Supporting Information

A Zero-Power Optical, ppt- to ppm-Level Toxic Gas and Vapor Sensor with Image, Text and Analytical Capabilities

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Contents Page

Section S1. The Occupational Safety and Health Administration (OSHA) regulations

The Occupational Safety and Health Administration (OSHA) from the United States Department of Labor defines the threshold of exposure from temporary injury to dangerous exposure, including the action level, the ceiling limit that a worker should not exceed, the short-term exposure limit, as well as a time-weighted average.

Table S1 summarizes the short-term at low- and high-level exposures to Cl_2 gas consequences on the health and safety without any protective equipment. Additionally, OSHA defined the workplace short-term exposure limit at 1 ppm for up to 15-minute exposures and the long-term exposure limit at 0.5 ppm for an up to 6-hour period. Regarding these regulations, it appears critical to monitor residual contamination from an emergency event that could potentially affect workers in a long-term period.

Table S1. Cl_2 gas inhalation levels and symptoms. Consequences for health and safety at low- and high-level exposure to Cl_2 gas (gathered from White and Martin).[S1]

Low-level Exposures (ppm)	
0.1 – 0.3	Odor detection
1.0 – 3.0	Mild mucus membrane irritation; can be tolerated for about 1h
5.0 – 15	Moderate mucus membrane irritation
30 and above	Immediate substernal chest pain; rapid onset of respiratory distress
40 – 60	Potential development of toxic pneumotitis and/or acute pulmonary edema
High-level Exposures (ppm)	
400	Lethal over 30 min
1000 and above	Fatalities ensues within few minutes

Section S2. Nanoparticle Synthesis

Synthesis:

Dodecanethiol-capped gold nanoparticles: A magnetic stir bar was placed in a two neck round bottom flask and the spin rate of the stir bar set to 350 rpm. Tetraoctylammonium bromide (TOAB) (492.1 mg, 0.90 mmol) was dissolved in 25 mL of dry toluene under nitrogen gas. $HAuCl_4 \cdot 3 H_2O$ (100 mg, 0.25 mmol) was dissolved in 10 mL DI water and added to the flask at once. Now, the spin rate of the stir bar was set to between 800 and 900 rpm, and the solution was stirred for 10 min to ensure the hydrogen tetrachloroaurate transferred to the toluene phase; indicated by a change in color from orange to red. Dodecanthiol (122.2 µL, 0.5 mmol) was added to the mixture, and the color of mixture gradually changed from red to white-gray. Sodium borohydride (100 mg, 2.6 mmol) was added to the flask and the color immediately changed from whitish gray to dark brown. The aqueous phase was separated from the nanoparticles carefully, and thereafter the temperature was set to 45 °C, and the mixture left overnight with the spin rate of the stir bar set to 400 rpm. A 1:1 (*v*:*v*) mixture of water and ethanol were prepared, and used to repeatedly wash the nanoparticles followed by centrifugation (12,000 rpm) and decanting the supernatant. The dried nanoparticles (dark brown color) were then dissolved in 1.5 mL of *o*-xylene to fill the ink cartridges for printing.

L-cysteine-capped nanoparticles: Hydrogen tetrachloroaurate (31.0 mg, 0.0787 mmol) was dissolved in 10.0 mL DI water and the flask immersed in an ice bath (0 °C) for a 15-minute period. L-cysteine (18.4 mg, 0.152 mmol) was added under the spin rate set between 600 and 700 rpm and stirred for 10 minuets. The color of the mixture turned to pale white after about 1 hour. $NaBH_4$ (28.5 mg, 0.753 mmol) dissolved in 6.5 mL cold DI water was rapidly added while the magnet stirring was set at 1,000 rpm, and the solution immediately turned dark blue. The reaction was left to stir overnight. The particles were precipitated by the addition of *iso*-propanol (20 mL), which was added slowly while stirring. The precipitate was collected by centrifugation (10,000 rpm, 5 min) and washed twice with a 1:1 ratio (*v*:*v*) of $MeOH/H_2O$. The dark blue nanoparticles were dissolved in 1 mL of a mixture of ethylene glycol/MeOH to fill the ink cartridges for printing.

6-Mercaptohexanoic acid-capped nanoparticles: Hydrogen tetrachloroaurate (40.7 mg, 0.012 M) was dissolved in 2.3 mL DI water and the flask immersed in a water bath set at a temperature of 20 °C and magnetically stirred at 600 rpm. A mixture of 6-mercaptohexanoic acid (12.8 µL) in 0.45 mL of ethanol was added to the flask. The color of mixture turned to pale white after 10 s, then $NaBH_4$ (54 mg, 0.143 M) dissolved in 1.75 mL cold DI water was rapidly added under magnetic stirring at 1,000 rpm. The sample was separated into three 2 mL centrifuge tubes and centrifuged at 12,000 rpm for 10 min and washed three times with a 10:1 ratio (*v*:*v*) of *iso*-propanol/H_2O, separated and then isolated by centrifugation. The dark gray nanoparticles were then dissolved in 0.5 mL of ethylene glycol/MeOH to fill the ink cartridges for printing.

^{1}H NMR Spectra:

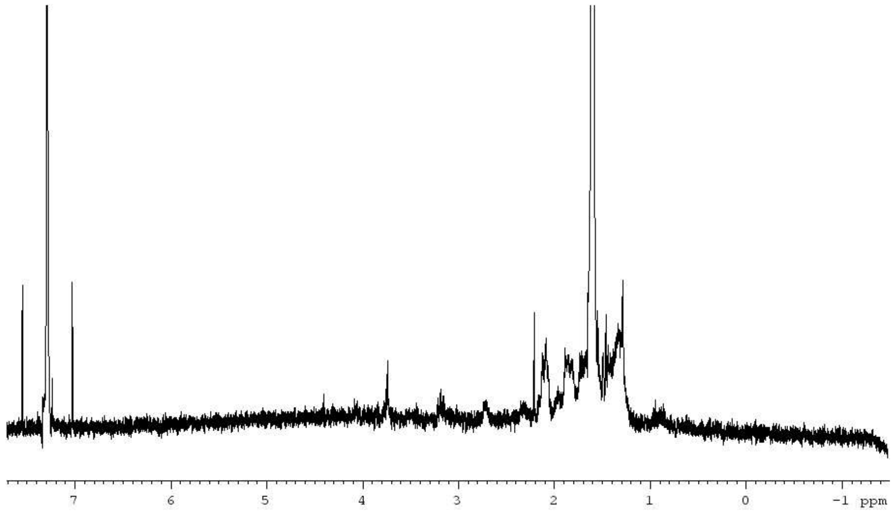


Figure S1. NMR characterization: ^{1}H NMR spectrum of dodecanethiol-capped Au NPs before Cl_2 gas exposure (peak broadening typical for Au NP ligand shells).

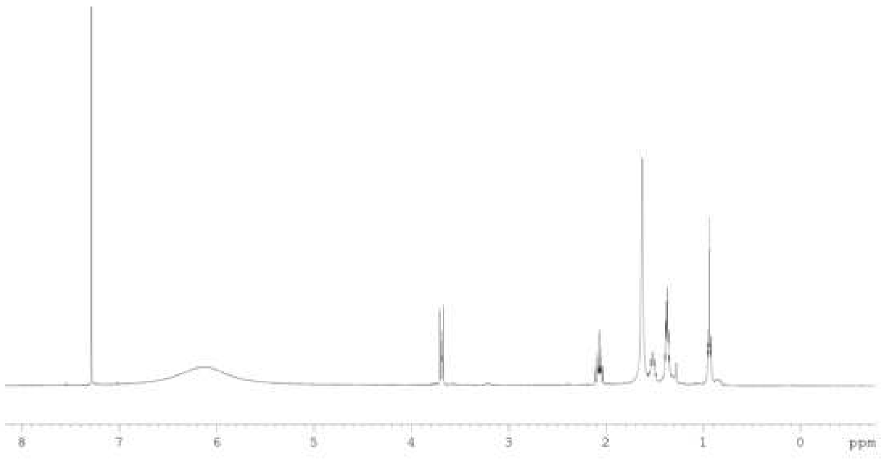


Figure S2. NMR characterization: ^{1}H NMR spectrum of the release didodecyl disulfide after Cl_2 gas exposure.

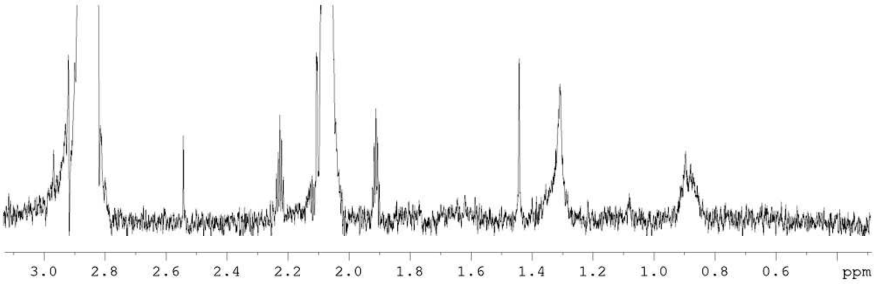


Figure S3. NMR characterization: ^{1}H NMR spectrum of 6-mercaptohexanoic acid-capped Au NPs (peak broadening typical for Au NP ligand shells).

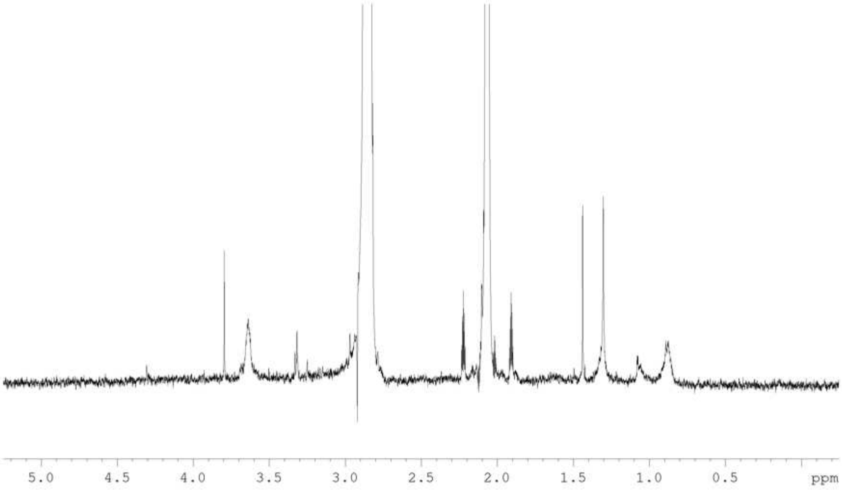


Figure S4. NMR characterization: ^{1}H NMR spectrum of L-cysteine-capped Au NPs (peak broadening typical for Au NP ligand shells).

Section S3. TEM Analysis (Imaging) of Gold Nanoparticles

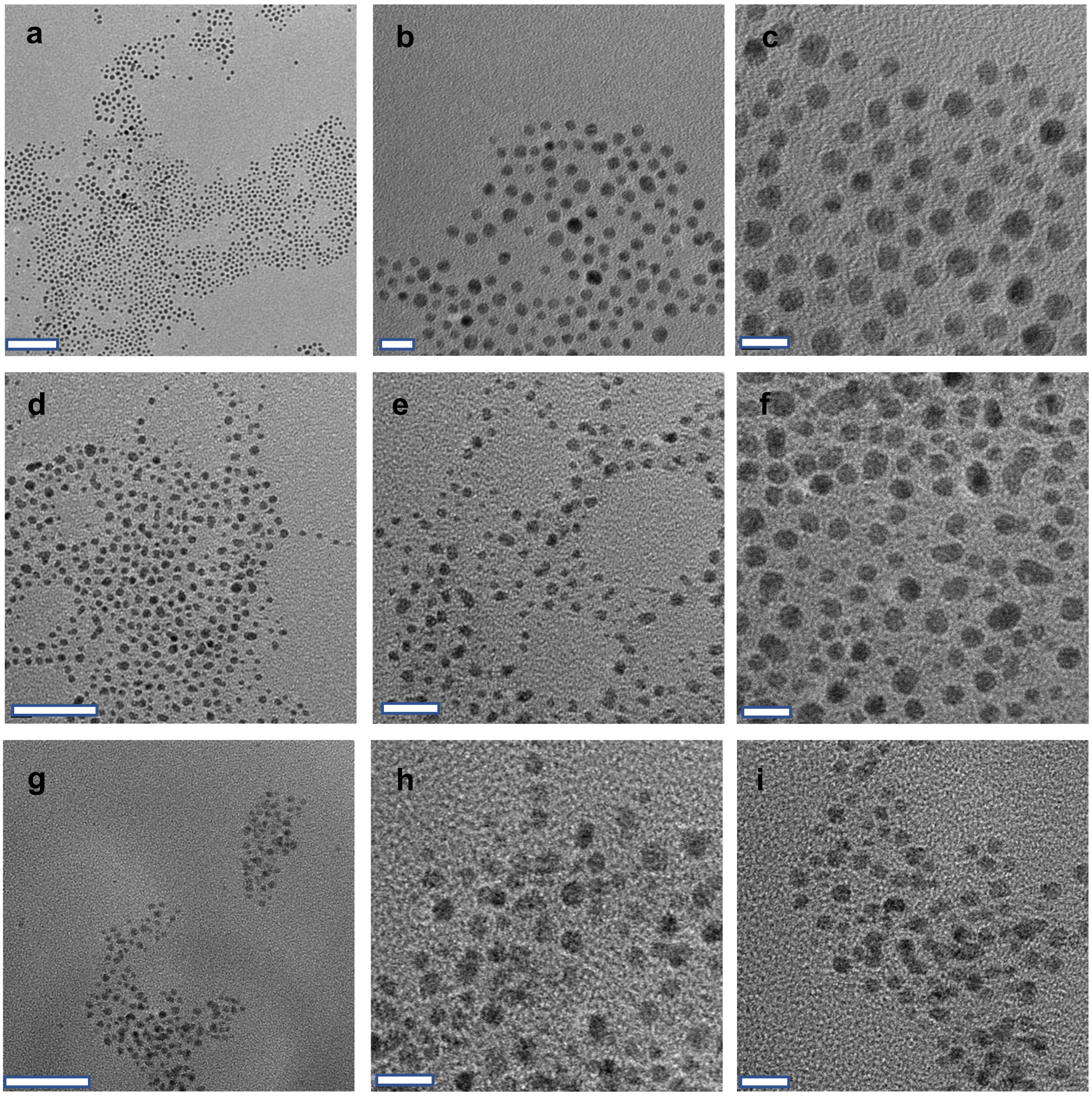


Figure S5. Additional TEM images of Au NPs: TEM grid (400 mesh), dried overnight, a – c) dodecanethiol-capped Au NPs, d – f) L-cysteine-capped Au NPs, and g – i) 6-mercapto-hexanoic acid-capped Au NPs; varying magnifications – scale bars: (a, d, g) 50 nm, (b, e, h) 10 nm, and (c, f, i) 5 nm.

Section S4. Vis-NIR Spectra

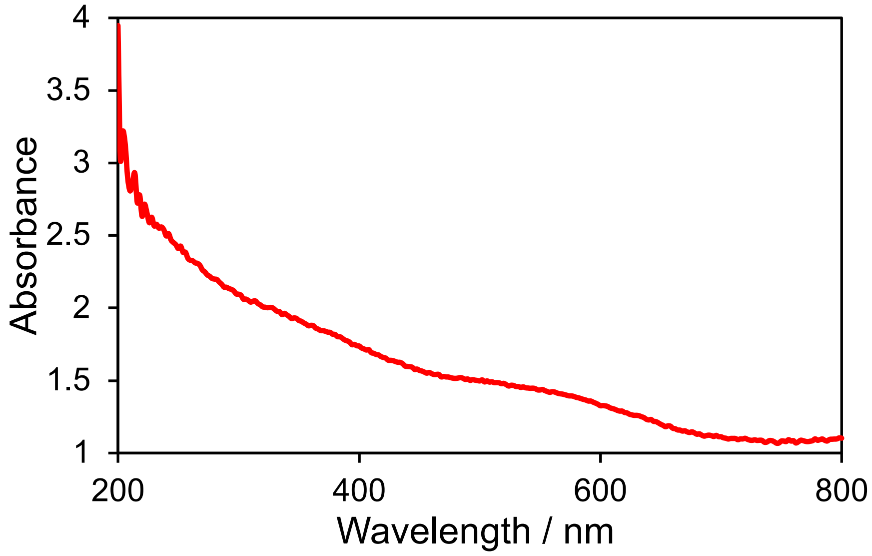


Figure S6. Vis-NIR spectra of dodecanethiol-capped Au NPs in *n*-hexane measured at room temperature (surface plasmon resonance band at ~ 550 nm).

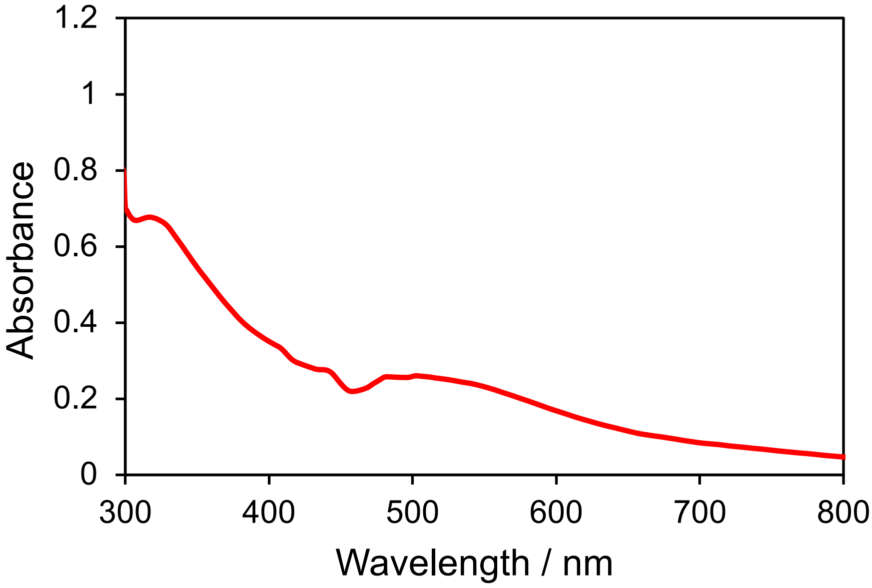


Figure S7. Vis-NIR spectra of L-cysteine-capped Au NPs in DI water measured at room temperature (surface plasmon resonance band at ~ 525 nm).

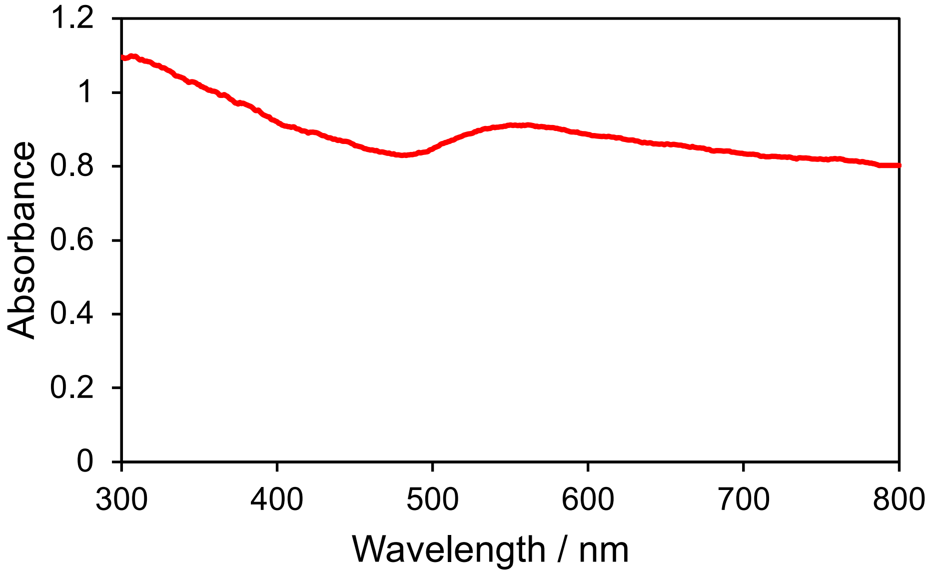


Figure S8. Vis-NIR spectra of 6-mercaptohexanoic acid-capped Au NPs in EtOH measured at room temperature (surface plasmon resonance band at ~ 550 nm).

Section S5. Thermogravimetric Analysis (TGA)

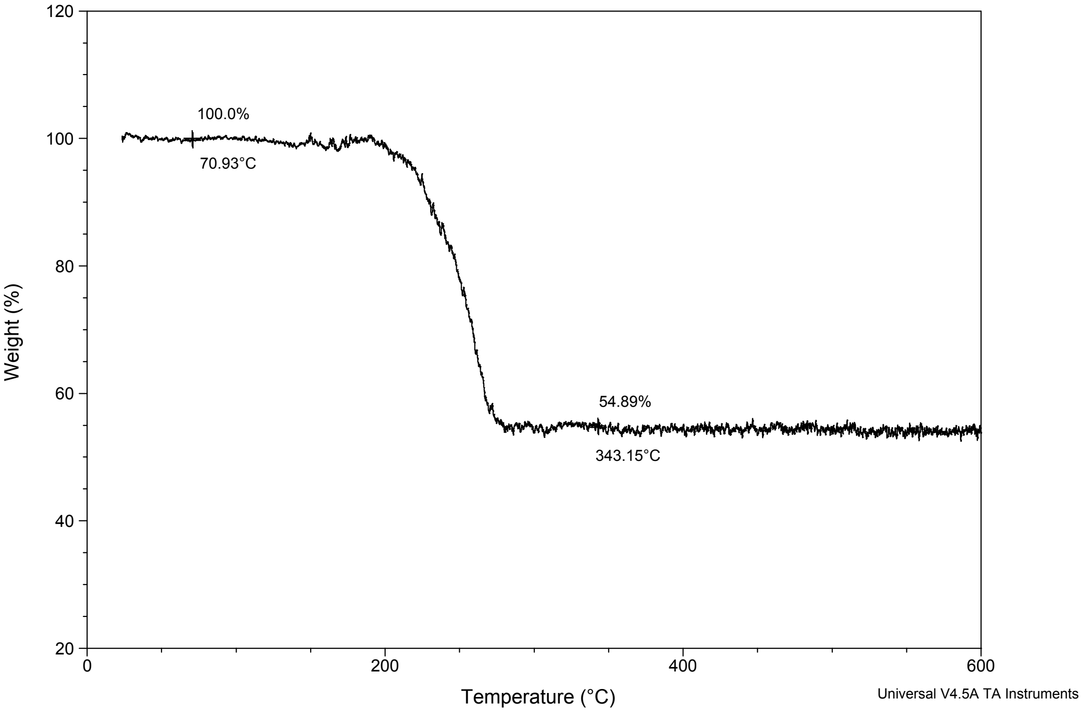


Figure S9. Determination of weight fraction of ligand shell of dodecane-thiol-capped Au NPs. Thermogravimetric analysis (TGA) plot for the dodecanethiol-capped Au NPs; sample weight: 5.37 mg, weight loss = 46%.

Section S6. FIB-SEM Imaging

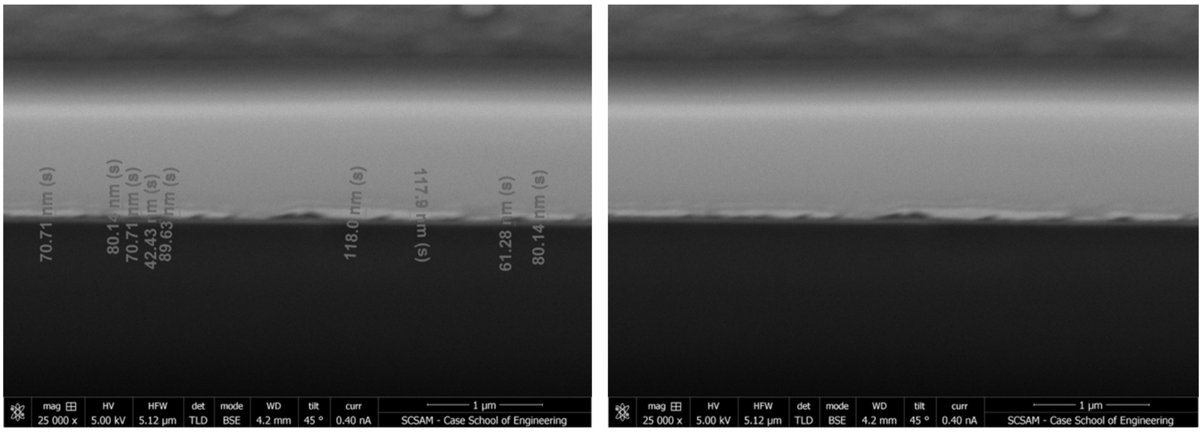
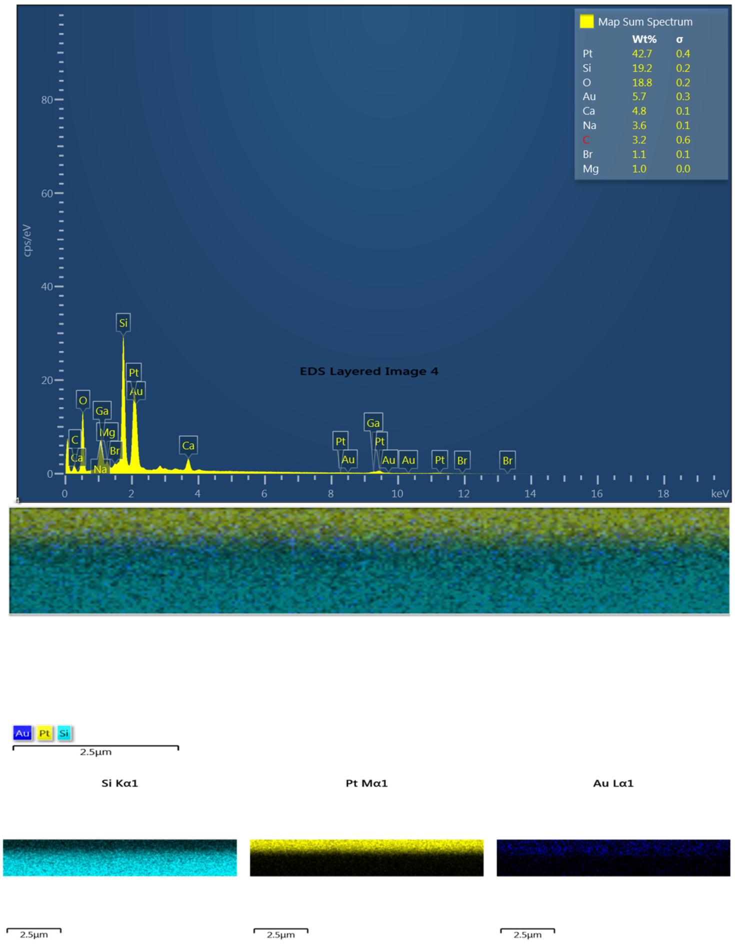


Figure S10. FIB-SEM images of the printed multi-layer of dodecanethiol-capped Au NPs. The average thickness of the NP multi-layer was calculated to be ~ 70 to 80 nm (averaging to about 10 NP layers); (left) with and (right) without measured thickness data.


Map Sum Spectrum

	Wt%	σ
Pt	42.7	0.4
Si	19.2	0.2
O	18.8	0.2
Au	5.7	0.3
Ca	4.8	0.1
Na	3.6	0.1
C	3.2	0.6
Br	1.1	0.1
Mg	1.0	0.0

Figure S11. EDX analysis of the printed multi-layer of dodecanethiol-capped Au NPs. Images show the material analysis: Si = substrate, Au = Au NPs, and Pt = coating layer used for FIB-SEM sample preparation.

Reference

[S1] C. W. White, J. G. Martin, *Proc. Am. Thorac. Soc.* **2010**, *7*, 257.