University of Louisville
Department of Chemistry
Prasadi Adhihetty

Dissertation Defense

When: April 14, 2022
Time: 10:00 a.m.
Location: SRB 139

MICROFABRICATED GOLD-BASED GAS SENSORS TO DETECT SELECT VOCs

Abstract

The development of gas sensors for detection of volatile organic compounds (VOCs) has been of interest in the sensing field for decades. To date, the use of metal nanoparticles-based chemiresistors for trace VOC detection, particularly gold monolayer protected clusters (Au MPCs)-based sensors, is of great interest due to methods for surface modification.[1,2] Herein, we present the results of our inspiration to exploit the advantages of functionalized Au MPCs chemiresistors for selective VOCs sensing by changing Au MPCs surface functionality. Our concept is to incorporate binding motifs onto Au MPCs to selectively bind target VOCs and thereby improve the sensing capabilities of chemiresistors derived from casting the functionalized Au MPCs on interdigitated electrodes (IDEs).

As inceptive studies, we were able to prepare urea-functionalized Au MPCs that demonstrated remarkable sensitivity and selectivity toward acetone serving as a representative carbonyl VOC.[3] We examined several structural elements of thiol urea ligands to change the degree of H-bonding between adjacent urea motifs on the Au MPCs surface as well as varied the steric properties of terminal groups on the urea-functionalized chains. The responses of the developed sensors were notably affected by the urea functional motifs. A *tert*-butyl end group on the thiol urea sensors resulted in high sensitivity and selectivity toward acetone and delivered a sensor capable of detecting acetone vapor at concentrations from 10 ppb to 10 ppm.[4]

To selectively detect aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylene (BTEX), at trace levels in outdoor and indoor air, we exploited the strong cation-π noncovalent interactions between metal cations bound to the Au MPCs-based chemiresistor surface and the π-systems of BTEX as a principal sensing mechanism.[5] We synthesized alkali-metal carboxylate-functionalized Au MPCs by modifying the surface chemistry of Au MPCs via an oxime ether approach.[6] The synthesized K^+ carboxylate-functionalized Au MPCs sensor show a higher response to electron rich BTEX VOCs over electron deficient nitrobenzene, cyclohexene, acetone, and methanol vapors at concentration range from 0.1 – 5.0 ppm than the other sensors developed in this work.[7] The developed sensors response to selected aromatic and non-aromatic VOCs suggests cation-π interactions arising between the positively charged cations and the electron-rich aromatic π-systems. The results open a promising research direction for harnessing cation-π interactions to create aromatic VOC-selective sensors.

Next, we utilized the binding ability of a cesium cation to chloride to detect trichloroethylene (TCE) vapor.[8] The developed Cs^+ carboxylate-functionalized Au MPCs chemiresistor was exposed to different alkyl and vinyl chloride vapors to explore the influence of structural features on TCE detection. The Cs^+-Au MPCs sensor exhibits a higher response to analytes with a vinyl 1,2-dichlorounit than other chloro-substituted analytes. Moreover, TCE shows a higher sensor response at 1 ppm – 5 ppm vapor concentration than the other declared harmful chloro analytes. This study revealed the different binding affinities of cesium cation toward the geminal, vicinal and vinyl halides and how it affects sensor response.[9]

Taken in sum, these results show that the outer ligand structure of thiolate-protected Au MPCs plays a major role in enhancing selectivity and sensitivity toward VOCs and suggests this approach as an effective means for targeting VOC analytes.

References

1. Wohltjen, H; Snow, A. W. *Anal.Chem.* **1998**, *70*, 2856-259.
2. Ibañez, F. J.; Zamborini, F. P. *Small* **2012**, *8(2)*, 174–202.
3. Xie, Z.; Raju, M. V. R.; Stewart, A. C.; Nantz, M. H.; Fu, X.-A. *RSC Adv.* **2018,** *8*, 35618–35624.
4. Xie, Z.; Raju, M. V. R.; Adhihetty, P. K.; Fu, X.; Nantz, M. H. *Sensors* **2020**, *20(24)*, 7024.
5. Mahadevi, A. S.; Sastry, G. N. Chem. Rev. **2013**, *113(3)*, 2100-2138.
6. Sibakoti, T. R.; Stinger, C. R.; Adhihetty, P. K.; Zamborini, F. P.; Nantz, M. H. *Part. Part. Syst. Charac.* **2019**, *36*, 1900093.
7. Adhihetty, P. K.; Halder, S.; Jasinski, J. B.; Fu, X.-A.; Nantz, M. H. *Sens. Actuators B Chem.* **2022**. (Manuscript is under review)
8. a. Smith, G. Acta Cryst. **2013**, *E69*, m22–m23. b. Levitskaia, T. G.; Bryan, J. C.; Sachleben, R. A.; Lamb, J. D.; Moyer, B. A. *J. Am. Chem. Soc.* **2000,** *122*, 554-562.
9. Adhihetty, P. K.; Halder, S.; Fu, X.-A.; Nantz, M. H. **2022**. (Manuscript preparing)