Synthesis and Characterization of Gold Nanosalts

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Abstract:

The purpose of this research is to develop a material containing gold nanoparticles that is a solvent-free liquid at room temperature. Gold nanoparticles have many optical and electrical properties that can be maximized by a high number density in solution. The best way to maximize the number density is to create a material that does not rely on solvent. Gold “nanosalts” have been prepared by functionalizing gold nanoparticles with a charged organic surfactant and balancing its charge with another bulky organic molecule. The gold nanosalt was characterized using UV-Vis spectroscopy, FT-IR spectroscopy, proton nuclear magnetic resonance spectroscopy, transmission electron microscopy, and atomic force microscopy. Spectroscopic evidence suggests that organic material has been attached to the gold nanoparticles and that it is an ionic liquid at room temperature. It has also been shown that the gold nanosalt is capable of forming ordered arrays and is capable of self-healing.

Introduction:

Ionic liquids have increasingly been drawing attention in research mainly due to their “green solvent” properties. These compounds exist as solventless cations and anions at room temperature. Iionic liquids have a variety of applications due to their tunable properties including polarizability, hydrophobicity, and solvent miscibility which are affected by the cation and anion present in the compound. These properties can be easily altered by changing either ion. Some of the desirable properties of ionic liquids include low viscosity, low melting points, thermal stability, nonflammability, and very low vapor pressure. Ionic liquids can provide an anhydrous polar environment for
chemical reactions, vital for the success of many reactions including synthesis of gold nanosheets.\textsuperscript{3,4}

Ionic liquids are useful for organic reactions, separations, electrochemical applications, and catalysis reactions. They act as environmentally friendly solvents for some reactions.\textsuperscript{2,3} More recently, inorganic syntheses have been investigated using gold nanoparticles, mesoporous materials, CoPt nanorods, and nanocrystalline metals with ionic liquids as a solvent.

Nanoparticles (particles with diameters on the order of $10^{-9}$ m) have also been attracting much attention in the literature because of their unique optical, magnetic, and electrical properties.\textsuperscript{3,5-8} They are used in a variety of applications including biodiagnostics, gas sensing, and catalysis.\textsuperscript{5-8} Nanoparticles, especially those of the coinage elements (i.e. gold and silver), express striking colors in the visible region of the electromagnetic spectrum. These color changes lend to many applications in the optical and optoelectrical fields.\textsuperscript{6} Changes in color are caused by the oscillation of the conductive electrons in response to the alternating electric field generated by the electromagnetic radiation. Even more interesting is the ability to modulate the color of the nanoparticles based on interparticle interaction, separation, and size.\textsuperscript{6,8}

In order to maximize the optical and electrical properties of nanoparticles, an optically clear, high number density suspension is needed. Nanoparticles possess characteristics that are significantly different than both their corresponding bulk materials and atomic properties.\textsuperscript{7} Many of these properties are related to the size of the nanoparticles; therefore being able to control nanoparticle growth is important.\textsuperscript{7}
It has recently been reported that gold nanosheets (thin layers of nanoparticles on the order of 1-30 µm long) have been synthesized using an ionic liquid as a solvent.\textsuperscript{3} Li et al. have been able to produce nanosheets that measure up to 30 µm long and 50 nm thick. It is suggested that these nanosheets may lead to fabricating new nanodevices or applications in electrochemistry.\textsuperscript{3}

The novelty of the current experiment is that it employs a functionalized gold nanoparticle as one of the ionic components of the ionic liquid. The ability to use the nanoparticle as a component of the ionic liquid allows for the optical and electrical properties of the nanoparticles to be more prominently displayed. This may allow for more effective and efficient applications.

Previous research has been conducted using silica and maghemite nanoparticles.\textsuperscript{2} Silica nanoparticles provided the most interesting data and were also easier to prepare. An ionic liquid containing a silica nanoparticle was created by functionalizing the surface of a 12 nm silica nanoparticle with a quaternary ammonium organosilane followed by an anion exchange with a bulky negatively charged organic group. After repeated washings, the result was a solvent-free substance containing silica nanoparticles that was a liquid at room temperature.

This concept was expanded to gold nanoparticles for the current experiment. Gold nanoparticles are more interesting and useful than silica nanoparticles because of their optical and electrical properties. Using a gold nanoparticle does, however, require some modifications. The first modification made is the use of a negatively charged thiol surfactant as the primary functionalizing molecule of the gold surface instead of a positively charged molecule. The molecule of choice in this experiment is the sodium
salt of mercaptoethanesulfonic acid (MES). The secondary surfactant is a bulky, positively charged quaternary ammonium molecule (Adogen 464) that replaces the small stabilizing sodium ion of the MES (Figure 1).

Mercaptoethanesulfonate was chosen as the primary surfactant because of its ability to bind to the gold nanoparticle surface and for the negative charge that it would place on the surface. The sodium ion that stabilizes the negative mercaptoethanesulfonate ion is easily removed in aqueous solution. Adogen 464 was chosen because of its large, branched chains and positive charge. The bulky side chains of the Adogen 464 assist in maintaining a liquid phase at room temperature. The chloride ion is readily removed in aqueous solution; this elimination drives the reaction to completion.

The resulting compound of this process is a stable ionic liquid with gold nanoparticles integrated into the system, commonly called a gold nanosalt. The nanosalt is a solvent-free ionic compound, liquid at room temperature, and displays some of the unique properties of the gold nanoparticles. This substance potentially has many
biotechnical and industrial applications. They can also provide better nanoparticle precursors for other applications.

**Experimental:**

**Synthesis:**

Gold nanoparticles with a 20 nm diameter were synthesized using the well-established Turkevich Method. Using this method, 400 mL of nanoparticles were prepared by bringing 3.4 mL of 29mM hydrogen tetrachloroaurate(III) hydrate (HAuCl₄ · 3H₂O, Aldrich) in 380 mL of nanopure water to a rolling boil. The Au³⁺ solution was then reduced by adding 20 mL of 1% sodium citrate. The solution was allowed to continue boiling until it turned ruby red, indicating 20 nm particles. Further modifications were carried out at room temperature after allowing the particles to cool and adding nanopure water to bring the volume up to 400 mL.

The particles were functionalized with a five times stoichiometric excess of 2 mM MES (Aldrich) in nanopure water by adding the MES and allowing it to stir for 24 hours at room temperature. An ion exchange was then performed using a ten fold excess of Adogen 464 (Aldrich) to replace the sodium ions. This was allowed to stir briefly (five minutes) then allowed to sit until the particles had precipitated out of solution (> 4 hours). The supernatant was decanted and the product was collected via toluene suspension. The solution was washed repeatedly with water until the water layer became clear. The solution of gold nanosalt in toluene could then be dried out, leaving behind a viscous gold nanosalt.
**Instrumentation:**

The products were analyzed using UV-Vis spectroscopy. A series of spectra were collected throughout the different stages of the synthesis with a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The wavelength range was set from 400-900 nm with a scan rate of 600 nm/min.

Fourier transform infrared (FT-IR) spectroscopy was performed on the gold nanosalts using a Thermo Nicolette Nexus 470 FT-IR ESP. Spectra were taken for each of the components of the gold nanosalt, as well as the final product for comparison.

Proton nuclear magnetic resonance (NMR) spectroscopy was also used to characterize the gold nanosalt. The gold nanosalt was suspended in toluene-d₈ and experiments were carried out with a 500 MHz spectrometer. In addition, relaxation time experiments of the protons were also performed.

Images of the gold nanosalt were obtained using transmission electron microscopy (TEM). High resolution TEM analyses were conducted on a Phillips CM200 Field Emission Gun instrument operating at 200 kV. A CCD camera was used for focusing at high magnification. Images were collected on SO-163 film and digitized using a Minolta DiMAGE scanner at 2400 dpi resolution. The gold nanosalt was prepared for TEM by placing a drop of the gold nanosalt on a porous carbon grid and allowing the toluene to evaporate.

Atomic force microscopy (AFM) was used to investigate the self-healing of the gold nanosalt, as well to clarify visually how the particles align themselves when drying. Experiments were conducted on a Dimension 3100 AFM with a Nanoscope IIIa
controller. Non-contact, or tapping, at a frequency of approximately 1 Hz was used to determine the phase, or hardness, of the gold nanosalt when affixed to a glass slide.

**Results and Discussion:**

The synthesis of the gold nanosalts provides an array of color changes. The beginning solution of hydrogen tetrachloroaurate(III) hydrate is a very pale yellow. After the addition of the sodium citrate, the particles go through a transition of bluish-purple, purple, pink, and finally to a deep ruby red color (Figure 2a,b). The addition of MES provides no color change, but the addition of Adogen 464 leads to the formation of a blue precipitate. This suggests that the surface of the nanoparticles has been functionalized as they are no longer water soluble and have also undergone a color change. After the removal of water, the particles were suspended in toluene or 1,2-dichlorobenzene, which causes the solution to turn dark red or purple, significantly darker than the unfunctionalized particles. Toluene was chosen as the suspending agent for the analyses due to the solubility of the nanosalt and also because it is safer than 1,2-dichlorobenzene. When the gold nanosalt is dried out onto a glass slide, it has a gold or copper colored sheen but turns red again when resuspended in toluene.
Figure 2. a) 20 nm gold nanoparticles make up a solution that is ruby red. b) The gold nanosalt is a darker red or purple color.

**Characterization:**

Using UV-Vis spectroscopy it was shown that the gold nanoparticles have a peak absorbance at 520 nm (Figure 3). After adding the MES, the particles had a peak absorbance of approximately 521 nm. Following the addition of the Adogen 464, resuspension in toluene, and a series of washings, the peak shifted to 529 nm. These shifts in maximum absorbance suggest that the organic surfactants have attached to the surface of the particles. The bonding of these organic molecules was further explored using FT-IR spectroscopy (Figure 4). However, this data was fairly inconclusive as good spectra of the different components were not obtained.
Figure 3. UV-Vis spectra for the stages of gold nanosalt synthesis. The particles absorb at 520 nm, the particles and MES absorb at 521 nm, and the final product absorbs at 529 nm after repeated washings to remove excess surfactants.

Figure 4. FT-IR spectra of the components of the nanosalt and the nanosalt. This data was fairly inconclusive as good spectra of the different components were not obtained. The waves present in the spectra are a result of interference from the sample cell. Curves are offset for clarity.
TEM images of the gold nanosalt confirmed the size of the particles to be approximately 20 nm (Figure 5). They also show the spacing between the gold particles and how these particles are stabilized by the surfactants attached to the surface. If the surfactants are not physically attached to the gold surface, the particles would aggregate when they are drawn out of solution. The individual particles (magnified in Figure 6) allow the organic layer surrounding the particle to be seen. The organic layer is the globular part hanging off of the surface of the nanoparticle. This is strong confirmation that the particles have been attached to the surface of the gold nanoparticle.

Figure 5. TEM image of the gold nanosalt. This image confirms the size of the nanoparticles and also shows that the particles are stabilized by the organic surfactants.
Figure 6. TEM of individual nanoparticles from the gold nanosalt. The arrows indicate the regions where the organic layer can be seen.

Proton NMR was also used as a method to explore the attachment of the surfactants to the gold. This data is incomplete although it does suggest that the surfactants are attached to the surface. The spectrum was obtained and analyzed to assign bonds to each peak of the spectrum (Figure 7). The peaks between 3 ppm and 5 ppm can be assigned to the methylene groups located nearest the thiol and the gold surface as well as the methyl group from the Adogen 464. The peak at 1.65 ppm may be from the Adogen 464 methylene nearest the nitrogen. The large peaks at 1.4 ppm were assigned to the methylene groups located in the alkyl chains of the Adogen 464. The splitting can be attributed to the different populations of surfactant molecules that arise from free and bound molecules or from parts of molecules that are shielded or exposed to the solvent. The peaks near 1 ppm are assigned to the methyl groups at the end of the Adogen 464 alkyl chains. Again, the splitting is most likely caused by the different
populations of the molecules. Spectra need to be obtained of the MES and Adogen 464 without the gold nanoparticles to be able to compare the shifts caused by the gold interaction in order to say anything more conclusive from this data.

![Proton NMR spectrum for the gold nanosalt](image)

Figure 7. The proton NMR spectrum for the gold nanosalt. Solvent peaks are marked. The peak labeled a is from the HS-CH₃ protons, b is the HS-CH₂-CH₃ protons, c is the methyl protons on the Adogen, d is signals from small molecules in solution, e is the methylene groups nearest the nitrogen, f is the methylene groups in the alkyl chains of the Adogen, and g is the methyl groups at the end of the alkyl chains.

NMR spectroscopy also allowed for the measuring of relaxation times for the protons in the gold nanosalt (Table 1). The proton T₁’s were obtained by inverting all of the protons at the beginning of the experiment and measuring the inversion recovery. It was found that the magnetization exchange between nearby protons was not very efficient. This varies from typical large macromolecules. It indicates that the dipole interactions between protons are not the main source of relaxation for the gold nanosalts.
as it is for most other macromolecules. The $T_2$ values are related to the line width by the equation

$$\Delta v_{1/2} = \frac{1}{\pi T_2}$$

where $\Delta v_{1/2}$ is the line width. From this data, it can be stated that protons nearest the gold surface relax faster than those protons in the outer periphery. The parallels in the calculated and observed line width values indicate that the lines are homogeneously broadened, suggesting that the broader lines are not caused by protons in different magnetic environments.

Table 1. Proton relaxation rates for the gold nanosalt along with the calculated and observed line widths for some of the peaks.

<table>
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<th>Shift (ppm)</th>
<th>$T_1$ (ms)</th>
<th>$T_2$ (ms)</th>
<th>$\Delta v_{1/2}$ (calc) (Hz)</th>
<th>$\Delta v_{1/2}$ (obs) (Hz)</th>
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AFM illustrated the packing arrangement of the gold nanosalt when the toluene was evaporated from the sample. Tapping lightly (with a small drive amplitude) on the surface of the gold nanosalt did not reveal the hexagonal self-packing of the particles (Figure 8a) where tapping with a larger drive amplitude on the surface did reveal this packing arrangement (Figure 8b). A closer view further illustrates the arrangement of the particles (Figure 8c).
AFM images further went on to show that the gold nanosalt is not a solid at room temperature and that it is still a liquid, albeit an extremely viscous one. Scratches approximately 150 nm thick were made in the surface of the gold nanosalt using the AFM tip (Figure 9a-f). Every 8-10 minutes, the same area of the nanosalt was scanned while the gold nanosalt healed the scratch made in the surface. It took approximately one
hour for the scratch on the right to heal. The required amount of time it takes for the scratches to heal is most likely a function of the thickness and depth of the scratch in the surface of the nanosalt.

Figure 9a-f. Three scratches were made in the gold nanosalt using the AFM tip of varying thickness and depth (left-most scratch is deepest and thickest). Over time, the gold nanosalt heals itself almost completely, indicating that the gold nanosalt is not a solid at room temperature. 9a insert: the scale bar indicating how thick the gold nanosalt is based on color.

Conclusions and Applications:

Gold nanosalts were successfully created and characterized in this experiment. Nanoparticles that were approximately 20 nm in diameter were made by reducing hydrogen tetrachloroaurate(III) hydrate with sodium citrate. The surface was functionalized with sodium mercaptoethanesulfonate. This was followed by a cation exchange with Adogen 464 to replace the sodium ion with a bulky organic group. These
gold nanosalts were characterized extensively. UV-Vis spectroscopy, FT-IR spectroscopy, and \(^1\)H NMR spectroscopy all suggest that the gold nanoparticles were functionalized. TEM allowed for the visualization of the particles as well as the organic layer surrounding them. NMR evaluated the effect of the gold particle on the relaxation times of the surfactant protons. These studies indicate that protons that are closer to the surface of the gold have a shorter relaxation time than protons on the outer edge of the surfactant, contrary to observations in most macromolecules. AFM revealed both the self-assembling and the self-healing characteristics of the gold nanosalt. This property of the nanosalt can be very useful to the Air Force and also to commercial companies as well.

The self-healing properties of the gold nanosalt make it extremely useful for many Air Force applications including radar switches. These radar switches operate based on Radio Frequency Micro Electro Mechanical Systems or RFMEMS. MEMS in a general sense is the integration of sensors, mechanical elements, electronics, and actuators on a common substrate through microfabrication technology.\(^{10}\) In order to create mechanical and electromechanical devices using MEMS technology, a circuit is formed by a micromachining process that etches away specific parts of a silicon wafer or applies a new structural layer to the silicon surface. The electrics are fabricated using a traditional integrated circuit process; this is where the nanosalts can be useful.

To prevent the circuit from breaking under the stress of repeatedly opening and closing as is needed in a radar switch, a lubricant is needed. The gold nanosalt fabricated in this paper has recently been applied to these switches. The nanosalt is conductive and can therefore be used to complete circuits in RFMEMS switches. Preliminary tests show
the ability of the switch to perform for over $10^5$ cycles whereas previous lubricants only allowed $10^4$ cycles. This is a very promising application for the nanosalts as more knowledge is gained about them regarding their properties and lifespan.

**Future Studies:**

Further study of gold nanosalts will be continued by exploring the characteristics of the gold nanosalt by neutron scattering, thermogravimetric analysis, differential scanning calorimetry, and nano indentation. Fundamental research in the areas of NMR and IR needs to be reexamined. Other cations for the system will also be explored such as hexadecyltributyl phosphonium and tetraoctylphosphonium to replace the Adogen 464. The nanosalts will also undergo further testing for their compatibility in RFMEMS switches.

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References:


