Effect of the Dispersion Process and Nanoparticle Quality on Chemical Sensing Performance

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ABSTRACT: On the surface of chemiresistive films, the scarce heterogeneity of a molecularly capped gold nanoparticle (MCGNP) colloidal dispersion and uneven evaporation of the MCGNP-contained drying drop applied to this surface are among the main factors that affect reproducibility, and repeatable fabrication of thin films of MCGNPs. This article shows that an increase in reproducibility and repeatability is possible using a dispersant and a surfactant during the deposition and annealing processes of the MCGNP. The results show higher sensitivity and accuracy of the sensors for the detection of volatile organic compounds in air and an increased limit of detection. These simple and practical additions might serve as a launching pad for fabrication of other types of thin-film-based sensors.

INTRODUCTION

Sensing volatile organic compounds (VOCs) using chemical sensors based on thin films of molecularly capped metallic nanoparticles (MCNPs) is a powerful potential technology that can be used in disease diagnosis, monitoring of outdoor and indoor air, and for the quality control of food products. There are many reasons why it is advantageous to design chemical assays around these nanomaterials, but there are three that are noteworthy here: (1) the versatility of the composition of the nanomaterial itself, (2) the ability to vary the nanomaterial size and/or shape and, therefore, the surface-to-volume ratio, and (3) the ability to prepare films of nanomaterials that have controllable porous properties, controllable mass transport (e.g., via diffusion), and controllable permittivity of the film.

The production of MCNP-based chemiresistors starts with the synthesis of nanoparticles with specific organic ligands, using two-phase, one-phase, and water-soluble approaches. This is followed by the assembly of thin films made of MCNPs between adjacent microelectrodes. There are several deposition methods on microelectrodes such as drop-casting, layer-by-layer deposition, spin coating, spraying, etc. However, most fabrication techniques lack reproducibility and repeatability mainly due to the uneven evaporation of the MCNP-contained drying drop applied on the surface. This phenomenon occurs despite strict control over the printing volume, particle size, temperature, relative humidity, and the surrounding gas atmosphere. The uneven evaporation forms coffee ring-like structures characterized by above average particle density inside the ring and a lesser amount of particles at the center of the surface of interest.

One approach for reducing the percentage of irregularity in the sensing film relies on the addition of a dipolar aprotic and high-boiling-point solvent to the water-based MCNP solution. This approach reduces the pinning effect of the contact line with the substrate and therefore the irregularities. However, water-based solutions are less suitable in the production of functioning MCNP-based chemiresistors. Other studies have shown that the addition of surfactants and different organic solvents with different vapor pressures to the MCNP solution and the application of electrowetting or surface acoustic waves, can lead to the production of fully homogeneous disk-shaped patterns. Still, the cost efficiency of sensing films using these approaches remains relatively low.

Here, we describe a method of increasing the stability and reproducibility of the chemical sensors based on molecularly capped gold nanoparticles (MCGNPs), by utilizing a dispersant and a surfactant for the deposition of ligand-capped GNP and removing them afterward. The sensor’s performance was measured via exposure to different pure VOCs and compared with sensors produced in the standard method. The validity of the fabrication steps was further confirmed using...
attenuated total reflectance (ATR) and scanning electron microscopy (SEM). The sensor performance was further enhanced using bromide instead of more commonly used chloride as the precursor for MCGNP synthesis since it produces higher yields of MCGNPs without the agglomerated byproducts. This finding was confirmed using transmission electron microscopy (TEM). The two processes were combined to provide a tunable sensor with superior properties.

**METHODS**

**Sensor Synthesis and Fabrication.** tert-Dodecanethiol (Sigma-Aldrich, 25103-58-6)-capped nanoparticles were synthesized using a modified Brust method with either HAuCl₄·3H₂O (Sigma-Aldrich, 16961-25-4) or NaAuBr₄·2H₂O (Alfa Aesar, 10378-49-1) as a precursor. Nanoparticles in toluene were mixed with 0.05% Byk-3760 (BYK Chemie GmbH) and 1% Solspere 75000 (Lubrizol) in an open glass chamber inside a hood. The sensors were submerged in a washing solution (50% v/v ethyl acetate:ethanol) and drop-casted (0.4ul) on a microelectronic transducer that consisted of circular interdigitated gold electrodes deposited by an anodic oxidation horizontal process (4 and 5) were repeated with the number of concentations that were needed. The applied voltage for each sensor was 5 V.

**Feature Extraction of Sensor Array Data.** The output of the gas exposure system was a vector of the resistance change for each sensor (a maximum of 40 sensors can be measured at once in the chamber). Using this output, we extracted one representative feature, which was the difference between the middle of the response step and the vacuum baseline before the response, divided by the baseline. Several exposure tests were performed in the same experiment, and therefore, several values of the features were extracted for every exposure.

**Sensor Imaging.** Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were outsourced and done at the Technion Center for Electron Microscopy and Soft Matter. TEM was performed with an FEI Talos 200 kV TEM with a Schottky FEG electron source. SEM was performed by a Zeiss Ultra Plus high-resolution SEM equipped with a field emission gun. Micrographs were taken at a low acceleration voltage of 1 kV and a working distance of 5 mm.

**RESULTS AND DISCUSSION**

**Experimental Design Scheme.** MCGNPs were synthesized using gold precursors (HAuCl₄·3H₂O or NaAuBr₄·2H₂O, Figure 1) by the Brust method. After synthesis, MCGNPs were mixed with additives and manually drop-casted onto an electrode surface to form a sensor. Finalization of the sensor was achieved after additive removal via a washout procedure and subsequent annealing. Sensor and MCGNP characterization was performed using SEM, ATR, and TEM analysis as well as pure-gas exposure tests.

**Surface Characterization of Additive-Supplemented HAuCl₄·3H₂O-Based MCGNP Films.** Each step of the fabrication process was monitored by SEM and ATR. SEM analysis reveals that drop-casting of MCGNPs on top of the electrode surface results in MCGNP congestion and the formation of coffee ring structures at the naïve drop periphery (Figure 2a). This nonuniformity on the sensor surface had been previously suggested to result in low reproducibility. On the other hand, these coffee ring structures were absent in the additive-supported sensor, which showed improved dispersion on the electrode surface where spheres...
cover the entire field of view (Figure 2b). This dispersion pattern was still present after washing, although fewer spheres are visible, explained by partial particle removal due to the washing step (Figure 2c). Preannealing, the MCGNPs are visible as small spheres (single or grouped nanoparticles), and after solvent vapor annealing (SVA), the spheres form a connected network that looks like a “smeared paste” on top of the electrode surface (Figure 2d). This is consistent with the SVA phenomena previously described in the literature.42

ATR can identify the chemical bonds of interest and therefore was used in this study to confirm the additive removal and the MCGNP ligand integrity. Naïve or additive-supplemented MCGNPs drop-cast on a cleaned silicon wafer confirmed the correct identification of the thiocarboxyl ligand, which is marked with a red arrow at approximately 2900 nm (Figure 3). This band was not visible in an additive-only-containing silicon wafer (Figure 3c) when compared with an MCGNP-containing silicon wafer (Figure 3a,b). In addition, two more visible bands are seen at values below 2900 nm. However, they are seen even when MCGNPs or additives are not present and therefore are not relevant either (Figure 3a–c). The ligand is still visible even after the MCGNP-containing silicon wafer is submerged in a washing solution for 2 h and subsequently annealed (Figure 3d,e), indicating that the ligand is undamaged and sufficient particles are still present on the surface. Additive removal was confirmed by identifying the additive-relevant bands at the 1300–1700 nm range. The composition is unknown of the patent-protected additives, so we searched for bands that are mutual in an additive-containing silicon wafer but absent when additives are absent (Figure 3f, red and green lines versus black line). Detection of materials in these wavelengths indicated that additives are present on the silicon surface. Indeed, we failed to obtain a signal at those wavelengths after washing or annealing (Figure 3f, purple and blue lines, respectively), suggesting full removal of the additives.

Controlled MCGNP Synthesis Using NaAuBr₄·2H₂O. Recently, Booth et al. showed that MCGNPs synthesized through the Brust method using HAuCl₄·3H₂O have a tendency to form an unstable active gold component that results in the formation of agglomerates during the synthesis step.40 These agglomerates are composed of thousands or perhaps millions of individual nanoparticles. Agglomeration results in two individually sized MCGNP populations. A sensor composed of such MCGNPs is expected to be faulty or with a reduced shelf life at best. The inability to control large particle positions on the sensing layer can result in sensor variability. In addition, large particle localization can influence the electron transport via reduced output,47 and agglomerated particles can be vulnerable to humidity, oxidation, heat, and other environmental cues. Particle agglomeration also increases the sensor recovery time.46,48 With this in mind, we have used NaAuBr₄·2H₂O as a precursor for MCGNP synthesis,47 to avoid agglomeration. Confirmation of the results was visually obtained with TEM analysis (Figure 4a,b), which showed lack of agglomeration in NaAuBr₄·2H₂O and the existence of agglomeration in HAuCl₄·3H₂O-based solutions. Specifically, nonagglomerated particles appear as single particles with no halo (Figure 4a). Meanwhile, agglomerated particles form a halo around them due to their size when injected on the TEM carbon membrane (Figure 4b). Switching the precursor to bromide from chloride has no detrimental effect on the particle diameter as shown via particle size histograms (Figure 4c,d).

Sensor Fabrication of Additive-Supplemented HAuCl₄·3H₂O-Based MCGNPs. This method produces drop-casted thin-film MCGNPs where coffee ring formation is inhibited. This method allows improved cover utilization of the electrode surface. This improved cover yields a sensor with reproducible performance when exposed to gas (Figure 5a,b showing five replicate sensors, each marked by a different color). Reproducibility was demonstrated with the sensor signals almost situated on top of each other (Figure 5a,b), which produced features with low standard deviation when exposed to p-xylene at different concentrations (Figure 5d). Furthermore, the signal produced is “clean” with a high signal to noise ratio when exposed to a pure gas such as hexanol at 0–80 ppm (Figure 5a) or 1,2,4-trimethylbenzene (TMB) at 0–80 ppm (Figure 5b) or p-xylene at 20 ppm (Figure 5c). The sensor performance can be attributed to the annealing step stabilizing the MCGNPs on the electrode surface forming thermodynamically favorable interactions (Figure 2d versus Figure 2b).42 On the other hand, the lack of additive usage in the fabrication results in a nonhomogeneous electrode MCGNP cover and coffee ring formation. When exposed, such sensors produce a noisy signal output (Figure 6a,b), demonstrating a low signal to noise ratio. Sensors produced in this manner are nonreproducible due to the uncontrolled particle deposition on the electrode surface and suffer from low performance. Specifically, such sensors cannot discriminate between different concentrations of a hexanol pure gas at 40 ppm versus 20 ppm (Figure 6a) or a TMB pure gas at 80 ppm versus 40 ppm (Figure 6b). They also cannot discriminate between a hexanol pure gas and a TMB pure gas since at 20 ppm, they provide a similar delta in resistance (Figure 6a,b). It was found that the addition of additives without their removal results in increased resistance changes when exposed to gas. However, this produces additional noise (Figure 6c) resulting in high sensor variance within batches and prevents reproducibility. This is demonstrated by features extracted...
from such sensors with high standard deviation when exposed to \( p \)-xylene (Figure 6d). To be noted, the inversion of the response in both Figures 5d and 6d was investigated in a previous study by Tisch and Haick.\(^{23}\) To further support this technique, we have synthesized MCGNPs with different capping agents (i.e., different ligands) and exposed the fabricated sensors to TMB and hexanol in different concentrations obtaining the same clean and reproducible signal (see Supporting Information, Figure S2 and Table S1).

The link between the improved cover of the nanoparticle dispersion on sensor signal reproducibility can be explained by the electron transfer on the electrode surface during exposure. Naturally, electrical current will pass through the least resistive route. The coffering milieu is a high-density environment of particles, and therefore, the resistance throughout the coffering structure is smaller than the resistance in other parts of the electrode that are less occupied by nanoparticles, where the interparticle distance is enlarged and substantially more affected by the particles’ ligand to ligand orientation. In essence, electrical current in coffee ring-containing devices is more prone to signal instability. Comparably, in higher-percolation thin films, the electrical current can move through various routes (similar to electrons passing from the anode to the cathode), and the complete electrode surface is efficiently utilized.\(^{23,50,51}\) This is shown macroscopically in Figure S3 in the Supporting Information where the coffee ring can be seen in the naïve sensors, whereas it is nonvisible in the additive-supported sensors. This figure also shows the reproducibility of the latter over the former where the density in the coffee ring compared with the center is hard to control.

**Fabrication of a NaAuBr\(_4\)·2H\(_2\)O-Based Tunable MCGNP Sensor with Desired Characteristics.** The use of the above-described additives for fabrication of a thin-layer MCGNP and the combination with the improved MCGNP synthesis protocol produced a tunable sensor. By modifying the particle ligand ratio, it was shown that the intrinsic sensing characteristics of these particles can be tailor-made and controlled. A sensor synthesized with a 0.5 S:Au ratio can discriminate a pure gas in 20 ppm concentration intervals, while a 1.5 ratio results in inaccurate measurements. This can be seen on the response curve (Figure 7a) and the feature values with variance in Figure 7bc, respectively. Lowering the ligand:gold ratio formed sensors with significantly lower baseline resistance (indicating that a lower interparticle spacing due to a reduced particle ligand cover is the dominant force and not the increased particle size\(^ {52}\)). Thus, the 0.5 S:Au ratio sensor with superior performance could be the result of flexible ligand orientation and mobility.\(^ {53}\) Either way, NaAuBr\(_4\)·2H\(_2\)O-
based MCGNPs offer advantages in the form of a homogeneous size and shape of these particles resulting in a sensor that is more efficient in electron transfer and possibly resistant to environmental insults (due to particle redundancy\textsuperscript{44} or reduced organic layer thickness).

### SUMMARY AND CONCLUSIONS

Most laboratory work that develops new sensors and the surrounding work encounter difficulties such as the irreproducibility of sensor performance, often leading to biased results, faulty conclusions, and wastage of raw materials. The sensors presented in this report are easily reproduced, and the surfactants used are simple to remove, guaranteeing pure, direct interactions of the target analyte with the MCGNPs. The results suggest that sensors produced via this method have an increased limit of detection, differentiation, and stability quality. The fabrication method is specifically aimed for laboratory research purposes but can be quickly adapted to...
scaled-up production of such sensors. The described method can also be adapted to produce other thiol ligand and metal-based nanoparticles on rigid or flexible surfaces.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01668.

Figure S1) Magnification of Figure 2d, (Figure S2) sensors produced via the described method using different ligands, (Table S1) detailed identification of the additional ligands used, and (Figure S3) macroscopic visualization of the electrode surface postnanoparticle casting (PDF)

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**Notes**

The authors declare no competing financial interest.
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