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Graphene Oxide - Gold Nanostar based sensor for chemiresistor and SERS sensing

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Background and Learning Objective

As part of a bigger project of building a multimodal electronic nose for 2,4 di-nitro toluene and 2,4,6 trinitrotoluene, the objective of this study was to develop a novel type of sensor to detect specific analytes and their concentrations. A chemiresistor based system involving gold and graphene nanostructures is proposed so that it has both chemiresistive and SERS sensing capabilities (fig. 1). It was expected that if succeeded, the sensor would show clearly the orthogonality between the optical SERS reading and the chemiresistive reading in terms of sensing analytes. This study hopes to eventually integrate chemiresistor sensing and SERS sensing for selective, qualitative and quantitative sensing of volatile organic compounds, especially explosives, but it is applicable to a wide range of sensing.
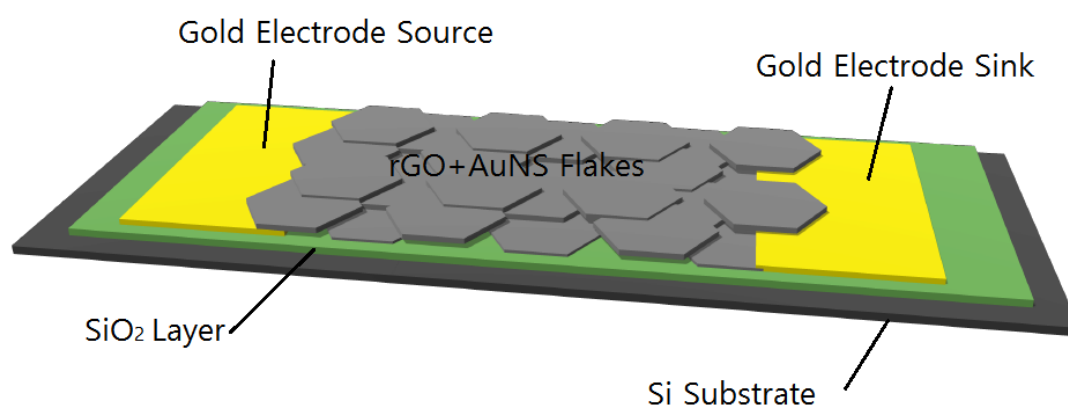
Figure. 1 Schematic of the electrode.

Materials:

Reduced Graphene Oxide sheets with patches of gold nanostars were used as SERS sensitive nanostructure. Graphene Oxide layers were synthesized by oxidative exfoliation of graphite flakes according to a modified Hummer method, where the concentration and the size of the layers were controlled by successive cycles of centrifugation and sonication. AuNS was synthesized using 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid(HEPES) as a reducing agent. 2ul of 0.1M $HAuCl_4$ was added to 1000ul of 0.1 HEPES solution at room temperature. After the completion of the AuNS synthesis, they were centrifuged at 10000rpm twice and redispersed in water. For the GO-AuNS

nanopatches, 5ug/mL graphene oxide was added to 1200uL of 0.1M HEPES followed by the addition of 2uL of 0.1M HauCl$_4$. The resulting hybrids were centrifuged and washed twice in water at 5000rpm for 10 minutes, then redispersed in water.

Chemiresistors

SiO2 layer was deposited on a silicon substrate. Then a thin layer of interdigitated gold electrode was deposited onto the SiO2 layer. The space between the interdigitated electrode was 20um. GO-AuNS hybrid solution was drop casted onto the interdigitated region and dried. This process was repeated multiple times, which was different for each sample of electrode produced.

GO reduction

The graphene oxide layer was reduced to make it conductive using hydrazine hydrate. 1ml of hydrazine hydrate solution was added into a clean vial. In another vial, the sample electrode with deposited graphene oxide was placed. The hydrazine vial was placed inside a 1L beaker and heated to 130 degrees Celsius. Once the hydrazine vapor was observed, the vial containing the graphene oxide was placed in the beaker as well, then the beaker was sealed. The electrode was exposed to the hydrazine vapor with 30 second increments until desired resistance was reached.

Results and Discussion

The resistance across the electrode was measured real time under analyte exposure of varying time steps and concentrations.
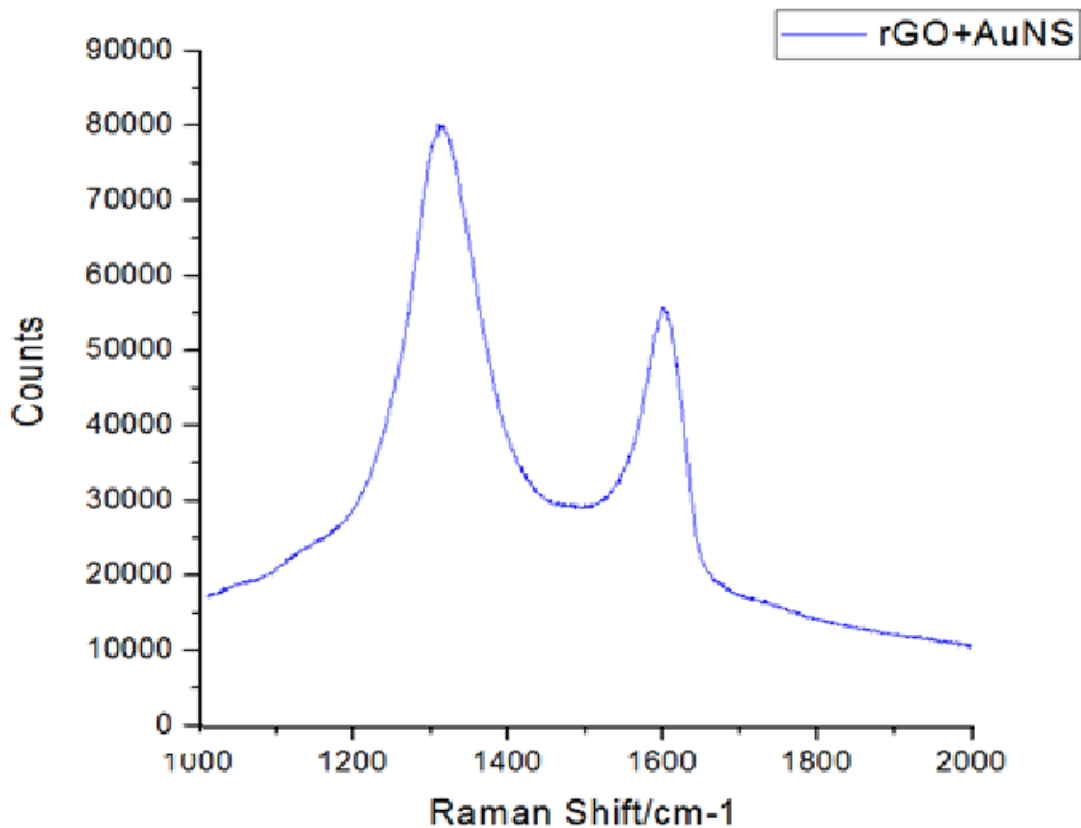
The gold nanostars concentration was very dense, as shown in the TEM image in fig. 2
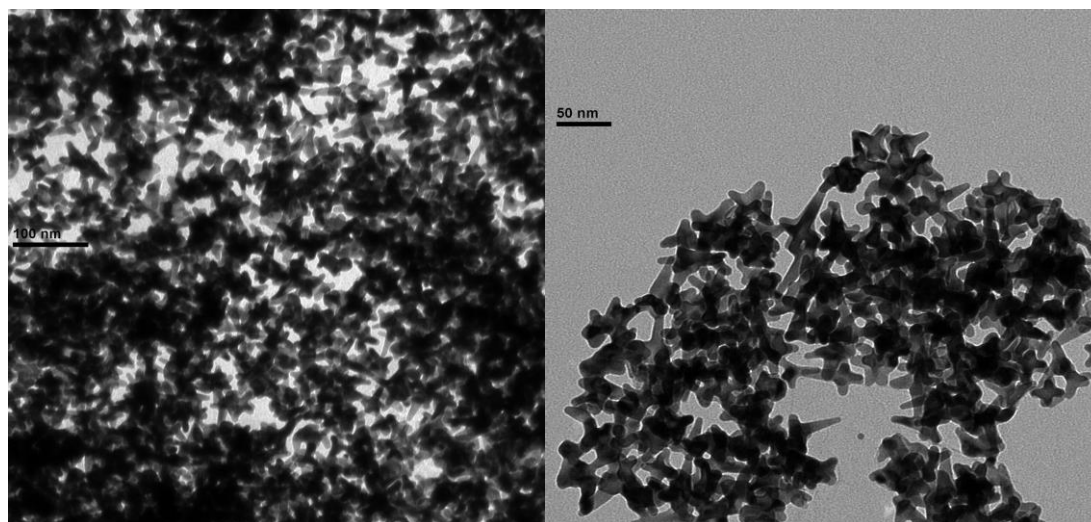
Figure. 2 AuNS grown on Graphene Oxide layers (TEM)

Graphene Oxide presence was confirmed using Raman Spectroscopy in fig.3 with the location of

the peaks.

Figure. 3 Raman spectrum of the GO-AuNS hybrid film deposited on the gold electrode

Various analytes, including hexane, ethanol and acetone were used to verify the resistance change of the electrode arrays. Figure 4,5,6 shows the change in resistance with respect to time. The grey bars show where the analyte pulses were applied. The analyte pulses were of 5, 10, 15 and 20 ppm in increasing order.
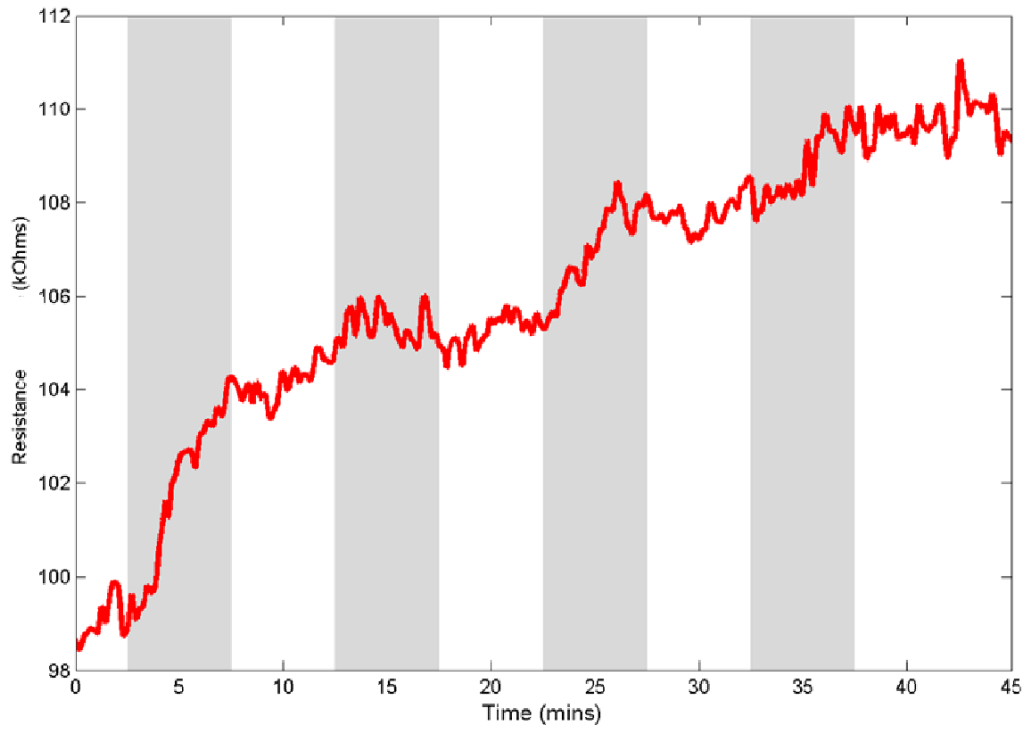
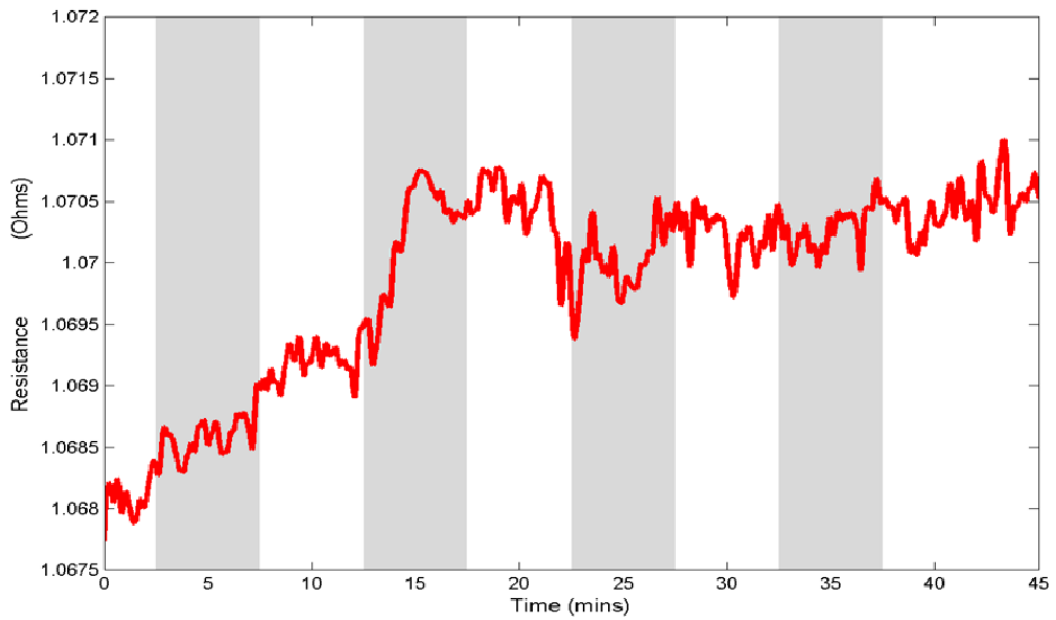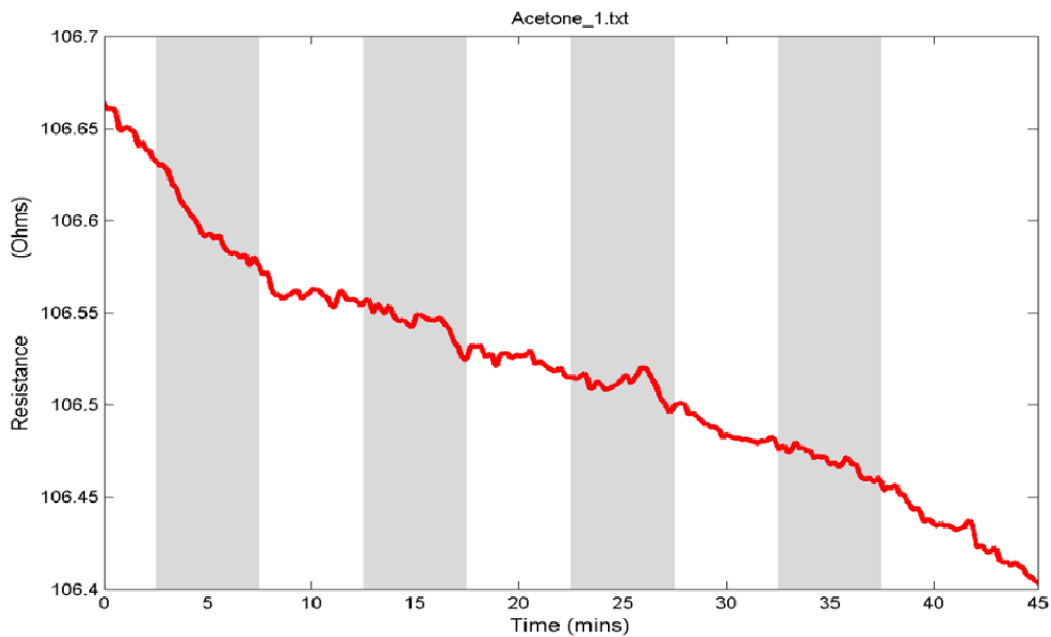**Figure. 4 Resistance change vs. Time under Hexane pulse**

Figure. 5 Resistance change vs. Time under Ethanol pulse

Figure. 6 Resistance change vs. Time under Acetone pulse

The results from these tests are mediocre. We suspect this because of several reasons. First, the produced sensors are extremely sensitive to moisture. Before each testing, the sensors were placed in vacuum overnight to remove all moisture. Two dehumidifiers were used in series to remove as much moisture from the carrier gas (air) as possible. However, the carrier gas used was building air, and not from a canister. On further research, nitrogen gas, helium, or argon is recommended. The second reason it might not have been able to detect changes of resistance under analyte exposure is because the concentration of the analyte is very high. A common trend that is shown in figure 4, 5 and 6 is a drastic change in resistance in one concentration, and then null response for other concentrations. We suspect that the high concentration of the analyte is saturating the sensor. With these hypotheses in mind, the experiment was repeated with hexane in fig. 7.
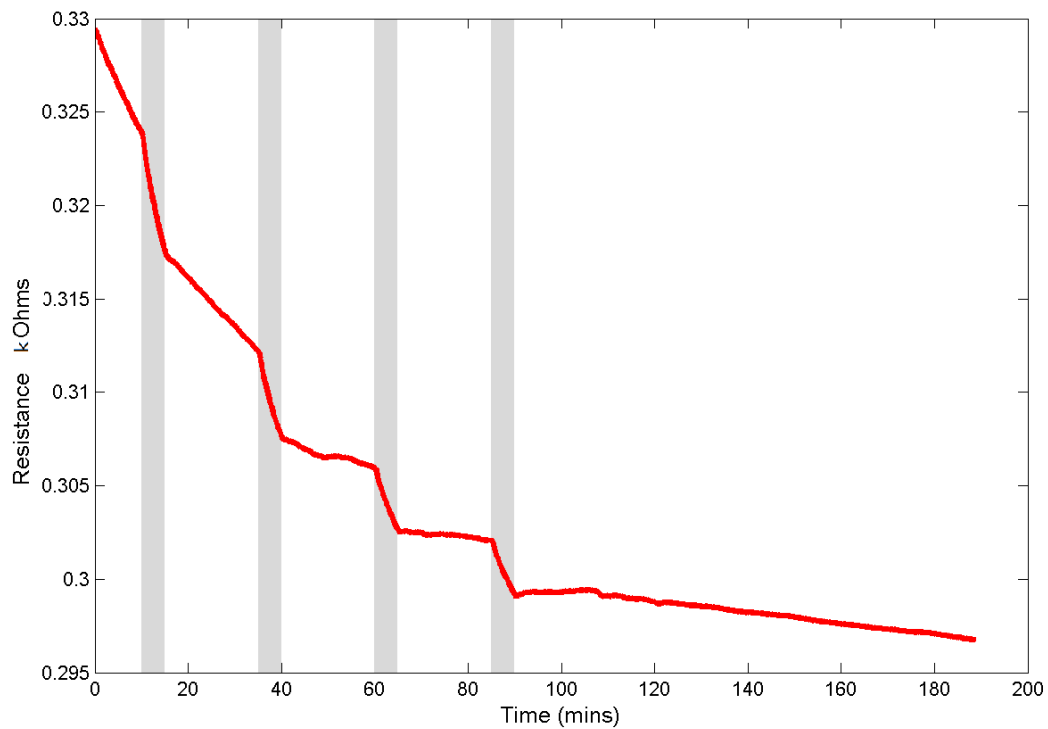
Figure 7. Resistance plotted against time under hexane exposure with 17ppm concentration

With longer recovery time between pulses, the signals are much easier to observe. Also, the initial resistance played a role where ideally, the resistance of the sensor straight out of the vacuum chamber is in the kOhm range.

The challenge encountered after this experiment was that the resistance was not recovering back to its initial level. With a lower concentration of analyte, small amount of recovery is exhibited, as shown in fig. 8.

Figure. 8 Resistance vs. Time under hexane exposure, concentration 2.5 ppm

Although with lower concentration it is easier to get a recovery in resistance, the response is very noisy. At this point, further experiments using graphene oxide was deemed futile because of the graphene flake's sensitivity to moisture and the noise in the readings.

Appendix*

Second Approach: Ordered Gold Nanoparticle (AuNP) array

After the failure of the initial proposed material, a monolayer of gold nanoparticle array on the gold electrode surface is proposed to achieve stable chemiresistor response and SERS reading. The process is outlined in fig. 9.
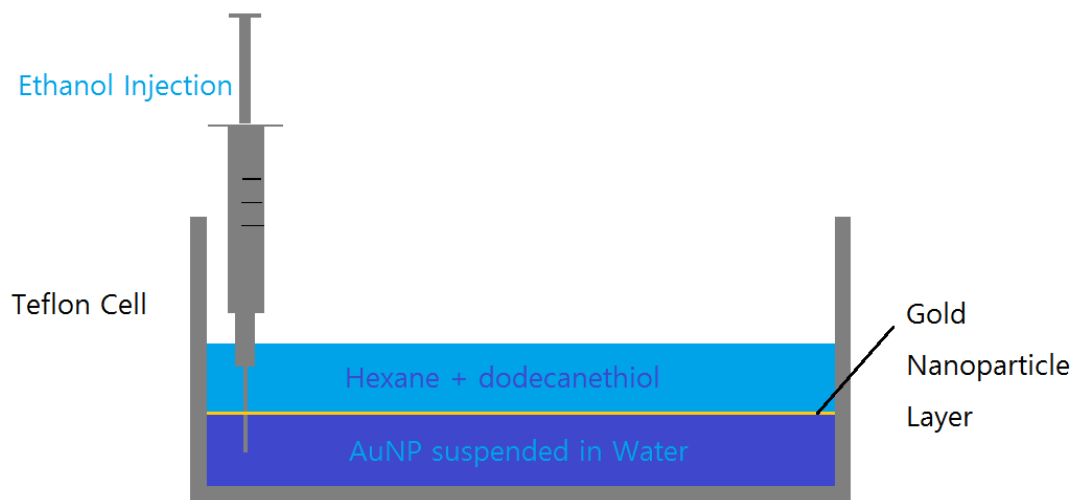

Figure. 9 Schematic of interfacial transfer of gold nanoparticles onto substrates.

Gold nanoparticles are first dispersed in water after twice centrifuged and placed in a Teflon cell. A hexane layer mixed with dodecanethiol is then carefully added to the container. Ethanol is injected dropwise into the water layer and moves the nanoparticles to the interface between the hexane and the water, where it is capped by the dodecanethiol. After hexane is spontaneously evaporated, a thin metallic sheen is observed on the surface of the water which could be transferred to a silicon substrate. The following image in fig.10 is an SEM image of the transferred nanoparticles.

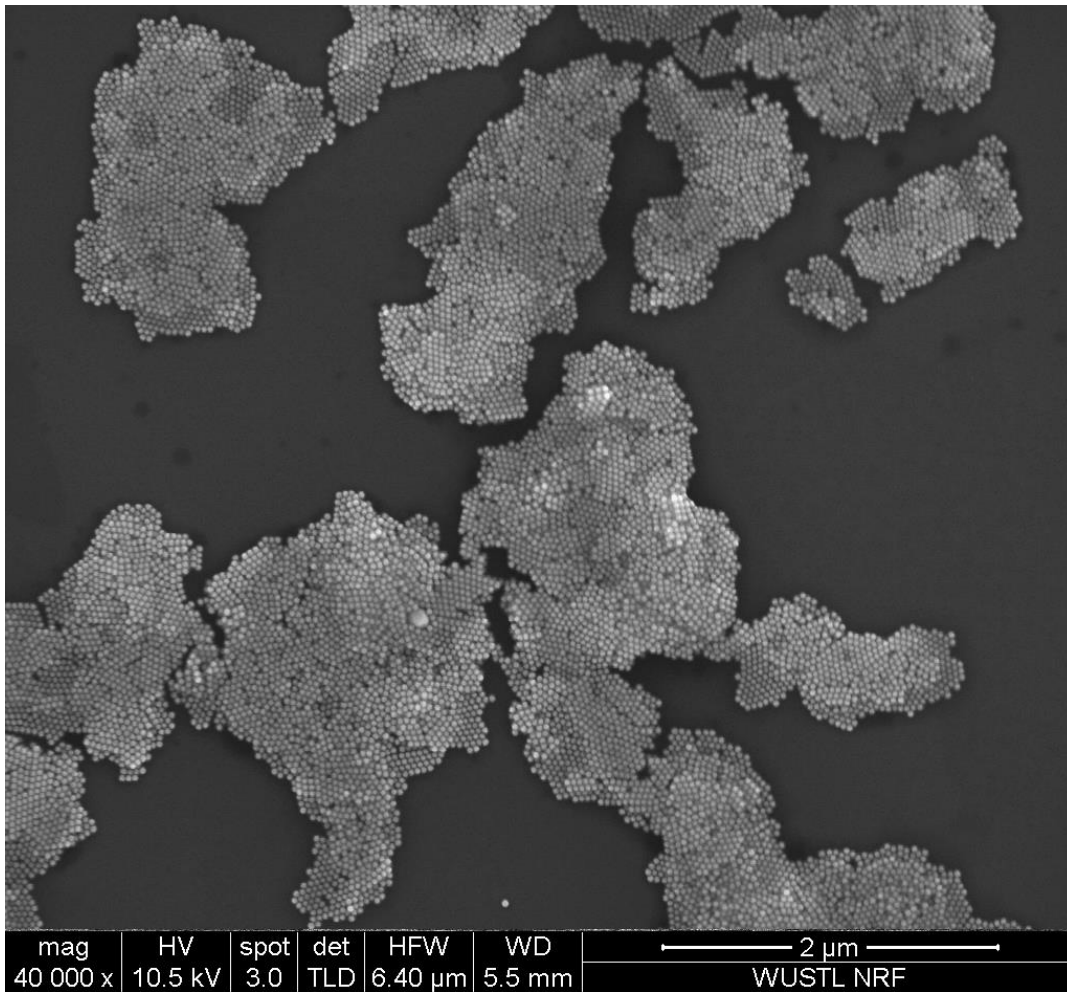| mag	HV	spot	det	HFW	WD	2 µm
40 000 x	10.5 kV	3.0	TLD	6.40 µm	5.5 mm	WUSTL NRF

Figure. 10 Gold nanoparticle multilayers from interfacial transfer

The concentration of dodecanethiol determines how clustered the nanoparticles are, because it is the capping agent that enables the gold nanoparticles to stick together. Further studies will be done in order to achieve a monolayer or a multilayer of gold nanoparticles that can span across microns and fill the gap between the electrodes to provide stable, ordered active sites for vapor analysis as well as SERS readings.

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