Sensitive Detection of Elemental Mercury Vapor by **Gold-Nanoparticle-Decorated Carbon Nanotube Sensors**

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Low-cost, low-power consumption gas sensors that can detect or quantify various gas analytes are of increasing interest for various applications ranging from mobile health to environmental exposure assessment and homeland security. In particular, miniature gas sensors based on nanomaterials that can be manufactured in the form of sensor arrays present great potential for the development of portable monitoring devices. In this study, we demonstrate that a chemiresistive nanosensor comprised of single-walled carbon nanotubes decorated with gold nanoparticles has impressive sensitivity to elemental mercury (Hg) gas concentrations, with a lower detection limit as low as 2 ppby. Furthermore, this nanosensor was found to self-regenerate, though slowly, without any external inputs. Finally, the mercury vapor sensing mechanism allowed for direct investigations into the origin of surface-enhanced Raman scattering in carbon nanotubes decorated with Au nanoparticles.

INTRODUCTION

Elemental mercury (Hg) is a hazardous material known to affect the lungs and kidneys as well as the central and peripheral nervous system.¹ The current personal exposure limit (PEL) for Hg as set by The United States Occupational Safety and Health Administration² is 0.1 mg/m³ (~ 11 ppb_v in air), whereas the World Health Organization³ has set their threshold exposure limit at half that value $(0.05 \text{ mg/m}^3 \text{ or } 5.6 \text{ ppb}_v \text{ in air})$. Hg exposure can originate from a large variety of sources including natural degassing of the Earth's crust,³ which causes Hg diffusion into the air, water, and soil as well as onto vegetation.⁴ Furthermore, Hg is still used in a variety of industrial applications including the manufacturing of some batteries, switches, and fluorescent tubes.⁴ As such, it is not surprising to find that Hg concentrations can vary depending on both the time and place of detection.⁵ Accordingly, there is a strong need for the development of personal Hg detection systems that are highly sensitive, portable, and durable.

Thus far, producing a sensor having all of these characteristics has been met with limited success. Many sensing systems encounter problems with portability,^{6,7} whereas others suffer from limited sensitivity.^{6,8} However, progress incorporating various nanomaterials into sensing platforms has fostered much hope for developing a variety of highly sensitive chemical sensors that are small and light and thus highly portable.9-14 Despite this encouraging progress, a Hg nanosensor embodying all of the desirable characteristics has yet to be demonstrated. Most current Hg sensors are plagued by the need for regeneration steps which often require high energy input and make it impractical for certain applications.^{8,15}

This work investigates the potential of single-walled carbon nanotubes (SWNTs) functionalized with gold (Au) nanoparticles for achieving a small, light, sensitive, and simple Hg sensor (Figure 1). The sensors described here were found to be extremely sensitive to low concentrations of Hg. In addition, it was discovered that no regeneration steps were necessary to recover this type of sensor; in all cases these sensors fully returned to their baseline resistance after exposure was complete. Interestingly, the structure of this nanosensor also makes it ideal for studying the

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A)



Figure 1. Schematic representation (A) and SEM images (B and C) of the sensor setup used in this study. As evidenced in parts B and C, the Au nanoparticles are deposited in a discontinuous manner. As a result conduction occurs through the SWNTs. The figure also shows that larger deposition charges (100 μ C in Figure 1C vs 5 μ C in 1B) results in larger Au nanoparticles being deposited on each SWNT. (Note: all scale bars are 2 μ m.).

mechanism of the surface-enhanced Raman scattering (SERS) effect. SERS is a valuable tool often used to enhance the intensities of otherwise weak Raman transitions. In the case of SWNTs, SERS can be used to observe every SWNT in a sample during Raman investigations.¹⁴ However, the exact mechanism of SERS is still a matter of debate. Many believe that the enhancement originates from a resonance coupling between the Raman active transitions in the SWNT and the plasmonic resonance of the species used to produce the enhancement.^{16,17} Others believe that the enhancement is a result of charge donation/chemical doping from the enhancing species to the Raman active materials (SWNTs).^{18,19} In this nanosensor system, SWNTs are decorated with Au nanoparticles which have been well established as capable of producing SERS in SWNTs.^{16,20} As will be discussed later, upon exposure to Hg, the Au nanoparticle donates electron density to the SWNTs, making Hg detection possible by simple resistance (R) measurements. Therefore, these Au nanoparticles can be utilized both to sense analytes and to investigate the true mechanism of SERS.

EXPERIMENTAL METHODS

Nanosensor synthesis followed a procedure previously described elsewhere.^{21,22} Briefly, 1.5 μ L of a SWNT suspension was drop-casted on the 3 μ m gap of microfabricated source and drain Au/Cr electrodes on a SiO_x/Si wafer. SWNTs were then aligned between these electrodes by applying 1 V_{pp} and 4 MHz (Keithley 3390 AC generator, 50 MHz arbitrary waveform generator). The sensor resistance was controlled by the alignment time. We utilized the sensor architecture as the functionalization cell, where the gold pads and SWNTs networks served as the working electrodes, a Pt wire as the counter electrode and a chlorinated Ag/AgCl wire as the reference electrode. Deposition of gold nanocatalysts was performed by using a commercially available ready to use electroplating electrolyte from Technic Inc. (CA), with neutral pH. A 5- μ L drop of the Au plating solution was

placed across the two electrodes completely covering the Au pads and SWNT networks, and a potential of -1.0 V vs pseudo Ag/AgCl was applied. Deposition was terminated by controlling the charge passed through the system from 0.5 to 500 μ C, which in turn determined the size and density of Au nanoparticles.^{21,22} Following nanoparticle deposition, the device was rinsed with nanopure water to remove any residual salt or impurities that could affect the device performance.

The morphology, size, and density of nanoparticle were analyzed using scanning electron microscopy (SEM) working at \sim 2 kV acceleration voltage. After SEM imaging, devices were wirebonded to a converter circuit board from ePBoards for ease and throughput of testing. These devices were then placed inside a 2 L polypropylene container with mounted inlet and exhaust lines. Hg exposure was accomplished as follows: UHP grade air (National Welders) was used to flush the exposure chamber for approximately 24 h or until a stable baseline resistance was achieved. After this period, a small metered stream of UHP air was passed through a 40-mL glass vial containing 5 mL of Hg. This flow displaced a concentrated Hg vapor which was then mixed with 200 sccm of UHP air prior to being directed to the exposure chamber. The resulting concentration of Hg inside the exposure chamber could therefore be varied simply by changing the flow rate of air to the Hg container (typically between 5 and 50 sccm). The actual Hg concentrations were determined using a digital Hg meter (Jerome J405, Arizona Instruments). Upon exposure, resistance measurements were taken at a rate of 6 data points/min using a custom built DAQ consisting of Field Point hardware and Labview software (both from National Instruments).^{12,21,22} Raman measurements were taken immediately after a 24 h exposure to saturated Hg vapor (\gg 10 ppm) using a Horiba Jobin Yvon LabRam ARAMIS Spectrometer operating at 633 nm. Resulting spectra were derived by averaging at least 30 spectra from at least 6 different sensors before and after Hg exposure. SWNT radial breathing mode (RBM) peaks were normalized to the Si peak (\sim 300 cm⁻¹) so as to accurately compare spectra before and after Hg exposure.

RESULTS AND DISCUSSION

Figure 1 displays both an artistic depiction (A) and SEM images (B and C) of the sensor setup used herein. Since Au deposits are discontinuous, conduction occurs through the SWNTs, and the overall behavior of the SWNT–Au nanostruc-tures is that of a semiconductor.^{21,22} Because these SWNTs have been exposed to air, and thus have absorbed O₂, they act as p-type semiconductors.²³ This means that their primary charge carriers are holes. The sensitivity of the hybrid nanostructure sensor to Hg will be governed by how Hg absorption into the Au nanoparticles will affect the relationship between the Au nanoparticle and the SWNT. Specifically, sensitivity will be dictated by how the Hg absorption affects the population of holes in the SWNTs. This could be accomplished by facilitating either electron donation or drainage in the SWNTs. If electrons are drained, the number of holes in the SWNT will increase. Alternatively, this drainage would effectively reduce the size of hole scattering regions at the sites of the nanoparticle/SWNT interface. Either mechanism would effectively decrease the resistance of the SWNT-Au system. As a corollary, if Hg absorption into the Au nanoparticle facilitates its donation of electrons to the SWNTs, this would decrease the number of available charge carriers (holes) or increase the size of hole scattering regions. Ultimately, this would manifest itself as an increase in electrical resistance. As can be seen



Figure 2. The real-time nanosensor relative responses to Hg vapor exposure at concentrations varying from 2 to 100 ppb_v as indicated. Direct responses are seen over the entire range of concentrations tested. The most consistent and impressive sensitivities are achieved from the sensors made using the highest depositions charges (100 and 500 μ C). Furthermore, after exposure is terminated, the sensors return to baseline resistance without any recovery steps.



Figure 3. Sensor relative response $[(R - R_0)/R_0]$ vs mercury vapor concentration. The sensor responses increase with the concentrations of mercury vapor. The consistency of these results is best for nanosensors made with the largest deposition charges implemented in this study (100 and 500 μ C). Similarly, the largest responses come from these sensors made from the largest depositions charges, and therefore those with the largest Au nanoparticles.

from Figure 2, exposure to Hg resulted in an increase in resistance in the SWNT—Au based sensors. This indicates that Hg absorption into the Au nanoparticle facilitates electron donation to the SWNT system. It should be noted that, while some change in resistance is observed in the case of undecorated SWNT sensors (sensor 4, Figures 2 and 3), this is negligible compared to the change in resistance observed for Au nanoparticle decorated SWNT sensors (Figures 2 and 3). The change in resistance in undecorated SWNT sensors primarily results from both adsorption of Hg onto SWNT as well as from changes in the contact resistance between the SWNT and Au electrodes as the electrodes absorb Hg. Therefore, it can be deduced that the largest contribution to the change in resistance results from Hg absorption by Au nanoparticles on the SWNT.

It was also observed that the change in resistance was proportional to the size and number of deposited Au nanoparticles and



Figure 4. Exposure of sensors made using $500 \,\mu$ C deposition charges to 1 ppm_v of SO₂, NH₃, and NO₂ did not register a significant sensor response when compared to the response to the much lower Hg concentration of 2 ppb_v. The sensor response to 500 ppb_v H₂S was only comparable to the sensor response at significantly lower Hg concentrations of 30 and 100 ppb_v.

therefore to deposition charge. From SEM images taken of four samples, the average particle size increased linearly from 18.3 \pm 6.2 nm to 139 \pm 39 nm with increasing applied charges of 1 to 500 μ C. The effect of size and density of the Au nanoparticles on the sensory response is obvious both in Figure 2, which displays the real-time response of selected nanosensors to Hg exposure, as well as in Figure 3, which displays the relative change in resistance vs the concentration of Hg. This trend results from the fact that as the diameter of the nanoparticle increases, so does the available surface area and the coverage of the SWNTs by Au deposits. Increasing the surface area as well as the amount of Au present increases the amount of Hg able to be absorbed by the nanoparticle. Therefore, increasing the size of the nanoparticle would increase the amount of Hg absorbed and ultimately the amount of charge transfer between the nanoparticle and the SWNT. Similarly, increasing the amount of Hg during exposure trials should increase the change in resistance. This trend is generally seen in Figures 2 and 3; however, two points should be discussed. First, the trend of increased change in resistance with increasing Hg concentration is not linear. Notably, the change in resistance is marginal at Hg concentrations ranging from 30 to 100 ppb_v. This may be due to a saturation event in the Au nanoparticles, as was observed with similar sensors probing different analytes.^{12,21,22} The second point to be made is that, along with sensitivity, consistency between sensors increases with Au nanoparticle particle number and size (i.e., deposition charge). In the case of sensors formed using smaller deposition charges (i.e., $1 \mu C$), the change in resistance is not as dependably dictated by the Hg concentration, as in larger deposition charge derived sensors (Figure 2 and 3). Ultimately, the most sensitive and consistent results come from sensors formed from larger depositions charges; specifically, the best results presented in this study come from sensors formed using 100 and 500 μ C depositions charges. (Figure 3)

For a sensor to be highly applicable, it must be specific for a small group of analytes if not for a single analyte. To test the specificity of this nanosensor, it was exposed to high concentration of some other common analytes: H_2S , SO_2 , NH_3 , and NO_2 . As can be seen from Figure 4, exposure to even 1 ppm_v of SO_2 , NH_3 , and NO_2 did not render a significant sensor response when compared to the response to 2 ppb_v of Hg. Despite this specificity, a noteworthy response to H_2S was observed at an analyte concentration of



Figure 5. Raman spectra (radial breathing mode) of virgin and Hgloaded nanosensors. Only very small increases in the intensity of the SWNT peaks at ~110 and 155 cm⁻¹, (corresponding to SWNT d = 2.25 and 1.6 nm, respectively) are noticeable. However, the intensity of the SWNT peak at ~175 cm⁻¹ (d = 1.42 nm) is actually larger before exposure to Hg. As such, no consistent increase in SERS is evident after exposure to Hg. Therefore, it appears that plasmonic resonance coupling rather than charge transfer is the primary mechanism of enhancement in the SERS of Au nanoparticle decorated SWNT systems. It should be noted that the peak ~320 cm⁻¹ arises as a result of scattering from two transverse phonons of crystalline silicon.²⁴

 500 ppb_{v} , which is consistent with previous results.²² However, this response was comparable to the sensor response at significantly lower Hg concentrations of 30 and 100 ppb_v.

Another key aspect which makes this nanosensor attractive for potential field application can be seen in Figure 2. Even after exposure to relatively large Hg concentrations, in most cases these sensors recovered back to their original baselines without any additional recovery steps, such as baking. It is a significant advantage that, by simply stopping Hg exposure, this system can self-regenerate without external intervention.

As was mentioned previously, the structure and sensing mechanism of this nanosensor makes it well suited to address the debate over the primary cause of SERS. In the case of Au nanoparticles enhancing the spectra of SWNTs, some believe that the SERS results from a charge transfer from the Au nanoparticle to the SWNT; others believe that it results from plasmon resonance between the Au nanoparticle and the SWNT. Since the mechanism of Hg sensing involves charge donation from the Au nanoparticles to the SWNTs, we know that charge transfer is facilitated by Hg absorption. Therefore, if the mechanism of SERS relies primarily on a charge transfer between the Au nanoparticle and the SWNT, Hg absorption should further enhance the intensity of the Raman spectra in these samples. However, Raman investigations show no real increased enhancement in samples with absorbed Hg. As is evident from Figure 5, only very small increases in the intensity of the SWNT peaks at $\sim \! 110$ and 155 cm⁻¹ (SWNT diameters = 2.25 and 1.6 nm, respectively, according to the relation $d = 248/\omega_{\text{RBM}}$ for carbon nanotubes on a surface¹⁶) are noticeable. However, the intensity of the SWNT peak at ~ 175 cm⁻¹ (SWNT d = 1.42 nm) is actually larger before exposure to Hg. As such, no consistent increase in SERS is evident after exposure to Hg. Therefore, it appears that charge transfer is not the primary mechanism of enhancement in SERS. It then stands to reason that the likely primary mechanism for SERS is the plasmonic resonance coupling of the Au nanoparticle with the SWNTs. More direct investigations into plasmon induced SERS

still need to be conducted. However, this work strongly suggests that charge transfer is not the dominant mechanism in the SERS of Au nanoparticle—SWNT systems.

CONCLUSIONS

In this paper, a Hg nanosensor capable of sensing Hg vapor concentrations down to ~2 ppb_v is described. Besides being extremely sensitive, because of its nanostructured components, it is highly portable, simple to make, and expected to be easy to integrate with conventional electronics. Furthermore, it requires no additional regeneration steps to recover its baseline resistance after exposure. Its structure was also ideal for probing the true mechanism of SERS, particularly in SWNT systems. It was found that no enhancement in SERS was observed despite direct evidence of charge transfer from the Au nanoparticles to the SWNTs. Therefore, it appears that the most likely origin of SERS primarily stems from plasmonic coupling between the Au nanoparticle and the SWNT.

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