1.2570418E-08	9.7160036E-01	3.9454370E-02
1.2211617E-08	9.7231307E-01	3.6861996E-02
1.1861380E-08	9.7320839E-01	3.4522819E-02
1.1519966E-08	9.7407224E-01	3.2492698E-02
1.1187559E-08	9.7478376E-01	3.0672803E-02
1.0873798E-08	9.7546925E-01	2.8916017E-02
1.0559151E-08	9.7623408E-01	2.7173068E-02
1.0253721E-08	9.7710531E-01	2.5573932E-02
9.9654642E-09	9.7790685E-01	2.4095562E-02
9.6778494E-09	9.7868687E-01	2.2794395E-02
9.3992447E-09	9.7939725E-01	2.1516723E-02
9.1295092E-09	9.8010573E-01	2.0243431E-02
8.8684796E-09	9.8081644E-01	1.9107878E-02
8.6159743E-09	9.8148321E-01	1.7894884E-02
8.3717969E-09	9.8225351E-01	1.6835815E-02
8.1304082E-09	9.8300176E-01	1.5926272E-02
7.8975194E-09	9.8377694E-01	1.5068100E-02
7.6728528E-09	9.8440279E-01	1.4303820E-02
7.4516534E-09	9.8502943E-01	1.3546328E-02
7.2386248E-09	9.8563106E-01	1.2869664E-02
7.0334484E-09	9.8618294E-01	1.2196435E-02
6.8320501E-09	9.8660988E-01	1.1523803E-02
6.6347610E-09	9.8711186E-01	1.0854212E-02
6.4451964E-09	9.8766360E-01	1.0260326E-02
6.2598401E-09	9.8811509E-01	9.7416272E-03
6.0818642E-09	9.8861650E-01	9.2234577E-03
5.9080967E-09	9.8901783E-01	8.7028992E-03
5.7386693E-09	9.8946905E-01	8.1852610E-03
5.5736761E-09	9.8984497E-01	7.7649856E-03
5.4131776E-09	9.9022085E-01	7.3347751E-03
5.2594332E-09	9.9064655E-01	6.9348551E-03
5.1078645E-09	9.9097217E-01	6.5574425E-03
4.9628012E-09	9.9132276E-01	6.1824322E-03
4.8201255E-09	9.9154826E-01	5.7975519E-03
4.6818879E-09	9.9194866E-01	5.4277663E-03
4.5480216E-09	9.9224899E-01	5.0879613E-03
4.4184484E-09	9.9254925E-01	4.7531274E-03
4.2915956E-09	9.9284947E-01	4.4407789E-03
4.1690198E-09	9.9314965E-01	4.1534209E-03

4.0492830E-09	9.9337485E-01	3.8859870E-03
3.9337359E-09	9.9367497E-01	3.6036041E-03
3.8210665E-09	9.9395005E-01	3.3187835E-03
3.7113380E-09	9.9425015E-01	3.0638914E-03
3.6056388E-09	9.9445023E-01	2.8214846E-03
3.5018354E-09	9.9475030E-01	2.5990779E-03
3.4019750E-09	9.9502530E-01	2.3966843E-03
3.3041286E-09	9.9525040E-01	2.2042252E-03
3.2100913E-09	9.9552539E-01	2.0295716E-03
3.1181209E-09	9.9575047E-01	1.8703548E-03
3.0283141E-09	9.9605050E-01	1.7146721E-03
2.9421397E-09	9.9627558E-01	1.5754625E-03
2.8574397E-09	9.9650066E-01	1.4495143E-03
2.7756159E-09	9.9675075E-01	1.2934437E-03
2.6965883E-09	9.9705107E-01	1.3197684E-03
2.6191689E-09	9.9725108E-01	1.3702031E-03
2.5445043E-09	9.9735076E-01	1.4205404E-03
2.4715145E-09	9.9742544E-01	1.3980962E-03
2.4007359E-09	9.9750019E-01	1.3365230E-03
2.3321434E-09	9.9752508E-01	1.2569530E-03
2.2652918E-09	9.9765000E-01	1.1686155E-03
2.2002133E-09	9.9769997E-01	1.0755461E-03
2.1372959E-09	9.9784995E-01	9.8948324E-04
2.0761384E-09	9.9792495E-01	9.1369993E-04
2.0167430E-09	9.9799994E-01	8.4667109E-04
1.9591036E-09	9.9814993E-01	7.7837054E-04
1.9029146E-09	9.9827494E-01	7.2888875E-04
1.8484808E-09	9.9834991E-01	7.0987931E-04
1.7955142E-09	9.9839988E-01	6.8434181E-04
1.7440263E-09	9.9844988E-01	6.2354297E-04
1.6942514E-09	9.9852489E-01	5.6977010E-04
1.6457094E-09	9.9859991E-01	5.1500005E-04
1.5986346E-09	9.9869992E-01	4.6900004E-04
1.5528164E-09	9.9877493E-01	4.3198381E-04
1.5084502E-09	9.9877494E-01	4.0048452E-04
1.4651633E-09	9.9887495E-01	3.6698568E-04
1.4233111E-09	9.9894996E-01	3.3697344E-04
1.3825499E-09	9.9900997E-01	3.0796575E-04
1.3428946E-09	9.9908747E-01	2.8022200E-04
1.3044899E-09	9.9913998E-01	2.5546722E-04
1.2671845E-09	9.9919249E-01	2.3296341E-04
1.2308535E-09	9.9926999E-01	2.1221913E-04
1.1952797E-09	9.9932750E-01	1.9311801E-04
1.1617044E-09	9.9941251E-01	1.7554168E-04
1.1279094E-09	9.9953752E-01	1.5956330E-04
1.0960250E-09	9.9959253E-01	4.2400663E-04
1.0640654E-09	9.9948251E-01	3.9050453E-04
1.0339169E-09	9.9946251E-01	3.6000372E-04
1.0046156E-09	9.9946501E-01	3.3275317E-04
9.7539332E-10	9.9947500E-01	3.0675268E-04
9.4782299E-10	9.9949750E-01	3.0825390E-04
9.2040081E-10	9.9949250E-01	2.7900248E-04
8.9452076E-10	9.9950000E-01	2.5225178E-04
8.6883774E-10	9.9951500E-01	2.2850131E-04
8.4401381E-10	9.9953750E-01	2.0650105E-04
8.1948501E-10	9.9955250E-01	1.8700074E-04
7.9634166E-10	9.9957500E-01	1.6950056E-04

7.7350393E-10	9.9958750E-01	1.5375042E-04
7.5102924E-10	9.9961000E-01	1.3900030E-04
7.2982371E-10	9.9963000E-01	1.2592527E-04
7.0897160E-10	9.9964250E-01	1.1390018E-04
6.8851293E-10	9.9966250E-01	1.0280016E-04
6.6884113E-10	9.9968250E-01	9.2825144E-05
6.4958131E-10	9.9969500E-01	8.3825085E-05
6.3107848E-10	9.9971500E-01	7.5750076E-05
6.1299422E-10	9.9972750E-01	6.8425034E-05
5.9534563E-10	9.9974500E-01	6.1725060E-05
5.7841506E-10	9.9975750E-01	5.5750027E-05
5.6191137E-10	9.9976750E-01	5.0275023E-05
5.4584263E-10	9.9978000E-01	4.5325000E-05
5.3021380E-10	9.9979750E-01	4.0925019E-05
5.1502711E-10	9.9980750E-01	3.6825016E-05
5.0028238E-10	9.9981750E-01	3.3250015E-05
4.8597740E-10	9.9982750E-01	2.9975013E-05
4.7192860E-10	9.9983750E-01	2.6975011E-05
4.5849974E-10	9.9984750E-01	2.4250010E-05
4.4533392E-10	9.9985000E-01	2.1900000E-05
4.3260122E-10	9.9986000E-01	1.9724999E-05
4.2014910E-10	9.9987000E-01	1.7749999E-05
4.0812510E-10	9.9988000E-01	1.5950000E-05
3.9651655E-10	9.9988250E-01	1.4349994E-05
3.8519103E-10	9.9989000E-01	1.2924999E-05
3.7415570E-10	9.9990050E-01	1.1609999E-05
3.6341544E-10	9.9990450E-01	1.0464998E-05
3.5297306E-10	9.9991075E-01	9.3974980E-06
3.4292435E-10	9.9991675E-01	8.4474964E-06
3.3307391E-10	9.9992525E-01	7.5899917E-06
3.2352029E-10	9.9992650E-01	9.9700211E-06
3.1426046E-10	9.9993225E-01	1.0522552E-05
3.0529043E-10	9.9993325E-01	9.4600137E-06
2.9653449E-10	9.9993675E-01	8.5175062E-06
2.8806601E-10	9.9994000E-01	8.3200003E-06
2.7981513E-10	9.9994275E-01	7.4924989E-06
2.7178539E-10	9.9994550E-01	6.7449938E-06
2.6403496E-10	9.9994900E-01	6.0849946E-06
2.5644901E-10	9.9995100E-01	5.4724908E-06
2.4913661E-10	9.9995400E-01	4.9399934E-06
2.4199343E-10	9.9995675E-01	4.4374947E-06
2.3507016E-10	9.9995875E-01	3.9924963E-06
2.2832173E-10	9.9996150E-01	3.5974888E-06
2.2179126E-10	9.9996375E-01	3.2374980E-06
2.1543676E-10	9.9996575E-01	2.9124909E-06
2.0929492E-10	9.9996775E-01	2.6124991E-06
2.0329351E-10	9.9996900E-01	2.3524965E-06
1.9746941E-10	9.9997075E-01	2.1174990E-06
1.9182132E-10	9.9997275E-01	1.9000003E-06
1.8631931E-10	9.9997400E-01	1.7057437E-06
1.8099202E-10	9.9997575E-01	1.5319959E-06
1.7581129E-10	9.9997700E-01	1.3749905E-06
1.7077774E-10	9.9997800E-01	1.2347525E-06
1.6589120E-10	9.9998000E-01	1.1079843E-06
1.6112991E-10	9.9998100E-01	9.9400351E-07
1.5651574E-10	9.9998200E-01	8.9276487E-07
1.5204661E-10	9.9998300E-01	8.0023537E-07

1.4768483E-10	9.9998425E-01	7.1900998E-07
1.4346673E-10	9.9998525E-01	6.4399054E-07
1.3935755E-10	9.9998625E-01	5.7702330E-07
1.3535897E-10	9.9998650E-01	5.1721199E-07
1.3148583E-10	9.9998725E-01	4.6301627E-07
1.2772290E-10	9.9998825E-01	4.1603338E-07
1.2407003E-10	9.9998925E-01	3.7223089E-07