Gas-Sensing Properties of Metal Oxide Nanostructured Heterojunctions

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Research Motivation

Much research has focused on developing sensors which are selective to either acetone or ethanol. Of the materials investigated, TiO_2 has demonstrated great potential as a resistive-type gas sensor used to detect hydrocarbons and volatile organic compounds (VOCs). The sensitivity of gas sensors is dependent upon its surface area and interfacial potentials.

This experiment is exploring the gas-sensing ability of MOX powders containing TiO_2 nanorods. Nanorods are high surface area structures and alter the potential at the interfaces and surfaces of the powders.

Application

Noninvasive Breath Analyzer for Disease Diagnosis

- Acetone is a biomarker for diabetes when present in high concentrations in human breath[4]

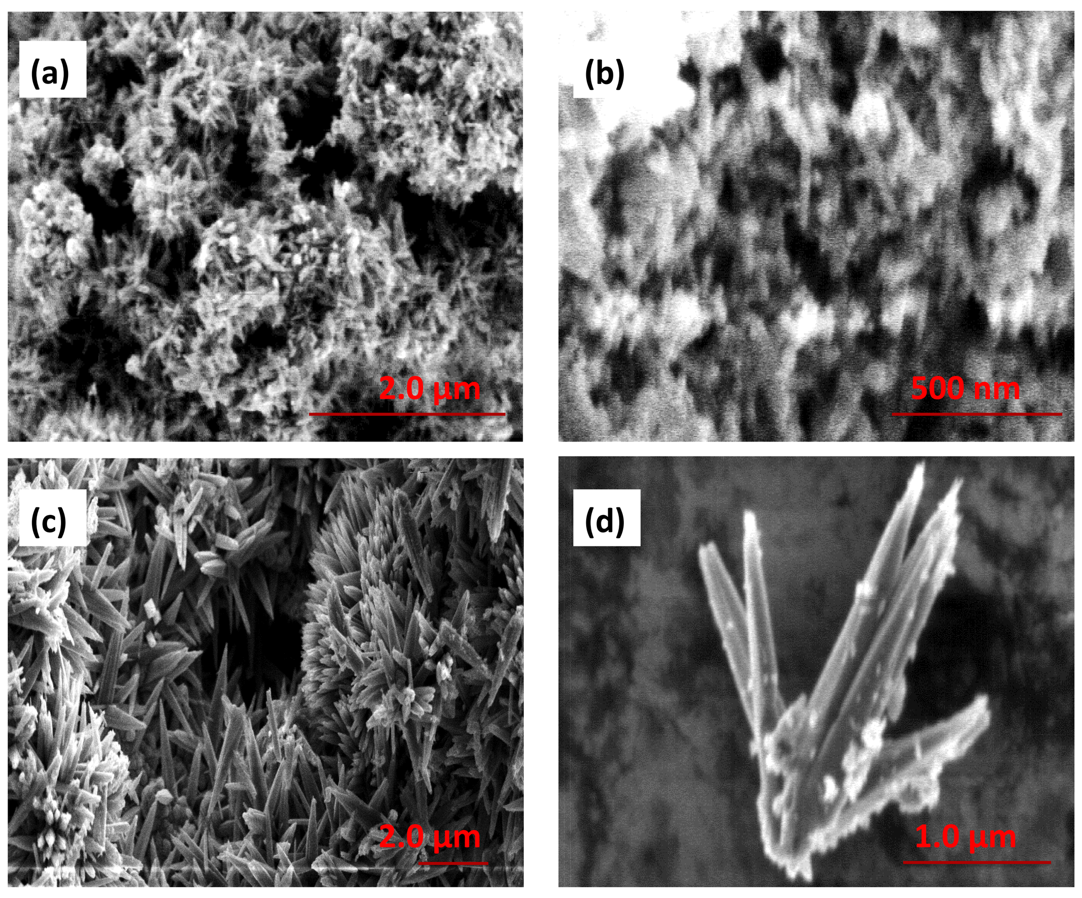
Application Requirements:

- Able to detect acetone in low concentrations (1 ppm) in a moist environment
- Selectivity to acetone when other VOCs and hydrocarbons are present
- Cost effective and patient friendly

Sensor Fabrication

- **Materials:** TiO_2 aerogel, CoO, TiO_2, NiO, and SnO_2
- **Hydrothermal Recipe**: 300 psi, 150˚C, 15 min.
- **Paste Composition:** 12.9 wt% metal oxide, 6.4 wt% ethyl cellulose, and 80.7 wt% alpha-terpineol
- **Laboratory Mixer:** 4.0 min.
- **Hand Brushing**
- **Firing:** 500˚C for 8 hours
- **Testing**: Ethanol and Acetone at 350˚C, 400˚C, 425˚C

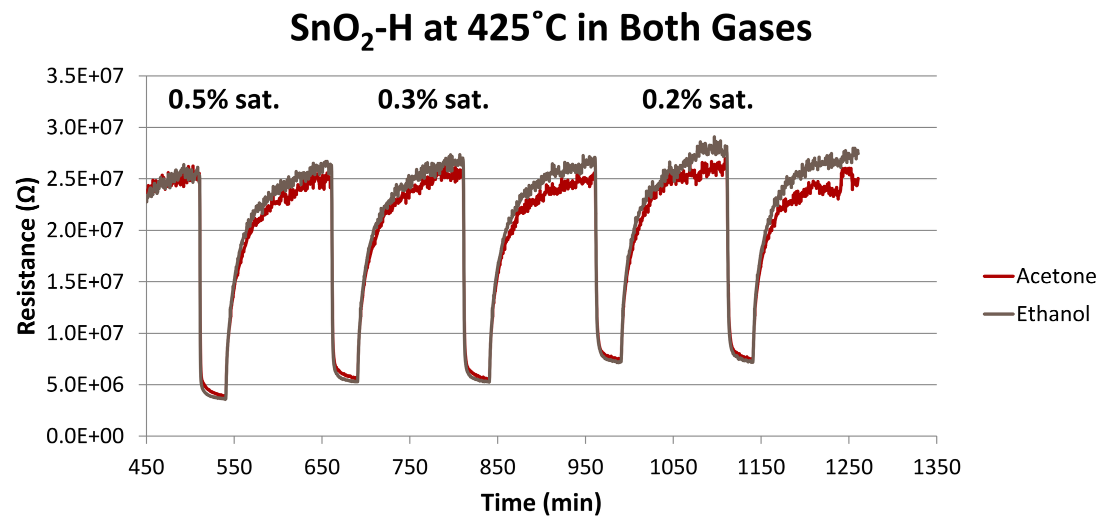
SEM Microscopy



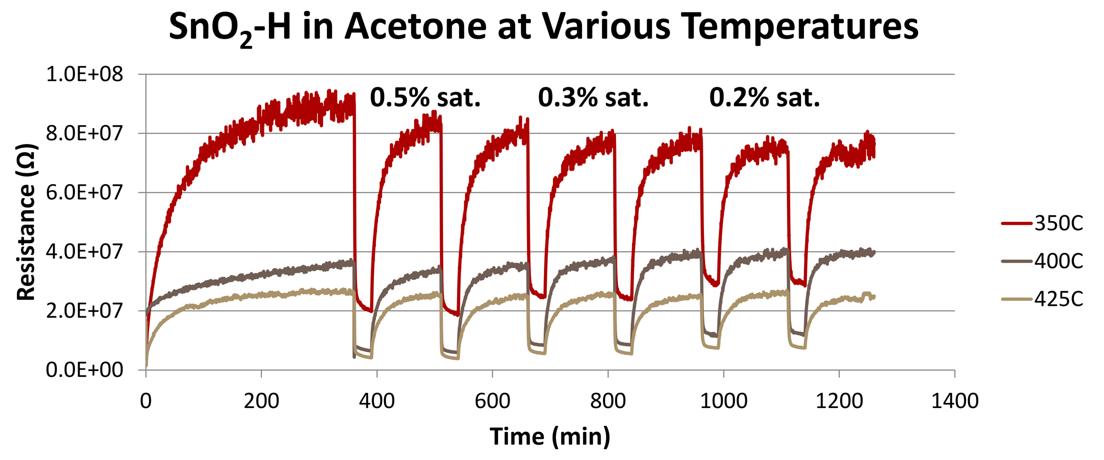
SEM micrographs of **(a)** TiO_2 hybrid powder **(b)** SnO_2 hybrid powder **(c)** CoO hybrid powder **(d)** TiO_2 nanorods

Hydrocarbon Selectivity

SnO_2-H at 425˚C in Both Gases



SnO_2-H in Acetone at Various Temperatures

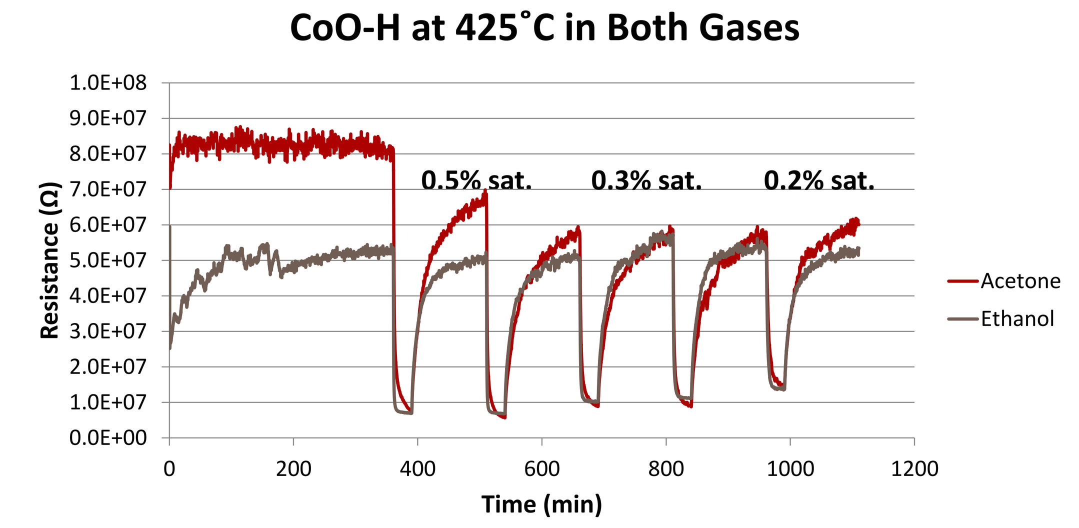


	0.5% Acetone Saturation		0.5% Ethanol Saturation	
Sample	SnO_2	SnO_2-H	SnO_2	SnO_2-H
Response* at 350˚C	2.72	4.75	2.88	5.03
Response* at 400˚C	3.06	5.88	3.43	5.71
Response* at 425˚C	-	6.69	3.49	7.17

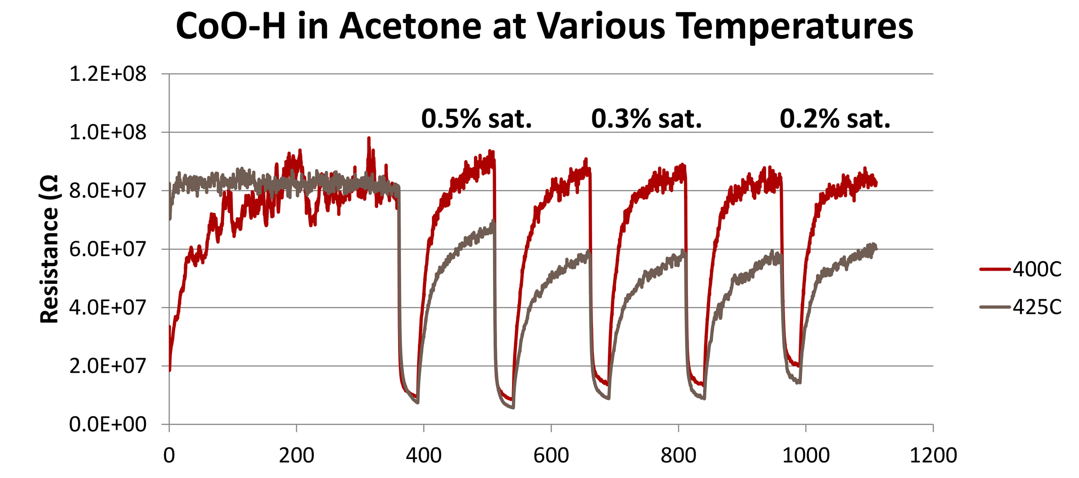
*Response = $\Delta R/R_g$

- The SnO_2–H sensor exhibited higher responses in both gases compared to the base SnO_2 sensor
- The measured responses of both SnO_2 sensors increased with increasing temperature and did not display noticeable selectivity towards acetone

CoO-H at 425˚C in Both Gases



CoO-H in Acetone at Various Temperatures



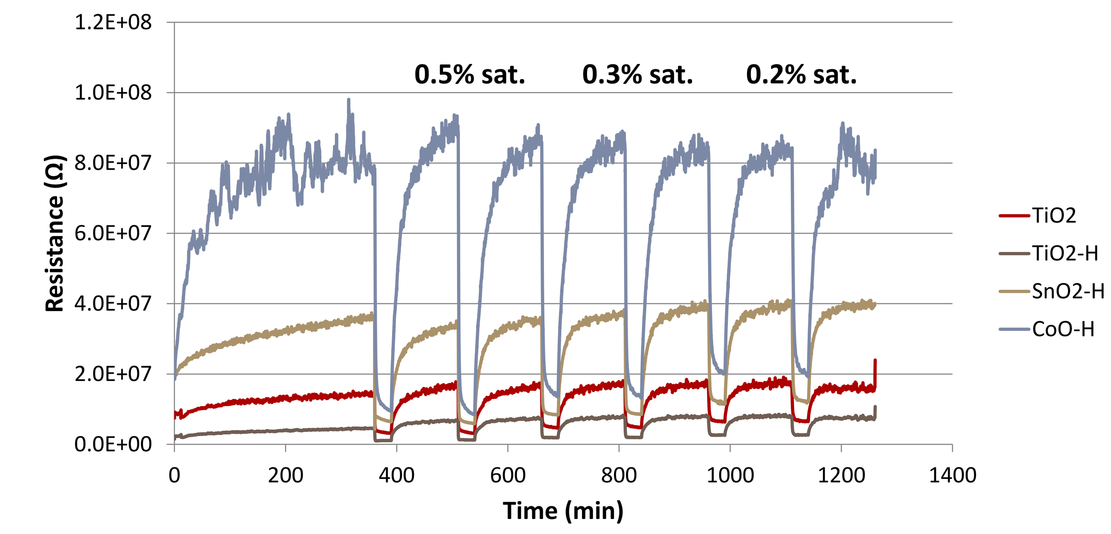
	0.5% Acetone Saturation		0.5% Ethanol Saturation	
Sample	CoO	CoO-H	CoO	CoO-H
Response* at 350˚C	1.07	-	1.08	-
Response* at 400˚C	1.09	10.80	1.06	10.76
Response* at 425˚C	1.07	12.04	1.07	8.14

*Response = $\Delta R/R_g$ for CoO-H, Response = $\Delta R/R_a$ for CoO

- The responses of the CoO-H sensor are about an orders of magnitude larger than the CoO sensor responses
- The CoO-H sensor was more selective to acetone than ethanol at a testing temperature of 425˚C
- The response of the Co-H sensor in acetone increased with increasing temperature, while the response in ethanol decreased with increasing temperature

Improving Response

TiO_2 and Hybrid Sensors at 400˚C in Acetone



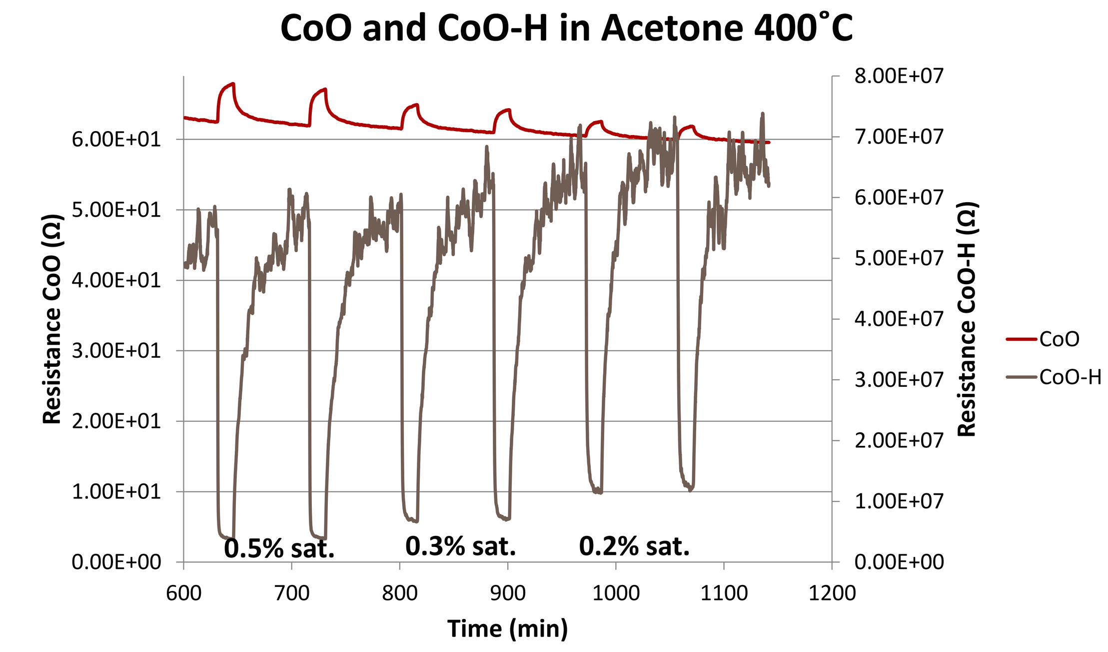
0.5% Acetone Saturation at 400˚C				
Sample	TiO_2	TiO_2-H	SnO_2-H	CoO-H
Response* at 350˚C	4.66	5.40	4.75	-
Response* at 400˚C	5.32	5.19	5.88	10.80
Response* at 425˚C	5.16	5.32	6.69	12.04

*Response = $\Delta R/R_g$ for n-type

- Growing the TiO_2 nanorods of the surface of the MOX powders increased the response of the sensors relative to the best base sensor, TiO_2

P-N Junction Effects

CoO and CoO-H in Acetone 400˚C



- The TiO_2 nanorods on the CoO surface caused the CoO sensing behavior to change from p-type to n-type
- Since TiO_2 is n-type, the CoO-H sensor response is likely controlled by the TiO_2 nanorods
- The depletion region formed at the p-n junction between the TiO_2 and CoO significantly increased the resistance, allowing for a larger response value

Conclusions and Future Work

Conclusions:

- Growing TiO_2 nanorods on the MOX powders significantly improves the sensors' responses
- The TiO_2 nanorods on the CoO surface caused the CoO sensor to exhibit n-type sensing behavior
- The CoO-H (p-n junction) exhibited the largest response when exposed to both gases
- Increasing the testing temperature made the CoO-H sensor more selective towards acetone than ethanol, demonstrating promise for selectivity

Future Works:

- Analyze the temperature dependence of response in greater detail
- Determine if nanorod/powder interfaces improve response compared to powder/powder interfaces
- Optimize sensor performance of most promising material through better processing and the testing temperature

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References

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