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**NANOPARTICLE LIQUIDS FOR
RECONFIGURABLE ELECTRONIC
MATERIALS (PREPRINT)**



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14. ABSTRACT High inorganic volume fraction, solventless nanoparticle liquids have many potential applications, including reconfigurable electronic materials. Materials such as conductive lubricants could find applications in MEMS devices to increase relay switch performance as one example. The ability of the conductive nanoparticles to reconfigure themselves and fill voids in damaged areas can increase the lifespan of devices where local defects can cause failure states. Solventless solid nanoparticles with liquid-like properties are an area of recent research interest. For example, Giannelis and colleagues have reported metal oxide and metal nanoparticle liquids which contain no free solvent but still can flow in a liquid-like fashion. These materials contain large organic ligands bound to the surface of the nanoparticle through a combination of covalent and electrostatic bonds. By optimizing the attractive and repulsive forces between the nanoparticles through the surface chemistry of these organic ligands, the properties of the resulting liquids can be tailored.					
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Nanoparticle liquids for reconfigurable electronic materials

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INTRODUCTION

High inorganic volume fraction, solventless nanoparticle liquids have many potential applications, including reconfigurable electronic materials. Materials such as conductive lubricants could find applications in MEMS devices to increase relay switch performance as one example. The ability of the conductive nanoparticles to reconfigure themselves and fill voids in damaged areas can increase the lifespan of devices where local defects can cause failure states.

Solventless solid nanoparticles with liquid-like properties are an area of recent research interest. For example, Giannelis^{1,2} and colleagues have reported metal oxide and metal nanoparticle liquids which contain no free solvent but still can flow in a liquid-like fashion. These materials contain large organic ligands bound to the surface of the nanoparticle through a combination of covalent and electrostatic bonds. By optimizing the attractive and repulsive forces between the nanoparticles through the surface chemistry of these organic ligands, the properties of the resulting liquids can be tailored.

EXPERIMENTAL

Synthesis. Gold nanoparticles were synthesized by two methods. The Brust method³ was used to generate 6nm citrate capped gold nanoparticles, while the Stucky method⁴ was used to generate 6nm dodecanethiol capped gold nanoparticles. The Stucky method was chosen for its highly monodisperse nanoparticles and easy ability to scale up to gram-scale quantity reactions. Gold nanoparticles were characterized by UV-Vis and TEM for concentration and sizing information. The number of surface gold atoms could be easily calculated from this data. Beta-functional alkylthiols and Adogen 464 were purchased from Sigma and used as received. Quaternary ammonium salts, such as Arquad S-50 and Ethoquad T/13-27W were purchased from Akzo Nobel and used as received. Gold nanoparticle solutions were added to alkylthiol solutions dropwise while constantly stirring, with a series of stoichiometries of alkylthiol:surface gold atom from 0.1:1 to 10:1. MPS functionalized nanoparticles were washed with milliQ water and collected by centrifugation to remove any unreacted alkylthiol. The pellet was resuspended in milliQ water and characterized by chemical analysis techniques. Ionic liquid coronas were formed by cation exchange of the surface species associated with the MPS and the organic cation in milliQ water. The MPS functionalized nanoparticles were added to the aqueous corona cation solution (ex-quaternary ammonium salts) dropwise while stirring, such that the final stoichiometry of cation:MPS was 1:1. The solvent was then evaporated at room temperature under nitrogen.

Chemical Analysis. Nanoparticle liquids were characterized by XPS, TEM, UV-Vis, Zeta Potential, ICP, and NMR.

MEMS Testing. Nanoparticle liquids were spin-coated onto gold-substrates to an average thickness of 2-3nm. The nanoparticles provided a sub-monolayer coverage of the substrate. A mechanical metal ball was brought into contact with a controllable, reproducible force, and the resulting contact resistance was measured. The physical contact was cycled at 5Hz for the duration of the test.

RESULTS AND DISCUSSION

A series of ligand exchange reactions was performed with varied stoichiometries between the number of surface gold atoms and the number of ligands added to the solution. 3-mercaptopropanesulfonic acid, or MPS, was used to functionalize 6nm citrate gold nanoparticles, and the zeta potential of the washed nanoparticles

was then collected to demonstrate the increased functionalization of the nanoparticles with the negatively charged sulfonic acid group. The results are summarized in Table 1, and show that above a 2:1 ratio of MPS:surface gold atoms, the surface of the nanoparticle is maximally functionalized with negatively charged sulfonic acid groups on its surface. This allowed optimization of the functionalization of the gold nanoparticles with MPS to achieve the maximum surface density of MPS possible with the least amount of excess or unused reagents. It is currently under investigation as to why the zeta potential varies near the 1:1 ratio and diminishes above the 2:1 ratio.

Table 1. Zeta Potential vs. MPS Ligand Concentration

Ligand:Surface Au atom	Zeta Potential (mV)	Std Error
0 :1	-8.16	3.65
0.1 :1	-14.54	1.66
0.5 :1	-19.95	2.56
1 :1	-21.27	3.84
2 :1	-21.92	3.28
5 :1	-22.10	2.69
10 :1	-35.61	3.02

In parallel to citrate stabilized Au nanoparticles, ligand exchange of alkane thiol stabilized Au nanoparticles also yielded controlled MPS surface functionalization. Reactions were performed in chloroform, with alkylthiol gold nanoparticles added dropwise to the chloroformic ligand solution, with a 1:1 ratio of MPS:surface Au atoms. The chloroform was evaporated at room temperature under nitrogen, and the resulting nanoparticles were resuspended in milliQ water. The ligand-exchanged nanoparticles were characterized by XPS, which demonstrated exchange had occurred by the altered C1s:S2p peak intensity ratio as well as the presence of an O1s peak.

A series of nanoparticle liquids were prepared from a series of cationic surfactants. The cationic species formed an ionic liquid corona around the anionic MPS-functionalized nanoparticles. An example of a nanoparticle liquid formed from 30nm citrate-capped gold nanoparticles exchanged with MPS followed by Adogen 464 is shown in Figure 1. The TEM shows the dark contrast of the 30nm gold nanoparticles, and a faint contrast from the remaining organic corona of Adogen linking the nanoparticles.

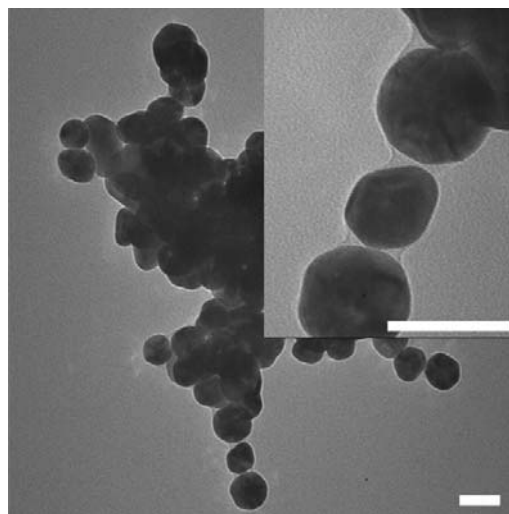


Figure 1. TEM of 30nm gold nanoparticle liquid from MPS and Adogen 464. Inset shows magnified region. Scale bars are 50nm.

Macroscopic quantities of nanoparticle liquids were found to flow on the time-scale of tens of minutes. Figure 2 shows a time-lapse series of photographs to display the fluid-like nature of a nanoparticle liquid after the solvent had been evaporated. The material shown comprised 6nm Stucky alkylthiol-capped gold nanoparticles exchanged

with MPS followed by Adogen 464. Figure 2a shows the vial initially after turning onto its side, Figure 2b shows 2.5 minutes, Figure 2c shows 5 minutes, and Figure 2d shows 10 minutes after turning the vial on its side.

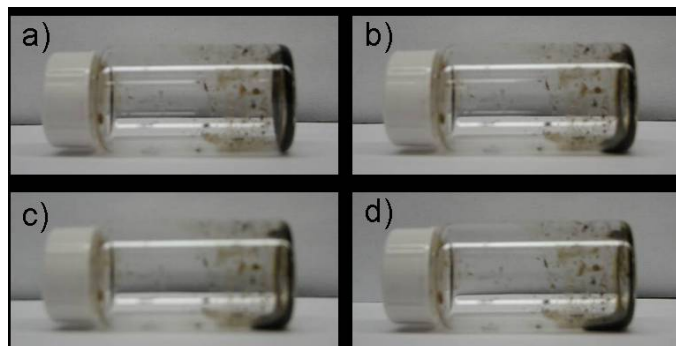


Figure 2. Time lapse series of a nanoparticle liquid flowing down the side of a vial. Time points are a) 0min, b) 2.5min, c) 5min, and d) 10 min.

Challenges to increasing the reliability of a MEMS relay switch currently include adhesion and stiction which results in shorting during an intended open circuit condition. Utilizing the MEMS testing platform described in the experimental section, the nanoparticle liquids were studied for their potential application to conductive lubricants for MEMS relay switches. Low and high current conditions were tested, to simulate two typical conditions MEMS relay switches would likely face in future devices. If the contact resistance between the two conductive components of the relay is greater than about two ohms, then the device is considered to be in a failure state.

The bottom contact of the MEMS testing platform shown in Figure 3 was coated with a sub-monolayer of Au nanoparticle liquid via spin-coating. These tests demonstrated that the Au NP liquids increased the durability (relay cycles) of the simulator by one to three orders of magnitude relative to uncoated contacts or self assembled monolayers.

It is speculated that the ability of these nanoparticle liquids, which could be imagined as solventless coated nanoparticles, to reconfigure themselves through fluid-like motion endows a self-healing property to the conductive lubricant layer. As the physical contact between the relay begins to wear out the conductive lubricant layer through physical deformation of the nanoparticles and ashing of the carbonaceous nanoparticle coating, the undamaged sections of the conductive lubricant layer can begin to flow in to the damaged areas and heal the coating.

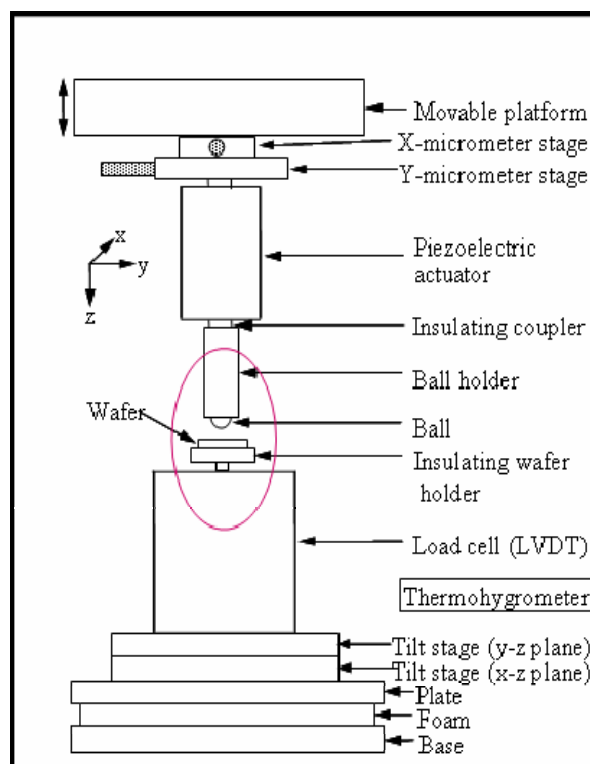


Figure 3. Schematic of MEMS testing platform.

CONCLUSION

A series of nanoparticle liquids were synthesized and characterized in detail. The ligand exchange efficiency of several beta-functional alkylthiol ligands was studied by a variety of chemical analysis methods in order to gain an understanding towards maximizing the efficiency of the synthetic protocol. A series of nanoparticle liquids with varied cationic corona molecules was synthesized, and the resulting materials were characterized for their application in MEMS relay switch conductive lubricants. The nanoparticle liquids had a self-healing properties and increased the useful life of the relay switch by one to three orders of magnitude. Future studies will focus on variations of the nanoparticle sizes and metal composition for their application towards conductive lubricants, as well as the uniformity and thickness of the conductive lubricant layer on the switch surfaces.

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