Chemiresistor Arrays Prepared by Simple and Fast Vapor-Phase Thiol Place-Exchange Functionalization of Gold Monolayer-Protected Cluster Films

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We describe a simple, versatile, and relatively fast method to alter the sensor selectivity of chemiresistors based on films of Au monolayer-protected clusters (MPCs) by varying their functionalization via vapor-phase thiol place-exchange reactions. Drop-cast deposited films of hexanethiolate (C6S)-coated Au MPCs are exposed to volatile thiol liquids, such as mercaptoethanol (HOC2S), mercaptopropionic acid (HOOCC2S), and mercaptopropyltrimethoxysilane (H3COSiC3S), which leads to thiol place-exchange and new functionalities in the film. Generally, the film is about 10–20% exchanged during the first 4 to 5 h and 80–90% exchanged after 24 h. The extent and the rate of exchange decreases as the thickness of the film of C6S Au MPCs increases, leading to irreproducibility issues if film thickness is not carefully controlled. Importantly, the chemiresistive sensing response ratio of 2-propanol relative to toluene vapor increased significantly from about 0.3 prior to exchange to 2.0 after 24 to 48 h of exchange with HOC2S, showing that the selectivity of the sensor could be significantly altered by this method, which is simpler, faster, and more amenable to a wide variety of ligands compared to solution-based functionalization methods. The chemiresistive response of an unexchanged C6S Au MPC films and those exchanged with HOC2S, HOOCC2S, and H3COSiC3S demonstrates potential electronic nose applications.

1. Introduction

For many years, researchers have been interested in the detection of volatile organic compounds (VOCs)[1–6] because of their importance in the food industry,[1] environmental protection,[2,6] bomb detection,[3,7] public safety,[4] and disease diagnostics,[8] as some examples. The detection is often performed by humans or animals, such as in the food industry, where humans directly detect VOCs given off by food using their sense of smell. Dogs are widely used for the detection of volatiles associated with bombs, drugs, and pursuit of suspects.[3] In many applications, though, the VOCs are toxic to humans and animals. There is also a large cost associated with employing humans and training dogs along with potential errors and lack of sensitivity or selectivity with the sense of smell. Accordingly, many sensor technologies and instrumental methods have emerged to identify and quantify VOCs, including colorimetric sensors,[9] electrochemical sensors,[7] acoustic wave devices,[10,11] piezoelectric devices,[12] gas chromatography–mass spectrometry (GC–MS),[13] localized surface plasmon resonance (LSPR) sensors,[14] and chemiresistors.[15–19] Miniaturized sensor arrays for sensitive and selective detection of VOCs based on pattern recognition are termed "electronic noses".[3,18] These devices combine the output signal of selective, chemical sensors with data analysis software, which is simpler and cheaper than instrumental methods like GC–MS.

Chemiresistors are an attractive method for the detection of VOCs[19] because they are simple, sensitive, and rugged hand-held devices.[20,21] The detection is based on a resistance change of some material in the presence of vapor phase analyte, which occurs by the vapor molecules partitioning into the material and altering its electronic properties. We have previously employed thin films of organic-coated Au and AuAg alloy nanoparticles (NPs), termed monolayer-protected clusters (MPCs), as chemiresistive transducers to detect various VOCs in the gas phase.[22,23] Au MPCs in particular consist of a metallic Au core that is surrounded by a monolayer of organic ligands, which is usually alkanethiolates. The metal core is responsible for electron transport while, the organic shell acts as an absorber of VOCs. Electron conduction through the film occurs by an electron hopping mechanism,[24–26] which, at constant temperature, depends exponentially on the distance between clusters and the dielectric constant of the environment. In the absence of VOCs, the conductivity depends on the spacing and dielectric properties of the alkanethiolate monolayer surrounding the Au MPCs. In the presence of VOCs, the target vapor molecule will partition into the film and can alter the spacing between the MPCs[27] and/or the dielectric properties of the original alkanethiolate monolayer. This leads to a change in the electron hopping conductivity and acts as

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a means to detect the VOC of interest. The degree of conductivity change depends on the properties of the alkanethiolate ligands and the analyte.

Wohltjen and Snow[28] first reported that metal MPCs could be used for sensing VOCs. They discovered that the resistance of drop-cast films of octanethiolate (C8S) Au MPCs decreased or stayed similar in the presence of polar vapors, such as 2-propanol and water, but increased in non-polar vapors such as tetrachloroethylene (TCE) and toluene. They attributed the increase in resistance to an increase in cluster-to-cluster separation due to film swelling in the presence of non-polar VOCs. Decreased resistance could be due to film contraction or increase in dielectric environment in the presence of polar vapors. While the response direction indicated the general polarity of the analyte in this case, MPC films lack high selectivity to specific analytes because they respond indistinctly to many VOCs. It was therefore proposed[28] that adding specific functional groups to the organic layer would improve the selectively for a wide range of vapor analytes.

In line with this, different approaches have been employed for improving the selectivity of chemiresistive devices based on MPCs, including those functionalized with aromatic, carboxylate, and alcohol-functionalized thiols,[29–32] dodecylamine-coated Au MPCs,[33] C6S Au MPCs exchanged with ethylene oxide oligomers, $CH_3(OCH2CH2)_nSH$, of specific length,[34] thiophene-terminated alkanethiol MPCs, mixed ligands of chlorobenzenemethanethiol (CBMT) and n-octanethiol,[35] and mixed films of C8S Au MPCs and a $PtCl_2$(olefin)-(pyridine) square planar coordination complex.[36] Selectivity can also be improved by varying the NP size, organic chain length, and NP separation within the film, as demonstrated for 2 and 8 nm diameter carboxylate (C5 and C15)-coated Au MPCs,[31] C2 to C12 thiophene alkanethiols[37] and C4 to C11 regular alkanethiols,[38] and dodecylamine-stabilized Au MPCs deposited via layer-by-layer with dodecanethiol,[39] respectively. In general, these reports demonstrate that films with non-polar ligands have better affinity to non-polar analytes and vice-versa, but the films still lack specific selectivity to just one or a very narrow class of analytes.

In order to improve selectivity various researchers have constructed sensor arrays[8,40–42] in which a particular sensor gives a distinct signal to a particular analyte. For instance, Zeller and co-workers placed an array of organic-coated Au NPs at the end of a GC column in order to separate and measure the response of a variety of analytes individually.[42] Later, Haick's group employed a similar approach and used GC–MS (and solid pre-concentrators) combined with a nine-sensor array based on Au NPs to identify 42 vapors associated with lung cancer biomarkers.[8] They found distinct responses between healthy and unhealthy patients and interestingly, sick patients exhaled eight biomarkers which were not otherwise detected. The response of chemiresistor arrays of organic-coated Au NPs combined with analytical analysis allows for much better selectivity and discrimination of vapor analytes.

In most sensor array applications, groups alter the functionality of MPCs by synthesizing the MPCs with a new type of thiol ligand and simply drop-cast depositing the different

MPCs as a film.[8] Normally, the synthesis of MPCs is a 24 h process. A second method to alter functionality is by performing a thiol place-exchange reaction. In the thiol place-exchange reaction, a MPC with one type of ligand (thiol 1) is co-dissolved with a new thiol (thiol 2) and stirred for a certain amount of time, where thiol 2 replaces some of thiol 1 on the MPC during the reaction. This leads to a final MPC with some mixture of thiol 1 and thiol 2, where the relative amount of the two ligands depends on the ratio of the thiols in the exchange solution, the time of exchange, and the affinity of the thiols for the MPC and the solvent.[43] This type of place-exchange reaction occurs in MPC solutions over a few days in order to reach equilibrium, followed by purification of the MPCs, filtering, and drying.[43] Both the synthesis of new MPCs and the place-exchange reaction have a few drawbacks. First, it takes a few days to synthesize the functionalized MPCs and the synthesis requires time-consuming procedures, such as rotary evaporation, filtration, rinsing, and drying. Second, and more importantly, the functionalities available are limited by the solubility of the MPCs. If the MPCs are not soluble with the new functionality, which is often the case, then they cannot be easily processed into films for sensing applications.

Here we describe the full synthesis and drop-cast deposition of just one type of Au MPC and use of a vapor-phase thiol place-exchange reaction to quickly and easily functionalize these solid-state films with a wide variety of volatile thiol ligands in order to alter the chemiresistive sensing response to different VOCs for electronic nose applications. This simple method only requires full synthesis and film formation of one type of Au MPC with the ability to then post-functionalize the film with a wide variety of functionalities, which successfully overcomes the disadvantages of solution-phase functionalization. Through vapor-phase thiol place-exchange reactions, we build sensor arrays easily and effectively that could potentially be scaled up for mass production. In this study, we specifically synthesize and prepare films of hexanethiolate (C6S) Au MPCs as our initial MPC and exchange the films with mercaptoethanol (HOC2S), 3-mercaptopropionic acid (HOOCC2S), and (3-mercaptopropyl)trimethoxysilane (H3COSiC3S) by vapor-phase thiol exchange. These four sensors show very different responses to toluene (Tol), isopropanol (IPA), ethanol (EtOH), and acetone (ACT) as model VOCs, demonstrating the potential for this method to create sensor array electronic nose devices.

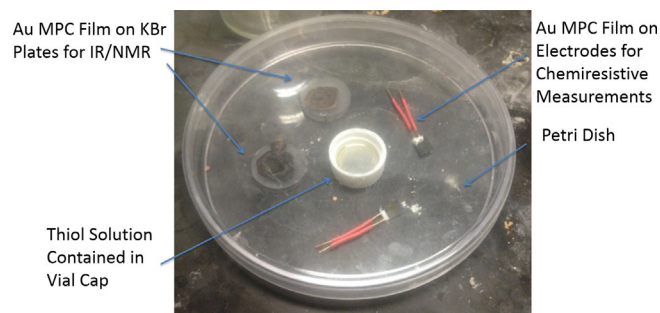## Experimental Section

Chemicals

Hexanethiol (C6S, 96%), mercaptoethanol (HOC2S, 99%), sodium borohydride (99%), tetraoctylammonium bromide (TOABr, 98%), toluene (Tol, 99.9%), isopropanol (IPA, 99.9%), ethanol (EtOH, 99.9%), acetone (ACT, 99.9%), 3-mercaptopropionic acid (HOOCC2S, 98%), and 3-mercaptopropyltrimethoxysilane (H3COSiC3S, 98%) were purchased from commercial sources and used as received. Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$) was synthesized from metallic Au. Barnstead Nanopure water ($R \geq 17.8\ M\Omega\ cm$) was employed for all aqueous solutions.

Synthesis of Au Monolayer-Protected Clusters (MPCs)

Hexanethiolate-coated Au monolayer-protected clusters (C6S Au MPCs) were synthesized according to the Brust reaction.[44] Briefly, 0.957 g of $HAuCl_4$ was dissolved in 25 mL of water and 2.18 g of TOABr was dissolved in 100 mL of toluene. The two solutions were combined and stirred until all of the $AuCl_4^-$ transferred into the toluene phase. The toluene phase was separated and 1.12 mL of hexanethiol, corresponding to a 3:1 thiol:Au ratio, was added to the toluene and stirred until the solution became colorless. The solution was cooled to approximately 0 °C using an ice bath and a 10-fold excess of $NaBH_4$ (1.01 g in 50 mL of water) was added to the toluene solution with stirring. The solution turned black within a few seconds, indicating the formation of metallic Au MPCs. 10 mL of additional water was added and the solution was stirred overnight. The toluene layer was separated from the aqueous layer and removed by rotary evaporation. The remaining black sludge was suspended in 200 mL of acetonitrile and collected by filtration on a glass fritted Büchner funnel. The black solid product was washed with an additional 250 mL of acetonitrile and 100 mL ethanol and thoroughly dried before collecting. Au MPCs prepared this way are 1.6 ± 0.4 nm.[45] UV/Vis spectroscopy, nuclear magnetic resonance (NMR), and thermogravimetric analysis (TGA) data were consistent with the synthesis of pure samples of this size MPC.

Film Deposition and Vapor-Phase Thiol-Exchange Reaction

10 mg of C6S Au MPCs was dissolved in 0.5 mL toluene. Then, 4–5 drops were used to drop-cast deposit a film onto a KBr salt plate and 2 drops used to deposit onto a Si/SiO_x substrate that contained two Au electrodes (rectangular in shape, 50 μm wide, and separated by 23 μm at closest point) in order to perform Fourier-transform infrared (FTIR) spectroscopy and chemiresistive sensing, respectively. These films were later exposed to thiol vapors for functionalization as shown in Figure 1. The KBr salt plate and electrodes coated with a film of C6S Au MPCs were placed inside a petri dish along with a vial cap that contained 1 mL of the thiol that was desired to be exchanged onto the C6S Au MPC film. Then, the container was closed in order to allow vapor exchange for various lengths of time up to 48 h. Mercaptoethanol (HOC2S), 3-mercaptopropionic acid (HOOCC2S), and mercaptopropyltrimethoxysilane (H3COSiC3S) liquids were placed in the vial cap as the ligands to replace the C6S ligands on the Au MPCs. Different thick-

ness films were formed in order to correlate vapor-exchange efficiency with thickness by drop-cast deposition of 1 to 4 drops (ca. 0.1 mL per drop) of the 20 mg mL^{-1} C6S Au MPC solution in a small container with a 0.79 cm^2 area, so that thickness was controlled by the number of drops used in the drop-cast deposition. The thickness was estimated at 5–10 μm per drop based on the 1.6 nm diameter of the Au MPCs and 1 nm length of the C6S ligand, assuming a cubic packing geometry, interdigitation of the C6S ligands in the film, and perfectly smooth layers.

Spectroscopy Analysis

An FTS 7000 Series Digilab FTIR spectrometer was used for characterization before and after C6S Au films were exchanged with the thiol vapors of interest. Before placing the film in the vapor exchange reactor, a background spectrum of the pristine KBr salt plate was run. Then, the C6S Au MPC films were prepared by drop-cast deposition on the KBr plate in a fume hood. After appearing visibly dry, they were characterized by FTIR spectroscopy under dry air, which further dried the films, making them free of solvent. Following FTIR analysis, they were placed into the vapor exchange container for the indicated times. Then the film was removed from the chamber and placed under a slow stream of N_2 for 30 min before the FTIR spectrum was measured again. The extent of exchange was determined by observing the peak height ratio of the corresponding functional group of the ligands at various times of exchange in the FTIR spectrum. For example, in the experiment of exchanging C6S ligands with HOC2S, we measured the peak height corresponding to the CH_3 and OH asymmetric stretch to estimate the ratio of C6S to HOC2S. For each exchange time a new sample was prepared and analyzed by both FTIR spectroscopy and by H^1 nuclear magnetic resonance (NMR) spectroscopy according to the procedure in the next paragraph.

H^1 NMR spectra were obtained with a 500 MHz INOVA spectrometer in chloroform-d solution for the vapor exchange of HOC2S onto the C6S Au MPC film in order to directly quantify the amount of thiol exchange as a function of time and compare to the results from FTIR. After FTIR spectroscopy of a specific sample exchanged for some amount of time, the thiol-exchanged films were rinsed off of the KBr plate with a chloroform-d solution and a small amount of iodine was added to the solution, followed by sonication for 30 min. This caused the thiolate ligands to be removed from the Au MPCs as disulfides and the Au to precipitate. The chloroform-d supernatant was removed from the Au precipitate and analyzed. The area of the peak corresponding to CH_2 hydrogens adjacent to the S group of HOC2S was compared to the area of the peak corresponding to the CH_2 hydrogens adjacent to the S group of C6S in order to determine the ratio of the HOC2S ligands relative to the original C6S ligands at different exchange times. This allowed easy quantitation of the different functionalities on the Au MPCs by NMR spectroscopy and correlation to FTIR spectroscopy.

Figure 1. Exchange reaction setup. C6S Au MPC films are drop-cast deposited onto KBr salt plates and two electrode devices and 1 mL of the liquid thiol used for exchange is placed in the white vial cap. The KBr plate allows measurement of the kinetics of the thiol vapor-phase place-exchange reaction by FTIR spectroscopy and NMR spectroscopy after film removal and the electrode device allows monitoring of the chemiresistive vapor sensing response. The petri dish is covered to confine and concentrate the exchanging thiol vapor above the MPC films.

Labels in figure:
Au MPC Film on KBr Plates for IR/NMR
Au MPC Film on Electrodes for Chemiresistive Measurements
Petri Dish
Thiol Solution Contained in Vial Cap

Vapor Sensing Experiment

Vapor sensing experiments were performed as described by our group previously.[23] Briefly, a gas line coming from a N_2 gas cylinder was split into two lines with a T-junction and the flow rate of each line after the split was controlled with two different Cole Parmer flow meters (2 % error at full scale). One of these split lines was pure N_2 and not altered while the other line was bubbled through the solvent of the vapor of interest in order to introduce

it into the vapor phase. The two lines were then recombined into one line again with another T-junction and the mixed (N_2 and N_2+ vapor) flowed into a two-arm (inlet and outlet) glass cell containing the electrode device with the specific Au MPC film of interest. Current flowing through the Au MPC films was monitored as a function of time using the chronoamperometry technique with a CH Instruments 660 A electrochemical workstation (Austin, TX). The current was monitored at a potential bias of 0.3 V while the device was exposed to alternating flow of pure N_2, 4% VOC vapor, or 52% VOC vapor, where the model VOCs were toluene (Tol), propanol (IPA), ethanol (EtOH), and Acetone (ACT). The response of the sensor was calculated using Equation (1):

$$\% \ \text{Response} = (i_r - i_b)/i_b \times 100$$

where i_r and i_b correspond to the response current in the presence of the VOC and initial baseline current in the presence of N_2 only, respectively. All of the chronoamperometry plots show $(i_r - i_b)/i_b$ indicated as $\Delta i/i_b$ versus time for easy comparison and the baseline current is provided for each device.

2. Results and Discussion

### 2.1. Vapor-Phase Place-Exchange Reaction

Figure 2 shows the results of FTIR and NMR analysis of films of MPCs at various stages of vapor-phase place exchange. In this experiment, a KBr salt plate with C6S Au MPC film was exposed to the vapor-phase HOC2S for the indicated time. Then, an FTIR spectrum was measured directly on the KBr salt plate and a NMR spectrum was measured from the same film after removal from the KBr salt plate and treatment to release the thiolate ligands. Figure 2 A is a series of FTIR spectra of five different C6S Au MPC films after 0 (as-deposited), 1, 4, 24 and 48 h of exchange with mercaptoethanol (HOC2S). The peak around 3300 cm^{-1} corresponds to the OH stretch of the HOC2S ligand and the peak at approximately 2900 cm^{-1} corresponds to the asymmetric CH$_3$ stretch of the C6S ligand. It is a shoulder peak of the asymmetric CH$_2$ stretch. For quantitation, we measured the height of the OH peak and the CH$_3$ peak from the CH$_2$ stretch background (Figure S1). The FTIR spectra show that the OH stretch peak increased in intensity with exchange time while the CH$_3$ stretch intensity decreased, as expected for exchange of C6S ligands with HOC2S. Figure 2 B shows the corresponding NMR results of the same five samples of Figure 2 A after removal of the film from the KBr plate and iodine treatment. The peak at 0.81 ppm corresponds to the CH$_3$ protons of the C6S ligands and the peak at 2.67 ppm corresponds to the CH$_2$ protons next to the sulfur of C6S. These two peaks decreased with increasing exchange time as expected for loss of the C6S ligands. The peak at 2.85 ppm corresponds to the CH$_2$ protons adjacent to the S of HOC2S and the peak at 3.85 ppm corresponds to the CH$_2$ protons adjacent to the OH of HOC2S. These two peaks increased with increasing exchange time. The NMR shows that HOC2S ligands replace C6S ligands in the vapor phase, which is consistent with the FTIR, but more quantitative. We calculated the percentage of HOC2S based on the FTIR peak heights and integrated NMR peaks (2.85 vs 2.67), as a function of exchange
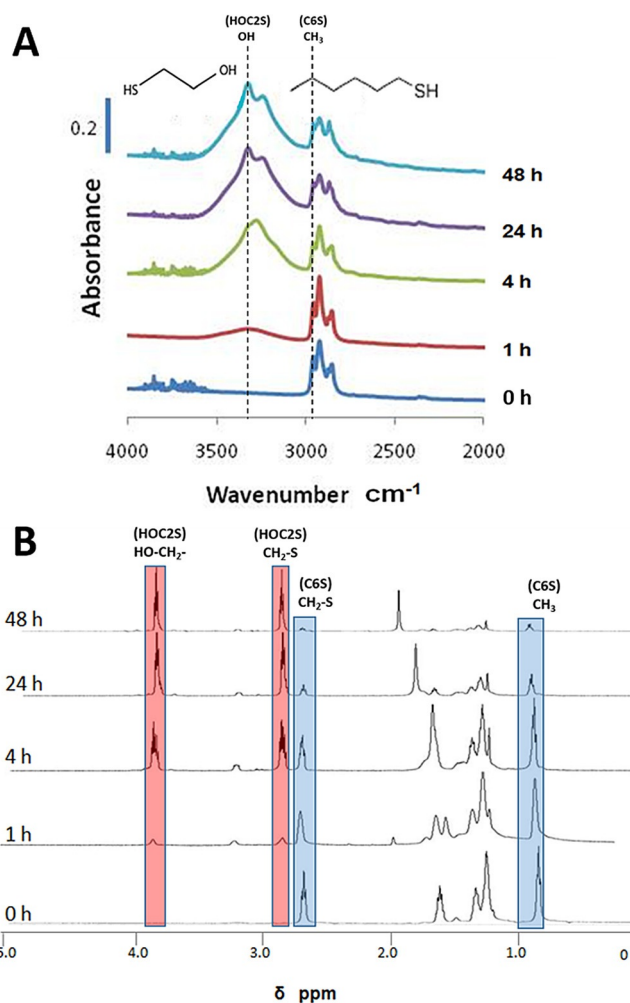

Figure 2. A) FTIR and B) NMR spectra of C6S films as a function of thiol vapor-phase exchange time from 0 to 48 h (bottom to top) with mercaptoethanol (HOC2S). The CH$_3$ peak for C6S and OH peak for HOC2S are indicated in the FTIR spectra. Peaks corresponding to HOC2S and C6S are marked in red and blue, respectively, in the NMR spectra. As expected, peaks corresponding to C6S decrease and those corresponding to HOC2S increase as the exchange proceeds.

time as shown in Figure 3. Both FTIR and NMR give a rough agreement. Based on the more accurate NMR results, the HOC2S ligands reach about 60% after 4 h of exchange and 80% and 90% after 1 and 2 days of exchange, respectively.

The comparison of FTIR to NMR shows that FTIR can be used as a rough estimate of the ligand percentage. We also monitored the exchange for three different samples by FTIR spectroscopy only. Two were performed on the same day and one on a different day. Figure S2 shows that the two samples prepared on the same day (labeled Day 1) were similar, but significantly different from a third sample treated the same but prepared on a different day (labeled Day 2). We attributed this to a possible difference in the film thickness on the two different days. In order to test this, we performed the vapor-phase thiol place-exchange reaction for 4 h on films with four different controlled relative thicknesses. The NMR spectra in Figure 4, labeled S1 to S4, are the results after exchange on the samples with four different relative thicknesses, where S1
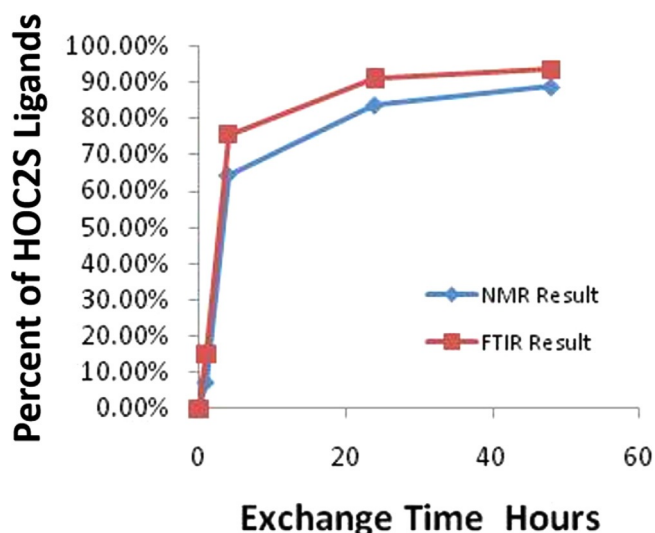
Figure 3. Percentage of HOC2S ligands in the MPC film relative to total ligands (HOC2S + C6S) as a function of vapor exchange time based on NMR and FTIR as indicated. Both methods showed fairly good agreement.
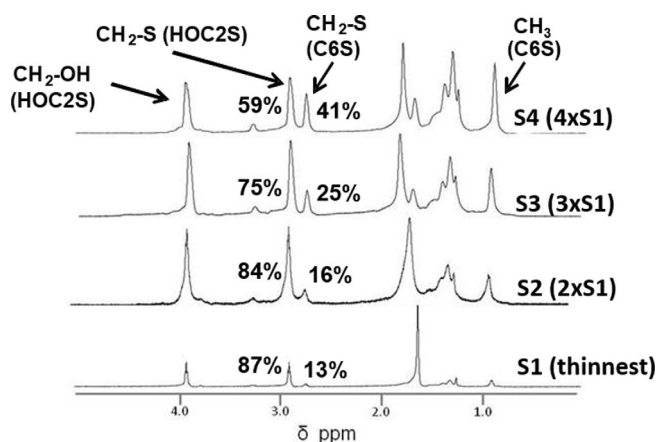

Figure 4. NMR spectra for four different C6S MPC films (S1–S4) of different thickness after a 4 h exchange with HOC2S. S2 is double the thickness of S1, S3 is triple the thickness of S1, and S4 is four times the thickness of S1. The percentage of HOC2S and C6S is shown for each sample based on the ratio of the peak areas for the CH_2 protons next to S for HOC2S (2.85 ppm) and CH_2 protons next to S for C6S (2.67 ppm). The S1 film thickness is estimated as 5–10 microns based on a 1.6 nm diameter Au core, cubic packing geometry, and interdigitation of the 1 nm C6S ligands surrounding the MPCs.

is the thinnest (5–10 microns), S2 is twice the thickness of S1 (10–20 microns), S3 is three times the thickness of S1 (15–30 microns), and S4 is four times the thickness of S1 (20–40 microns). As the thickness of the film increased, the percentage of HOC2S in the film decreased from 87% for S1 to 59% for S4. This is presumably due to some hindrance experienced by the HOC2S ligands to penetrate deep into the thicker films. The two thinnest films were similar (84% and 87%). A significant drop in % exchange did not occur until film S3 and thicker. These results show that good exchange reproducibility requires a similar film thickness during the vapor-phase place exchange and the thiol exchanges well into the film to a depth of about 30 microns within 4 h. It also shows that one can

reach a large exchange percent in 4 h for relatively thin films (5–20 microns). Other factors could also affect the exchange kinetics, such as film roughness, humidity, and extent of film dryness.

2.2. Chemiresistive Sensing Response to 2-Propanol and Toluene

Figure 5 shows two examples of chemiresistive sensing of 2-propanol (IPA) (blue line) and toluene (Tol) (red-dotted line) for a C6S Au MPC film exchanged with HOC2S ligands for different times. Figures 5 A–C show the sample after 0, 1.5, and 48 h vapor exchange, respectively. The arrows in Figure 5 A provide an example to show the time that the vapor was turned on and off. "On" (green arrow) corresponds to the 52% vapor in N_2 and "off" (red arrow) corresponds to 100% pure N_2. In the
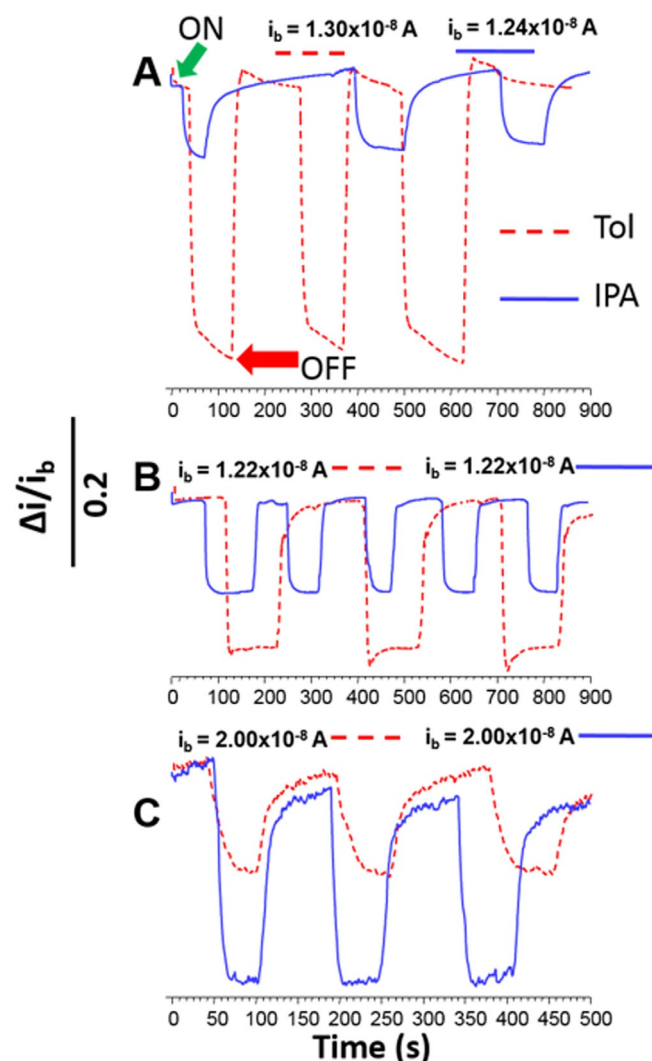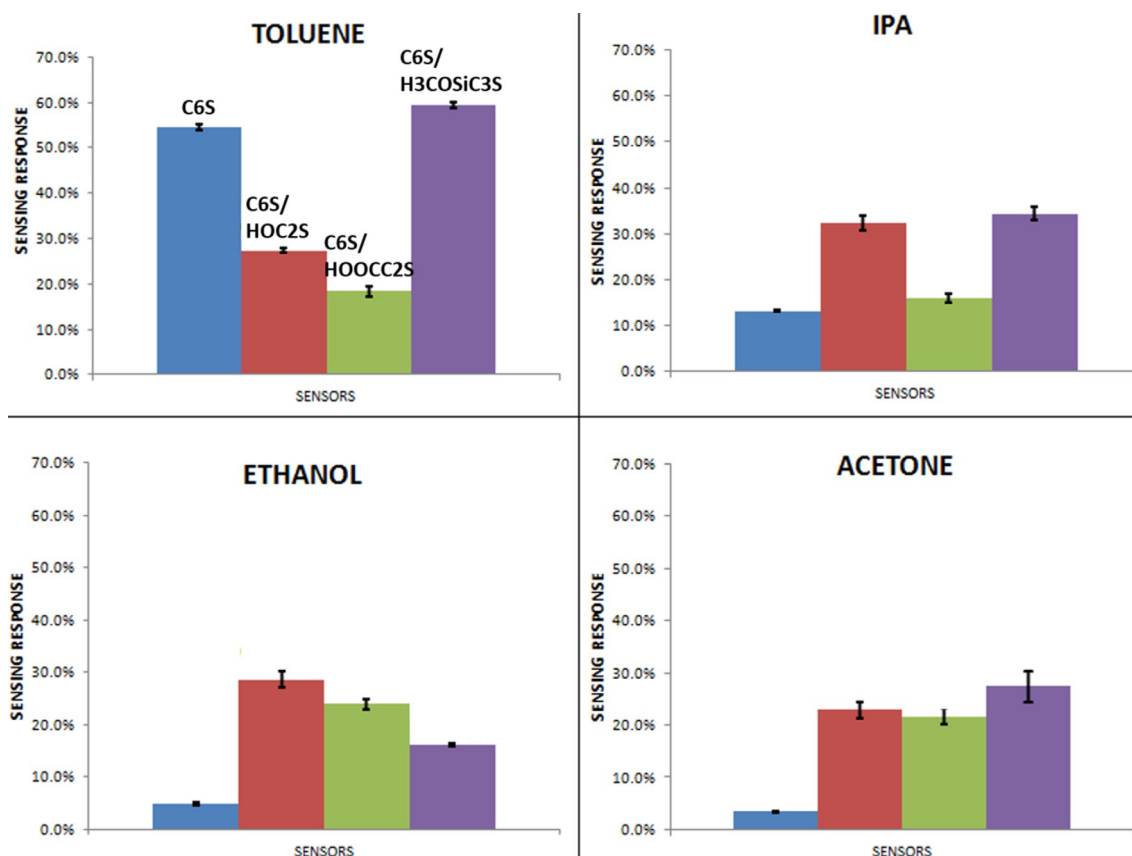

Figure 5. The chemiresistive sensing response of a film of C6S Au MPCs to 52% IPA and Tol after exchange with HOC2S for A) 0 h, B) 1.5 h, and C) 48 h. The ON and OFF arrows give an example showing when the sensor is exposed to the N_2 + Vapor (ON) and N_2 only (OFF). The sensor becomes more responsive to IPA as more HOC2S is exchanged into the film. The film should be approximately 24% exchanged in 1.5 h and 80–90% exchanged after 48 h.

presence of the vapor, the film of MPCs expands as the vapor molecules partition into the film, increasing the cluster-to-cluster distance[27] and reducing the film conductivity. The *y*-axis displays the change in current relative to the original baseline current divided by the baseline current. It is equivalent to the percent response of the device to the vapor-phase analyte. The scale bar of 0.2 is equal to a 20% response of the device, which is the relative change in conductivity in the presence of the vapor. Before HOC2S exchange, the relative current change was 10.1 ± 0.8% for IPA and 34.7 ± 0.8% for Tol, with a response ratio (response IPA/response Tol) of 0.29. The response was larger for the non-polar Tol relative to IPA because the film was non-polar with all C6S ligands. After 1.5 h of exchange, approximately 20% of the C6S ligands were replaced by HOC2S, leading to an increase in response to IPA of 12.3 ± 0.4% and decrease in response to Tol to 19.6 ± 0.4%, with a response ratio of 0.63. The response was still larger for toluene. After 48 h of exchange, 80–90% of C6S ligands were replaced by HOC2S, making the film more sensitive to hydrophilic vapors. In this case, the response to IPA was 26.9 ± 2.0%, which is larger than Tol at 13.7 ± 0.7%, giving a larger response ratio of 2.0. Table S1 in supporting information shows all of the device studied and their responses to 4% and 52% IPA and Tol along with their response ratio, or selectivity.

We also performed FTIR and chemiresistive sensing on films of C6S Au MPCs vapor-phase exchanged with mercaptopro-

pionic acid (HOOCC2S) and 3-mercaptopropyltrimethoxysilane (H3COSiC3S). Figure S3 shows a series of FTIR spectra after a 0 h exchange and vapor-phase exchange at different times up to 48 h and 30 h for H3COSiC3S and HOOCC2S, respectively. The plots indicate as the time of exchange increases the CH₃ stretching peak diminishes whereas the carbonyl peak increases for HOOCC2S and the Si—O peak increases for H3COSiC3S. Figure S4 shows a rough estimate of the percent exchange based on the FTIR peak heights of CH₃ relative to C=O and CH₃ relative to Si—O, which are likely not very accurate, but give the general trend. Figure S5 shows chemiresistive sensing plots generated by four different types of sensors, including the parent C6S Au MPCs and C6S Au MPCs exchanged for 24 h in the vapor phase with HOC2S, HOOCC2S, and H3COSiC3S, where all samples should have a high percentage of the new ligand (70–90%). The four films (C6S, C6S/HOC2S, C6S/HOOCC2S, and C6S/H3COSiC3S) were exposed to 52% concentrations of Tol, ethanol (EtOH), IPA, and acetone (ACT). They exhibited significantly different sensitivities to the different vapors depending on the affinity between the analyte vapor and the MPC functionalities. The response of the four devices to each vapor is displayed in Figure 6 in box plots. In general, the non-polar C6S Au MPCs responded more to non-polar vapors and the more polar C6S/HOC2S and C6S/HOOCC2S Au MPCs responded better to more polar vapors. The C6S/H3COSiC3S surprisingly responded well to Tol despite

Figure 6. The chemiresistive sensing response patterns to Tol, IPA, EtOH, and ACT vapors provided by the Au two electrode devices coated with films of C6S MPCs only and films of C6S/HOC2S, C6S/HOOCC2S, and C6S/H3COSiC3S Au MPCs prepared by thiol vapor exchange for 24 h (70–90% exchanging ligands). A unique signature results for the four different vapors, indicating that this simple exchange strategy could be useful for making chemiresistive-based electronic nose devices from these MPCs.

the polar Si—O bonds and was a bit unpredictable. It is clear that the response pattern of the four different devices is different for each analyte vapor. This could therefore be utilized to discriminate between the different analytes using the electronic nose concept.[3, 18] We did not perform principal component analysis or other pattern recognition analysis since the purpose of this paper is to simply show that vapor-phase thiol-exchange functionalization could be a useful method for altering the response of chemiresistors based on Au MPCs for electronic nose applications. H3COSiC3S exchange is a particularly good example in this work because it would not be possible to synthesize Au MPCs coated with this ligand in solution due to its crosslinking nature. Vapor-phase thiol exchange is a unique way to access this functionality in the Au MPC film.

3. Conclusions

We described the use of vapor-phase place-exchange to easily and quickly vary the functionality of Au MPC films, where the full synthesis of only one parent Au MPC is necessary, in this case C6S Au MPCs. FTIR and NMR spectroscopy of HOC2S exchange show that the reaction is effective, generally reaching 10–20 % within 1 h, 60 % after 4 h, and saturation around 80–90 % after 24 h. The rate and extent depends on film thickness, where the thinnest films displayed 84–87 % exchange after 4 h. Exchange with HOOCC2S and H3COSiC3S works equally well for functionalization. It would not be easy to functionalize C6S Au MPCs in solution with these short, volatile ligands due to their weakly passivating nature and strong hydrogen bonding or Si—O—Si cross-linking, which generally makes them insoluble in most solvents. The chemiresistive response of the parent film and exchanged films to Tol, IPA, EtOH, and ACT are distinctly different, allowing the possibility to discriminate between different vapor-phase analytes using sensor arrays and electronic nose concept, with vapor-phase thiol exchange as an easy method to provide a wide variety of functionalities.

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Keywords: Au nanoparticles · chemiresistors · electronic noses · thin films · sensors

[1] F. Biasioli, F. Gasperi, C. Yeretzian, T. D. Märk, *TrAC Trends Anal. Chem.* **2011**, *30*, 968.
[2] B. J. Finlayson-Pitts, J. N. Pitts Jr., *Science* **1997**, *276*, 1045.
[3] J. Yinon, *Anal. Chem.* **2003**, *75*, 98A.
[4] M. P. Martí, O. Busto, J. Guasch, R. Boqué, *TrAC Trends Anal. Chem.* **2005**, *24*, 57.
[5] O. Barash, N. Peled, F. R. Hirsch, H. Haick, *Small* **2009**, *5*, 2618.
[6] J. S. Cooper, B. Raguse, E. Chow, L. Hubble, K.-H. Müller, L. Wieczorek, *Anal. Chem.* **2010**, *82*, 3788.
[7] A. Díaz Aguilar, E. S. Forzani, M. Leright, F. Tsow, A. Cagan, R. A. Iglesias, L. A. Nagahara, I. Amlani, R. Tsui, N. J. Tao, *Nano Lett.* **2010**, *10*, 380.
[8] G. Peng, U. Tisch, O. Adams, M. Hakim, N. Shehada, Y. Y. Broza, S. Billan, R. Abdah-Bortnyak, A. Kuten, H. Haick, *Nat. Nanotechnol.* **2009**, *4*, 669.
[9] J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 5321.
[10] R. M. Crooks, A. J. Ricco, *Acc. Chem. Res.* **1998**, *31*, 219.
[11] J. W. Grate, *Chem. Rev.* **2000**, *100*, 2627.
[12] M. Sepaniak, P. Datskos, N. Lavrik, C. Tipple, *Anal. Chem.* **2002**, *74*, 568A.
[13] W. H. Steinecker, M. P. Rowe, E. T. Zellers, *Anal. Chem.* **2007**, *79*, 4977.
[14] M. C. Dalfovo, R. C. Salvarezza, F. J. Ibañez, *Anal. Chem.* **2012**, *84*, 4886.
[15] M. E. Franke, T. J. Koplin, U. Simon, *Small* **2006**, *2*, 36.
[16] B. J. Holliday, T. B. Stanford, T. M. Swager, *Chem. Mater.* **2006**, *18*, 5649.
[17] E. C. Walter, F. Favier, R. M. Penner, *Anal. Chem.* **2002**, *74*, 1546.
[18] D. J. Strike, M. G. H. Meijerink, M. Koudelka-Hep, *Fresenius J. Anal. Chem.* **1999**, *364*, 499.
[19] F. J. Ibañez, F. P. Zamborini, *Small* **2012**, *8*, 174.
[20] W. Zhao, T. Rovere, D. Weerawarne, G. Osterhoudt, N. Kang, P. Joseph, J. Luo, B. Shim, M. Poliks, C.-J. Zhong, *ACS Nano* **2015**, *9*, 6168.
[21] E. Chow, T. R. Gengenbach, L. Wieczorek, B. Raguse, *Sens. Actuators B* **2010**, *143*, 704.
[22] F. J. Ibañez, U. Gowrishetty, M. M. Crain, K. M. Walsh, F. P. Zamborini, *Anal. Chem.* **2006**, *78*, 753.
[23] F. J. Ibañez, F. P. Zamborini, *ACS Nano* **2008**, *2*, 1543.
[24] F. P. Zamborini, L. E. Smart, M. C. Leopold, R. W. Murray, *Anal. Chim. Acta* **2003**, *496*, 3.
[25] R. H. Terrill, T. A. Postlethwaite, C.-H. Chen, C.-D. Poon, A. Terzis, A. Chen, J. E. Hutchison, M. R. Clark, G. Wignall, J. D. Londono, R. Superfine, M. Falvo, C. S. Johnson Jr., E. T. Samulski, R. W. Murray, *J. Am. Chem. Soc.* **1995**, *117*, 12537.
[26] F. P. Zamborini, M. C. Leopold, J. F. Hicks, P. J. Kulesza, M. A. Malik, R. W. Murray, *J. Am. Chem. Soc.* **2002**, *124*, 8958.
[27] M. C. Dalfovo, L. J. Giovanetti, J. M. Ramallo-López, R. C. Salvarezza, F. G. Requejo, F. J. Ibañez, *J. Phys. Chem. C* **2015**, *119*, 5098.
[28] H. Wohltjen, A. W. Snow, *Anal. Chem.* **1998**, *70*, 2856.
[29] S. D. Evans, S. R. Johnson, Y. L. Cheng, T. Shen, *J. Mater. Chem.* **2000**, *10*, 183.
[30] H.-L. Zhang, S. D. Evans, J. R. Henderson, R. E. Miles, T.-H. Shen, *Nanotechnology* **2002**, *13*, 439.
[31] A. W. Snow, M. G. Ancona, D. Park, *Langmuir* **2012**, *28*, 15438.
[32] M. G. Ancona, A. W. Snow, F. K. Perkins, B. Pate, D. Park, *Sens. Actuators B* **2013**, *177*, 936.
[33] S. M. Briglin, T. Gao, N. S. Lewis, *Langmuir* **2004**, *20*, 299.
[34] E. E. Foos, A. W. Snow, M. E. Twigg, M. G. Ancona, *Chem. Mater.* **2002**, *14*, 2401.
[35] Y. J. Kim, Y. S. Yang, S.-C. Ha, S. M. Cho, Y. S. Kim, H. Y. Kim, H. Yang, Y. T. Kim, *Sens. Actuators B* **2005**, *106*, 189.
[36] M. P. Rowe, W. H. Steinecker, E. T. Zellers, *Anal. Chem.* **2007**, *79*, 1164.
[37] H. Ahn, A. Chandekar, B. Kang, C. Sung, J. E. Whitten, *Chem. Mater.* **2004**, *16*, 3274.
[38] E. García-Berríos, T. Gao, M. D. Woodka, S. Maldonado, B. S. Brunschwig, M. W. Ellsworth, N. S. Lewis, *J. Phys. Chem. C* **2010**, *114*, 21914.
[39] Y. Joseph, B. Guse, T. Vossmeyer, A. Yasuda, *J. Phys. Chem. C* **2008**, *112*, 12507.
[40] L. Han, X. Shi, W. Wu, F. L. Kirk, J. Luo, L. Wang, D. Mott, L. Cousineau, S. I.-I. Lim, S. Lu, C.-J. Zhong, *Sens. Actuators B* **2005**, *106*, 431.
[41] K. J. Albert, N. S. Lewis, C. L. Schauer, G. A. Sotzing, S. E. Stitzel, T. P. Vaid, D. R. Walt, *Chem. Rev.* **2000**, *100*, 2595.
[42] Q.-Y. Cai, E. T. Zellers, *Anal. Chem.* **2002**, *74*, 3533.
[43] M. J. Hostetler, A. C. Templeton, R. W. Murray, *Langmuir* **1999**, *15*, 3782.
[44] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* **1994**, 801.
[45] M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, *Langmuir* **1998**, *14*, 17.