Multi-Gas Sensors for Enhanced Reliability of SOFC Operation

DOE/NETL Cooperative Agreement: DE-FE0031653

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SUNY Polytechnic Institute: Michael Carpenter, Nora Houlihan

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21st Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, July 21-23, 2020

Project goal and objectives

Goal:
to build gas sensors for in situ monitoring of H_2 and CO gases of SOFC systems

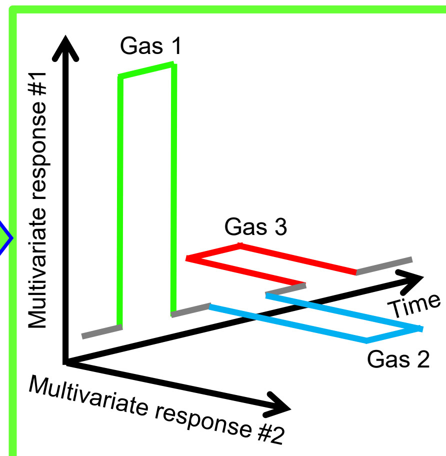
Objectives:
to achieve multi-gas monitoring capability with a single multivariable sensor and to achieve its long-term sensor performance

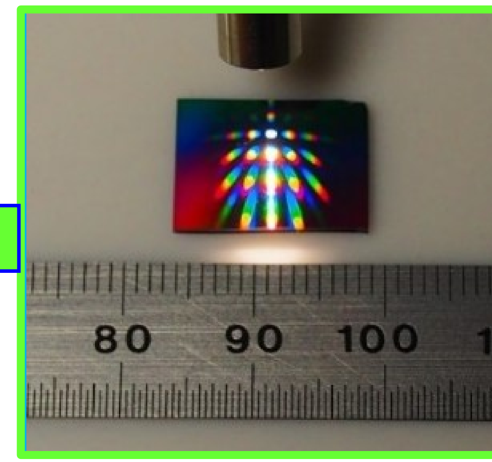
Real-time knowledge of H_2/CO ratio of anode tail gases:
- will allow control of efficiency of reforming process in the SOFC system
- will deliver a lower operating cost for SOFC customers

Status quo:
Mature traditional detector concepts

Performance need:
Compact system for multi-gas discrimination

Our approach:
Multivariable photonic gas sensors





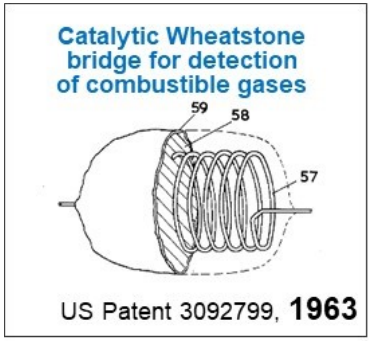
In-line sensing is not straightforward, requires traditional analytical instruments

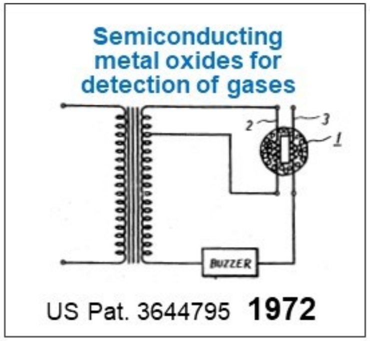
Modern conventional gas sensors:
"For the revolution to take off, accuracy must improve"

alphasense.com
figaro.com
sgxsensortech.com

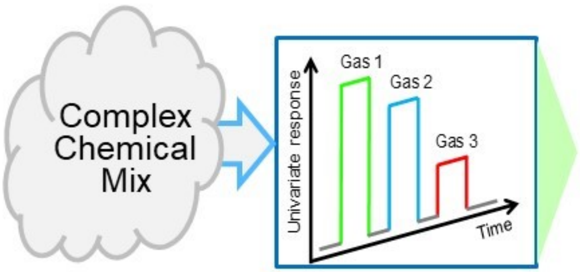
✓Miniaturization
✓Reduced power
✓Low cost

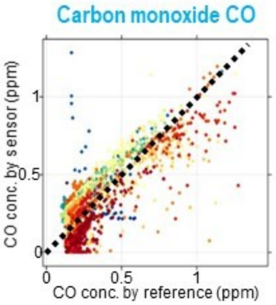
The roots: industrial safety
single-output devices for detection of expected gases at high concentrations



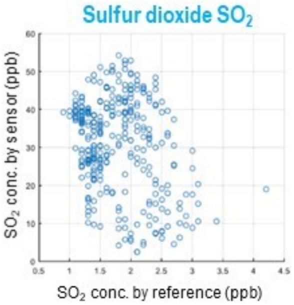


Gas cross-sensitivity: undesired response to interfering gases





Hagler et al., *Atmospheric Meas. Tech.* **2016,** 9, 5281



Borrego et al., Atmospheric Environment **2016**, 147, 246

EPA
No low cost sensors meet the Regulatory Monitoring requirements.
-Air Sensor Guidebook, EPA/600/R-14/159, 2014

nature
The biggest headaches are caused by interfering chemicals.
-Lewis, Edwards, 2016

High performance analytical instruments:
Diverse designs to reject known and unknown interferences

Gas chromatography

Photo by R. Potyrailo

Qin, Gianchandani, *Microsyst. Nanoeng.* 2016

Mass spectrometry

Photo by R. Potyrailo

May 28, 2018

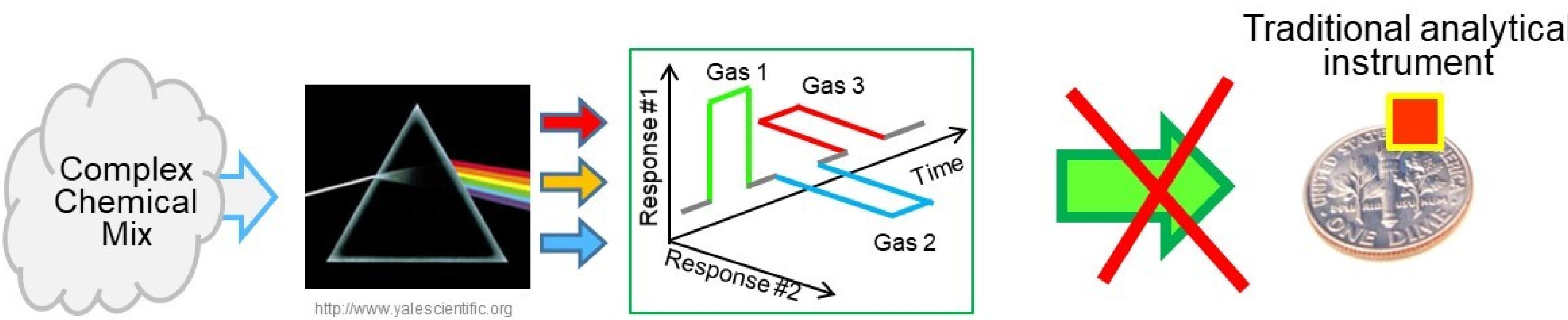
Laser spectroscopy

www.eol.ucar.edu

alliedscientificpro.com

Multi-detectors

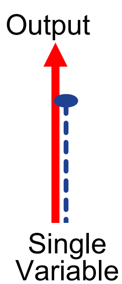
emersonprocess.com



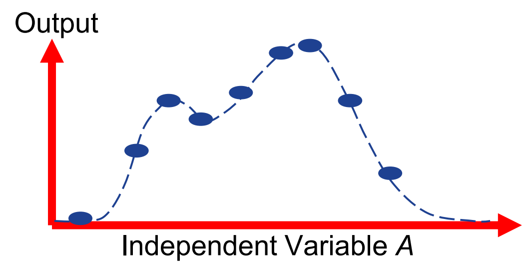
Diverse instrument-design rules to operate in complex conditions

Design principles of analytical instruments:
Different orders of measurements

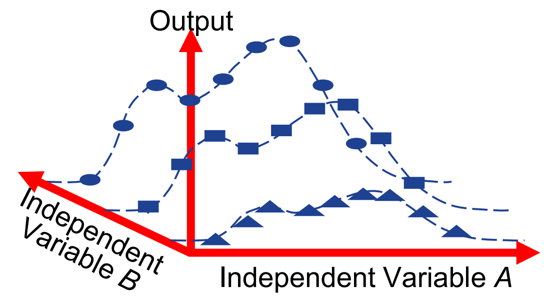
Zero order



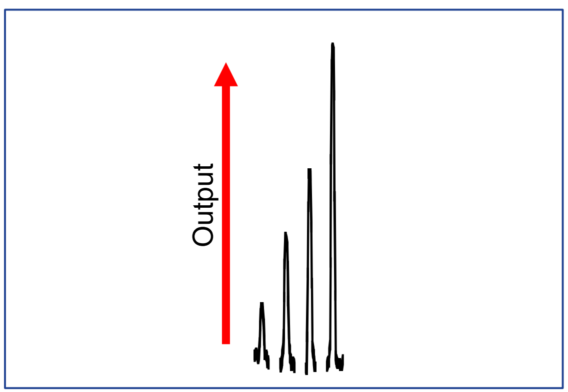
First order



Second order

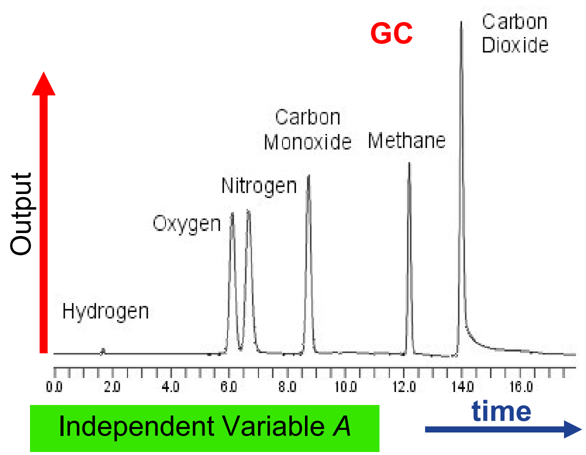


Zero order

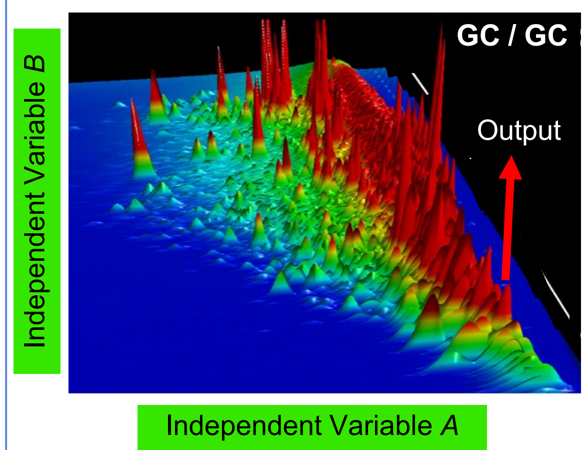


No independent variables

First order



Second order



Mathematically, interferences are not noticed, cannot be rejected

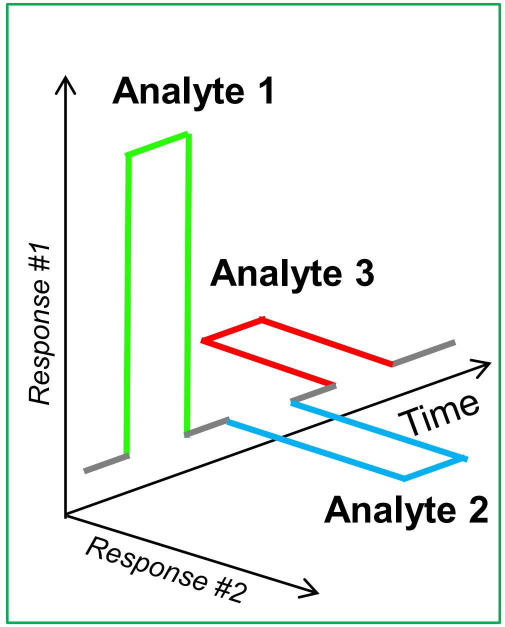
One independent variable allows rejection of KNOWN interferences

Two or more independent variables reject UNKNOWN interferences

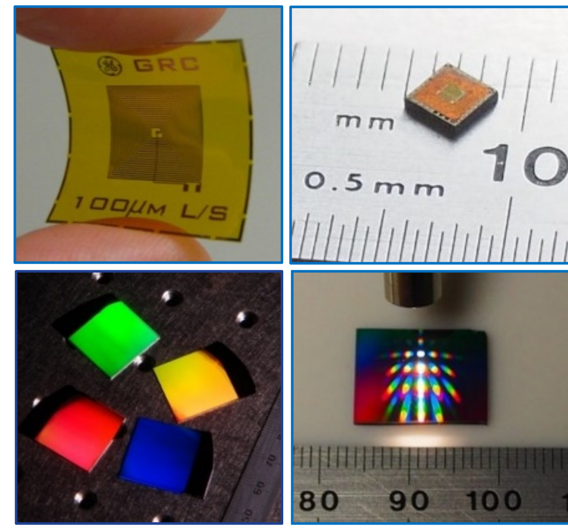
GE Research:
multivariable sensor solutions for demanding applications

Instruments based on mature analytical concepts

Qin, Gianchandani, *Microsyst. Nanoeng.* **2016**
alliedscientificpro.com
emersonprocess.com
C&EN May 28, **2018**



Sensors and systems based on multivariable sensing concepts

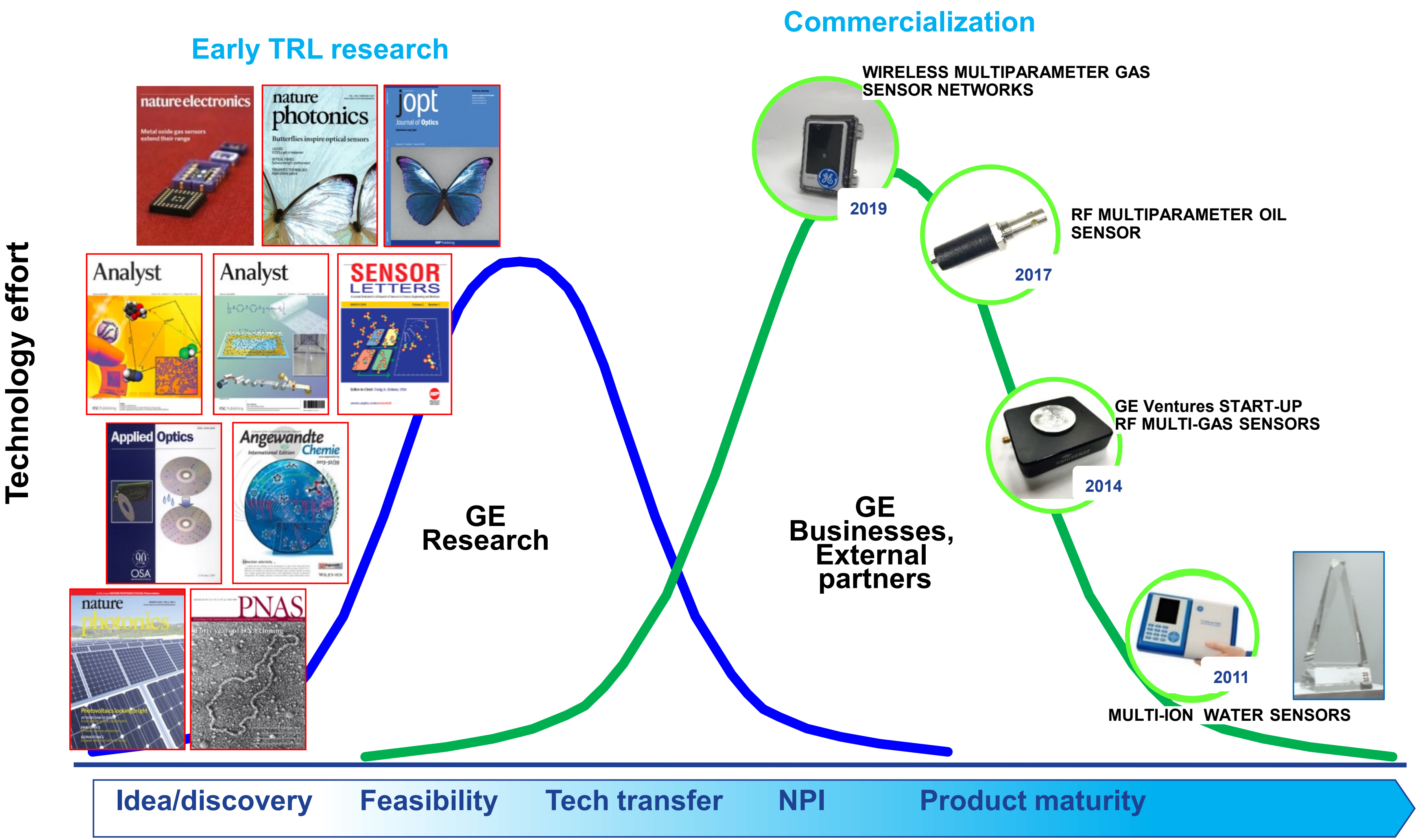


Photos by R. A. Potyrailo

Bringing contemporary sensing solutions to society using mathematics and physics

Our industrial R&D goal:

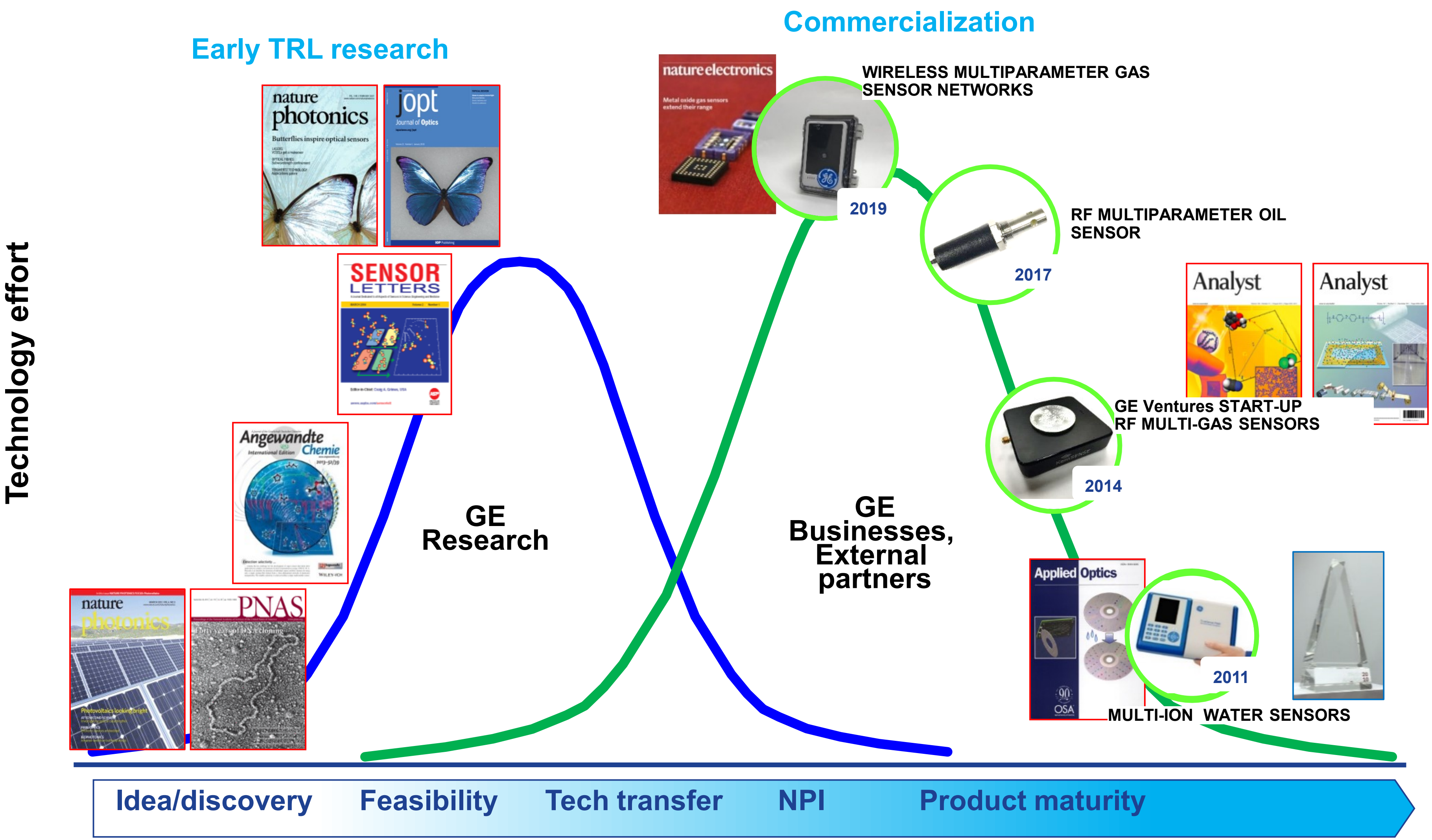
Develop sensors with new capabilities, transition for commercialization



TRL = technology readiness level
NPI = new product introduction

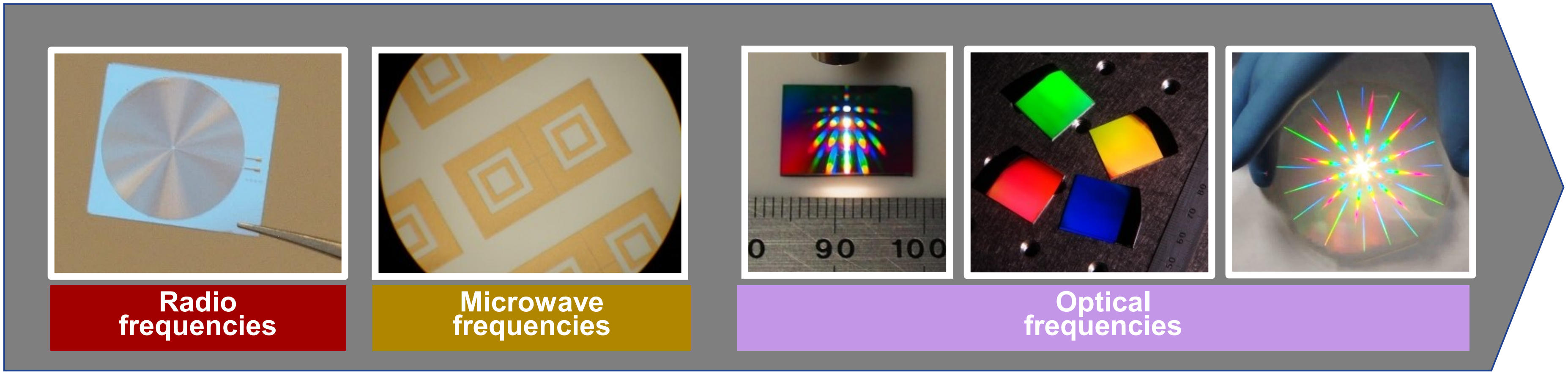
Our industrial R&D goal:

Develop sensors with new capabilities, transition for commercialization



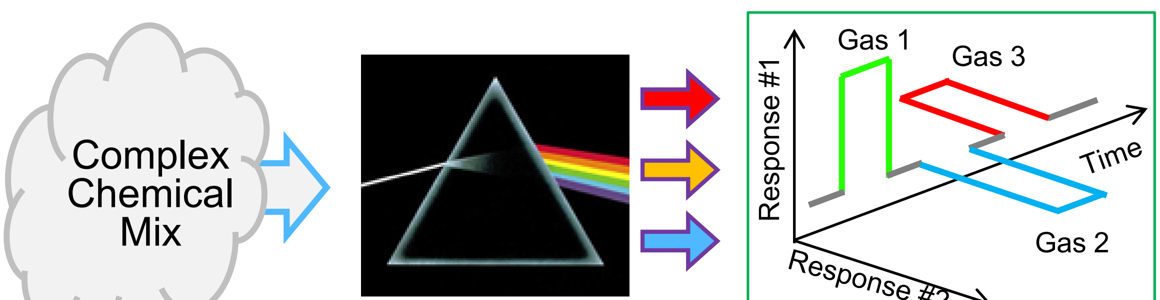
TRL = technology readiness level
NPI = new product introduction

Our design principles for multivariable gas sensors



Potyrailo et al., *Nature Electronics* **2020**

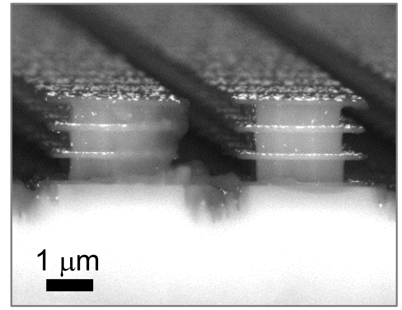
Potyrailo et al., *Nature Photonics* **2007**
Potyrailo et al., *Proc. Natl. Acad. Sci. USA* **2013**
Potyrailo et al., *Nature Communications* **2015**

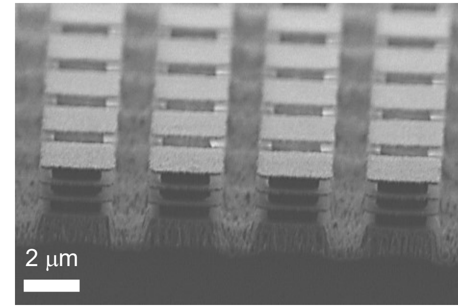


http://www.yalescientific.org

New philosophy for selective gas sensing across different frequency ranges

Learning from Nature

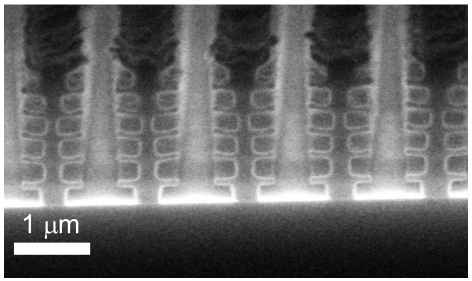


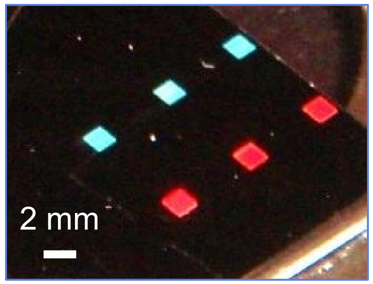


Bioinspiration -
new functionality, beyond Nature

High temperature

Potyrailo et al., *J. Opt.*, **2018**
Potyrailo et al., *ECS Transactions* **2019**
Potyrailo et al., *Faraday Transactions* **2020**

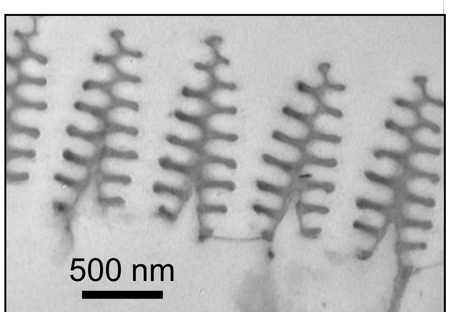




Biomimetics -
recreation of observed functionality

Room temperature

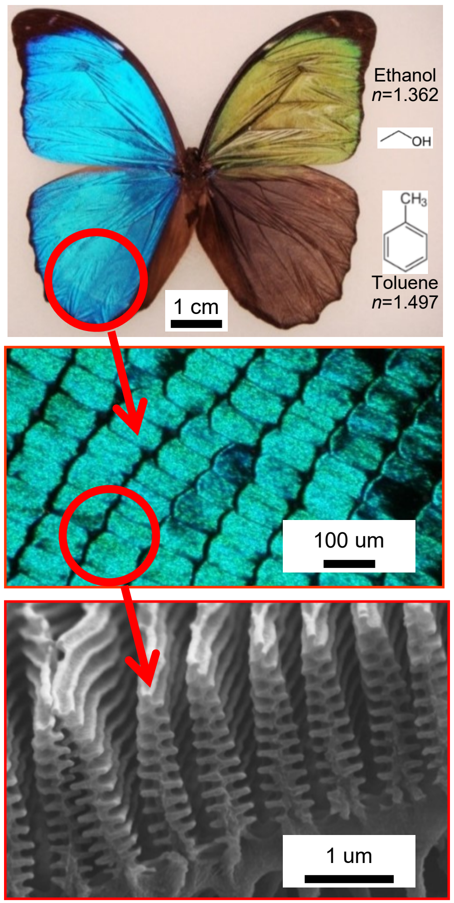
Potyrailo et al., *Nature Communications* **2015**



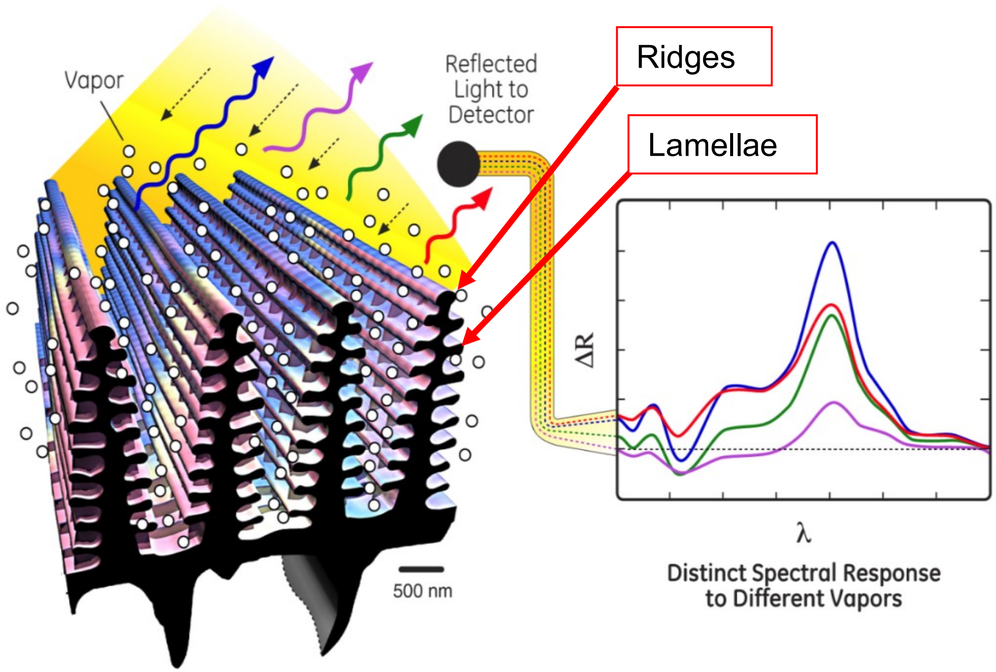
Biomimicry -
imitation of biological systems

Potyrailo et al., *Nature Photonics* **2007**
Potyrailo et al., *Proc. Natl. Acad. Sci. U.S.A.* **2013**

Structural color in nature:
from understanding to functional applications



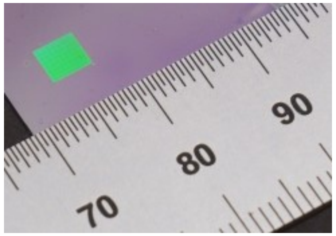
Operation principle of multivariable sensors utilizing natural *Morpho* butterfly scales

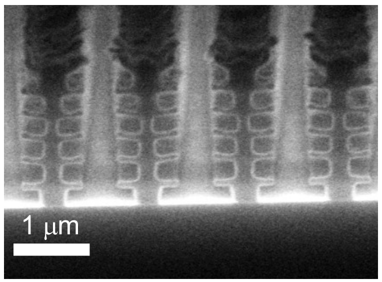


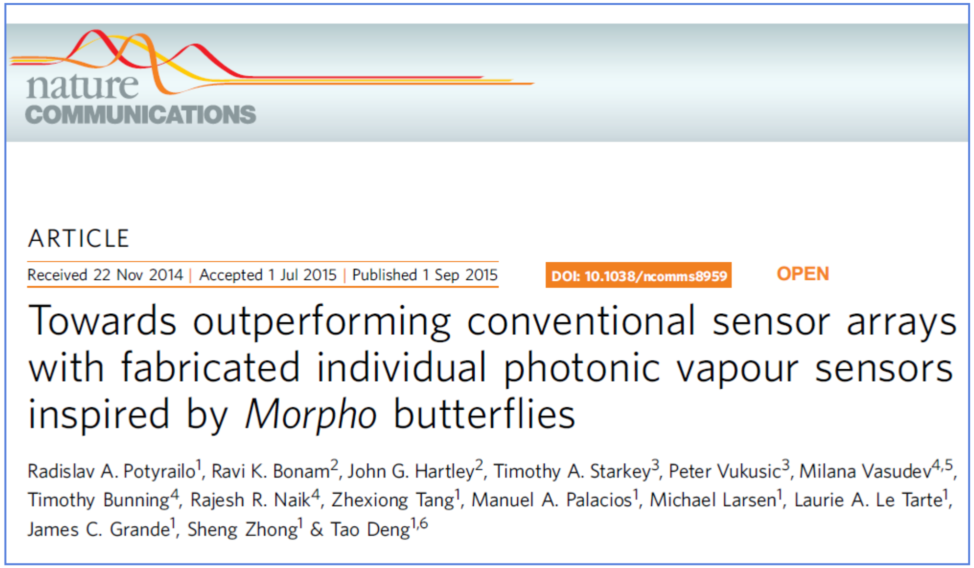
Potyrailo et al., *Nature Photonics*, **2007**

Research curiosity brings a potential for useful performance

Single multivariable sensor
outperforms classic QCM and MOS sensor arrays







nature COMMUNICATIONS

ARTICLE

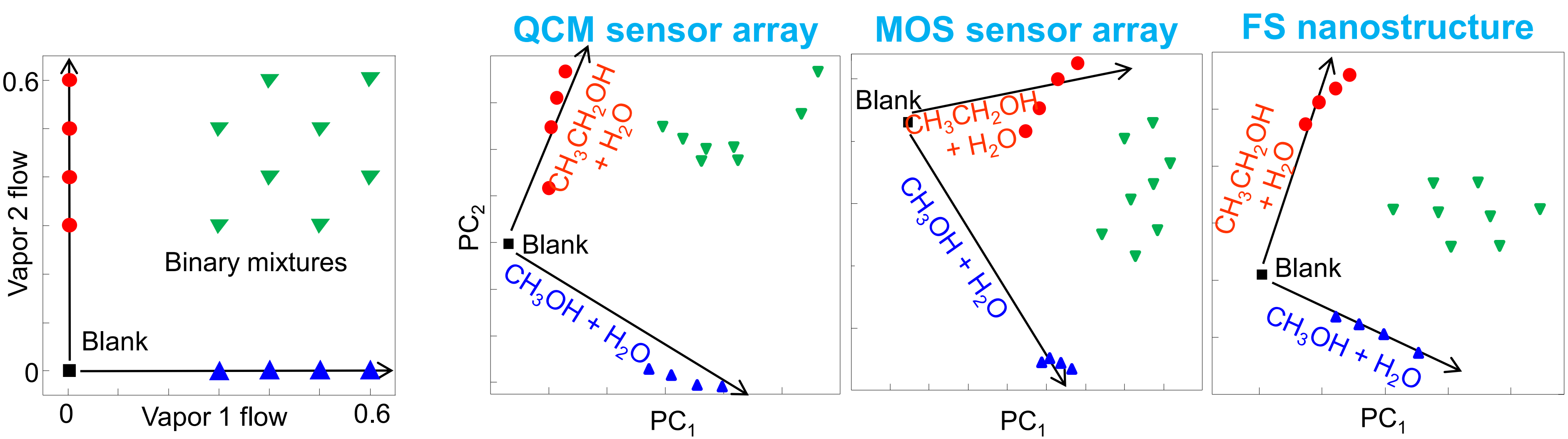
Received 22 Nov 2014 | Accepted 1 Jul 2015 | Published 1 Sep 2015

DOI: 10.1038/ncomms8959 OPEN

Towards outperforming conventional sensor arrays with fabricated individual photonic vapour sensors inspired by *Morpho* butterflies

Radislav A. Potyrailo[1], Ravi K. Bonam[2], John G. Hartley[2], Timothy A. Starkey[3], Peter Vukusic[3], Milana Vasudev[4,5], Timothy Bunning[4], Rajesh R. Naik[4], Zhexiong Tang[1], Manuel A. Palacios[1], Michael Larsen[1], Laurie A. Le Tarte[1], James C. Grande[1], Sheng Zhong[1] & Tao Deng[1,6]

FS = nonafluorohexyl-trimethoxysilane
QCM = quartz crystal microbalance
MOS = metal oxide semiconductor

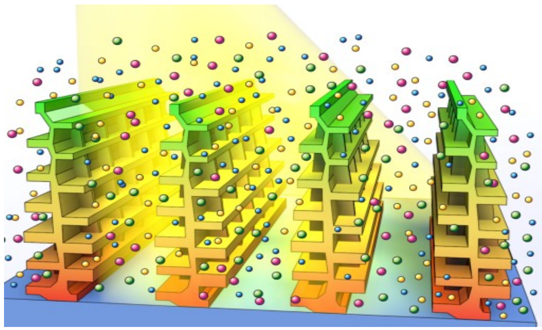


Ethanol, methanol vapors, their mixtures + water background

Potyrailo et al. *Nature Communications* **2015**

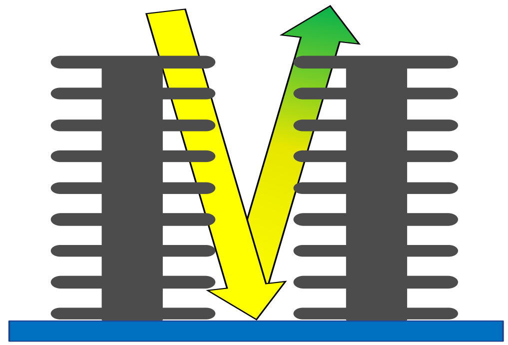
Advancing design rules of nanostructures for high temperature SOFC gas-sensing applications

Selectivity control for vapors at room temp.



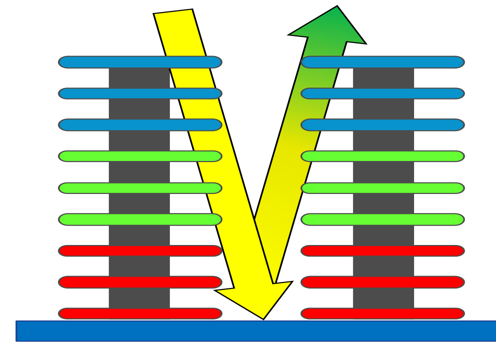
- Polymeric nanostructure
- Absorption and adsorption of vapors

Selectivity control for gases at high temp.

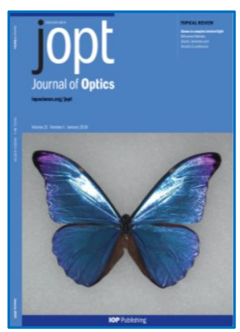


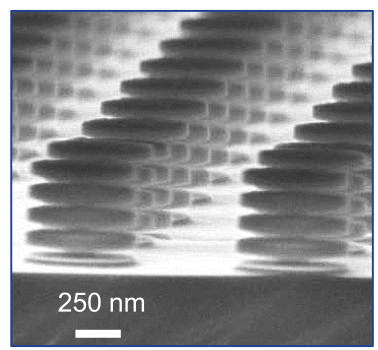
- Inorganic nanostructure
- Catalytic reactions of gases

Interference rejection control



- Multi-material inorganic
- nanostructure
- Catalytic reactions of gases

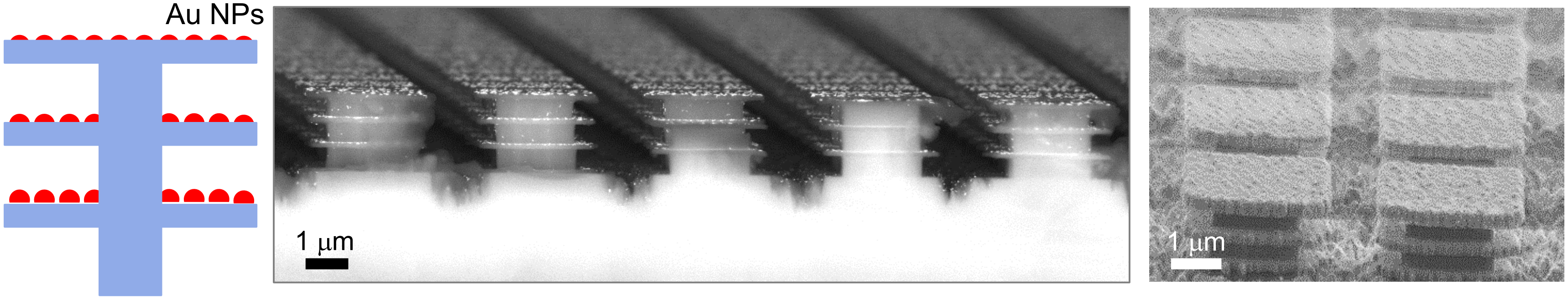




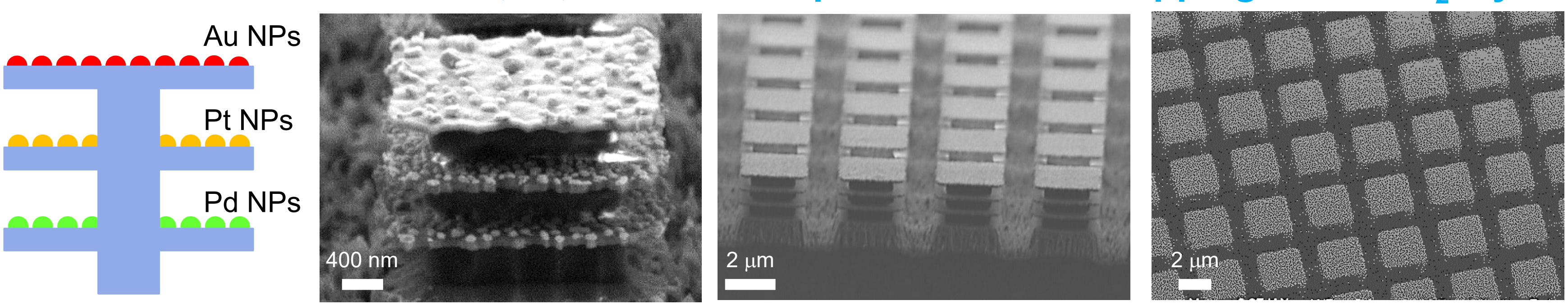
Potyrailo et al., *J. Opt.*, **2018**
Potyrailo et al., *ECS Transactions* **2019**
Potyrailo et al., *Faraday Transactions* **2020**

Nanostructures for gas sensing at high temperature

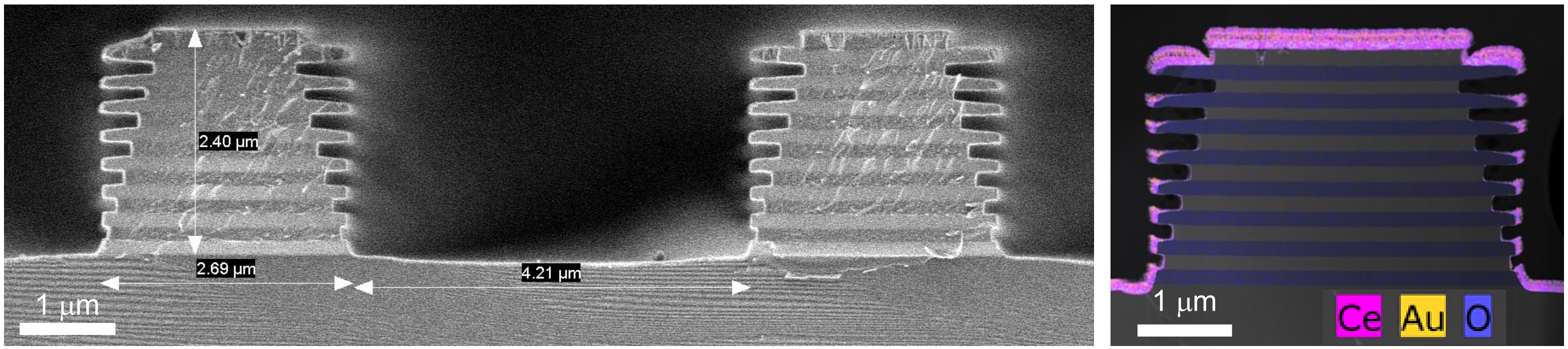
Nanostructure with Au nanoparticles before and after capping with CeO_2 layer



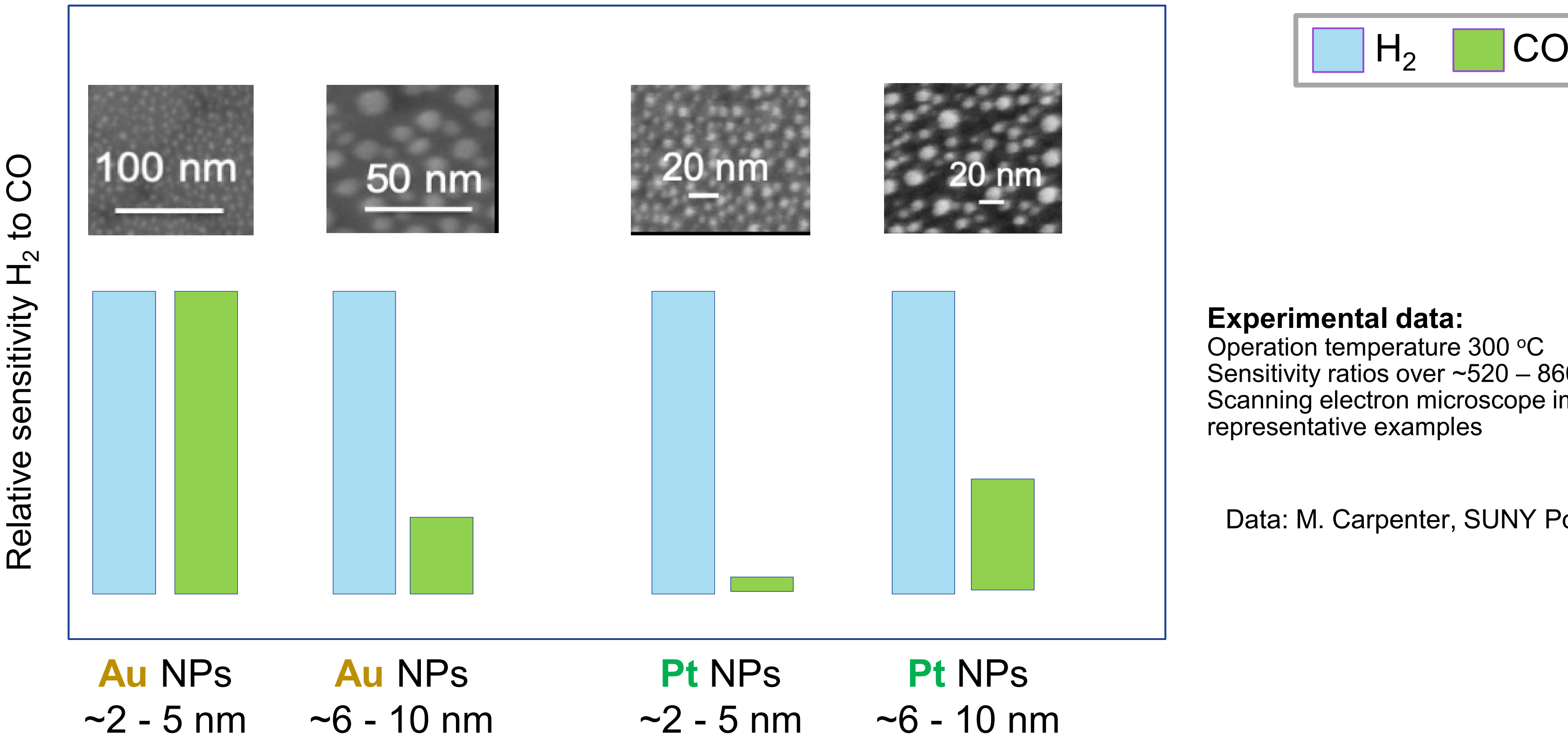
Nanostructure with Pd, Pt, and Au nanoparticles before capping with CeO_2 layer



Nanostructure with Au nanoparticles after capping with CeO_2 layer



Size and metal type effects on diversity of sensitivity to H_2 and CO



Experimental data:
Operation temperature 300 °C
Sensitivity ratios over ~520 – 860 nm
Scanning electron microscope images are representative examples

Data: M. Carpenter, SUNY Poly

Machine learning support:

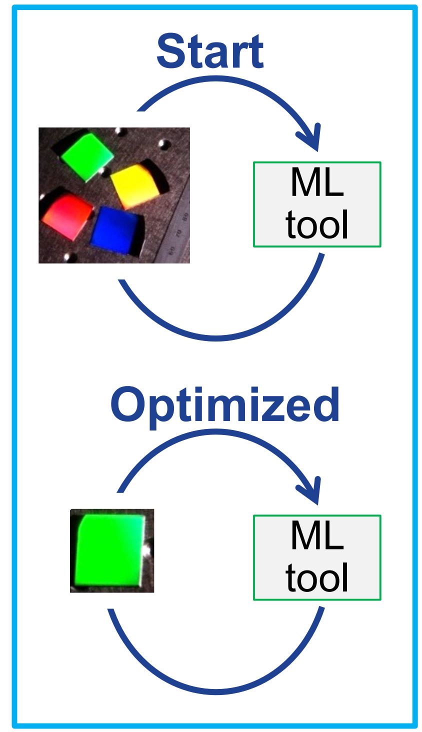
Data analytics =
a.k.a. chemometrics, multivariate statistics, machine learning (ML)

Examples of our ML tools

- Support Vector Machines (SVM)
- Principal component analysis (PCA)
- Hierarchical cluster analysis (HCA)
- Discriminant Analysis (DA)
- Artificial Neural Network (ANN)
- Independent Component Analysis (ICA)
- Partial least squares (PLS) regression
- Principal Component Regression (PCR)
- **New tools for boosting sensor stability**

R. A. Potyrailo, Multivariable sensors for ubiquitous monitoring of gases in the era of Internet of Things and Industrial Internet, *Chem. Rev*. **2016**, *116*, 11877–11923

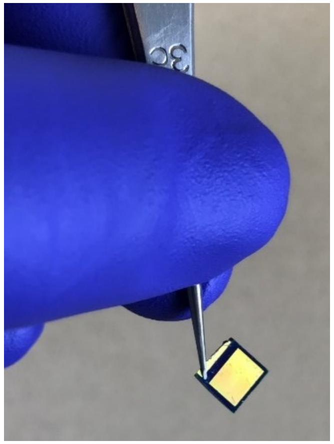
ML for sensor system optimization

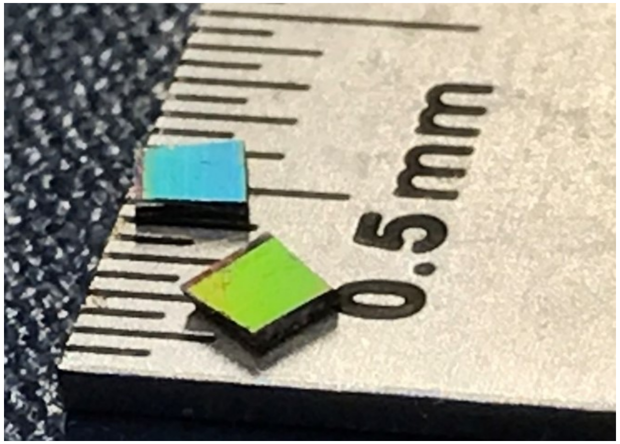


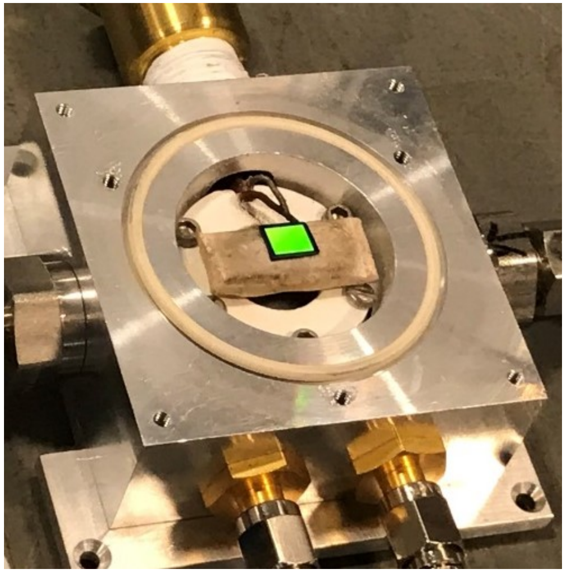
Potyrailo et al., *Faraday Transactions* **2020**

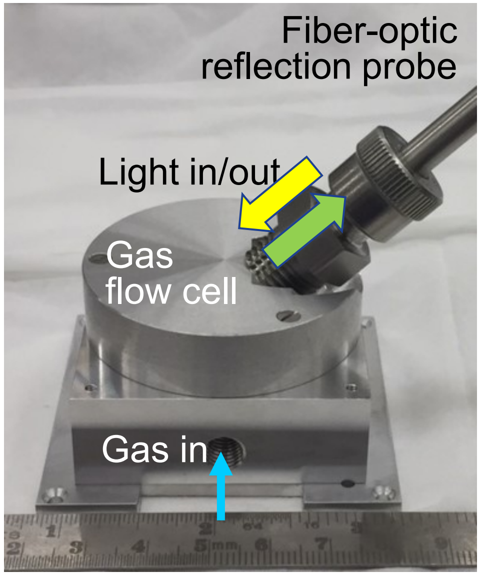
Increasing role of data analytics in high performance sensing

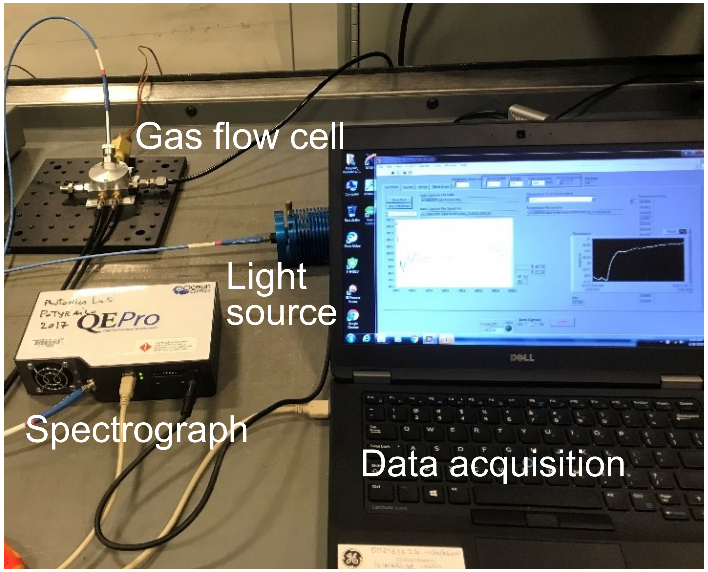
Fabricated bio-inspired photonic 3-D nanostructures and their gas testing



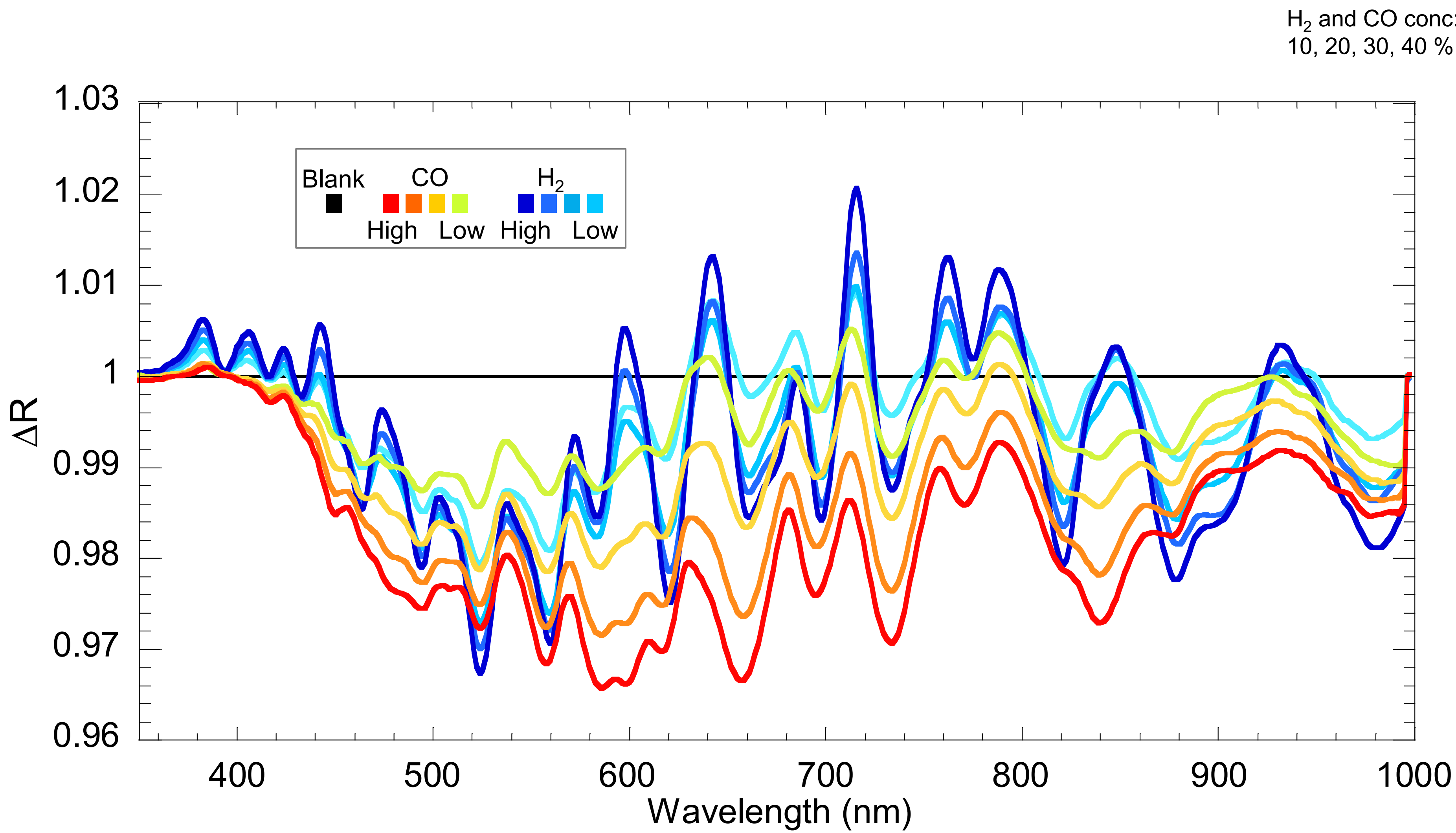






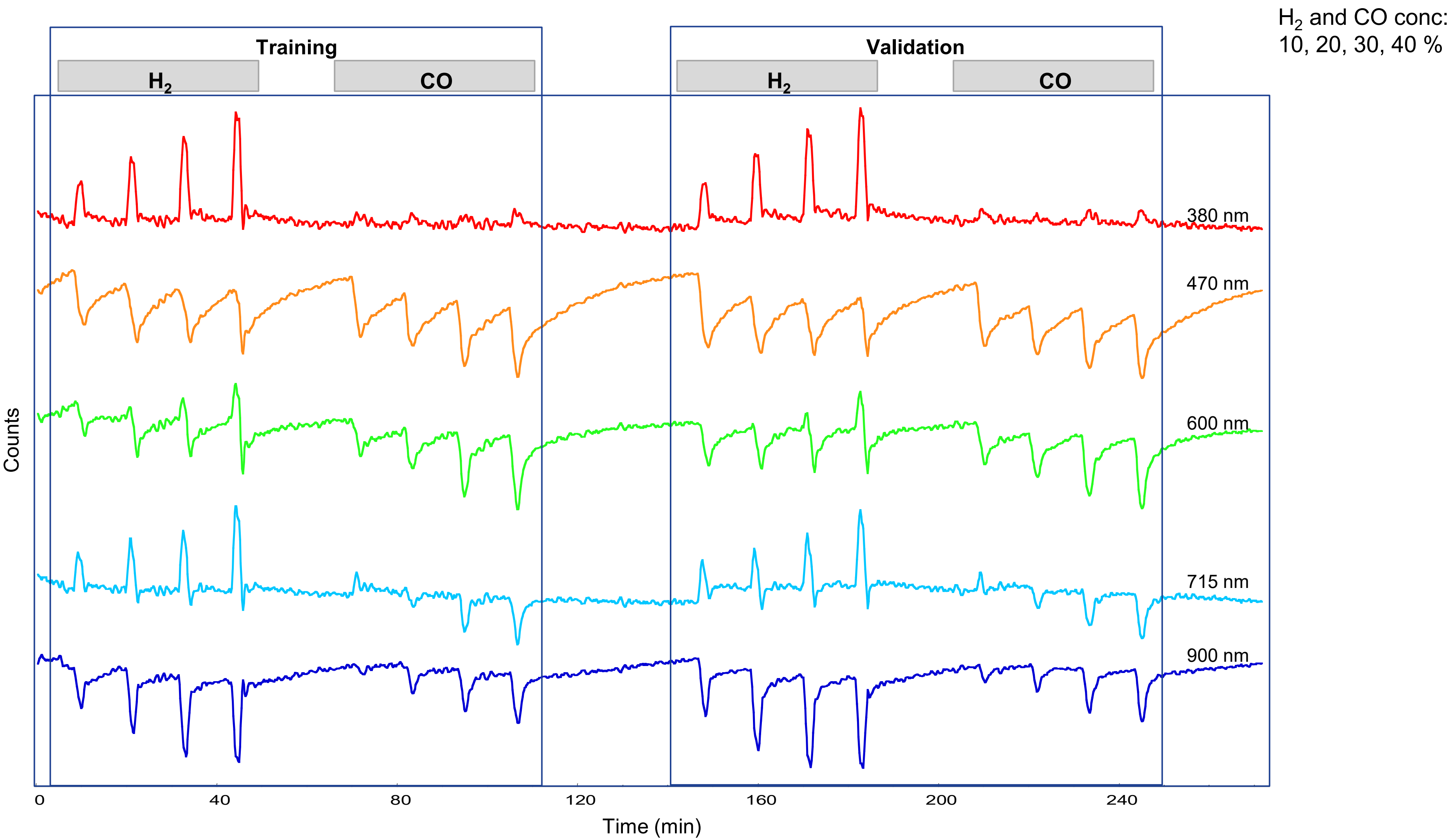


Spectral response to H_2 and CO



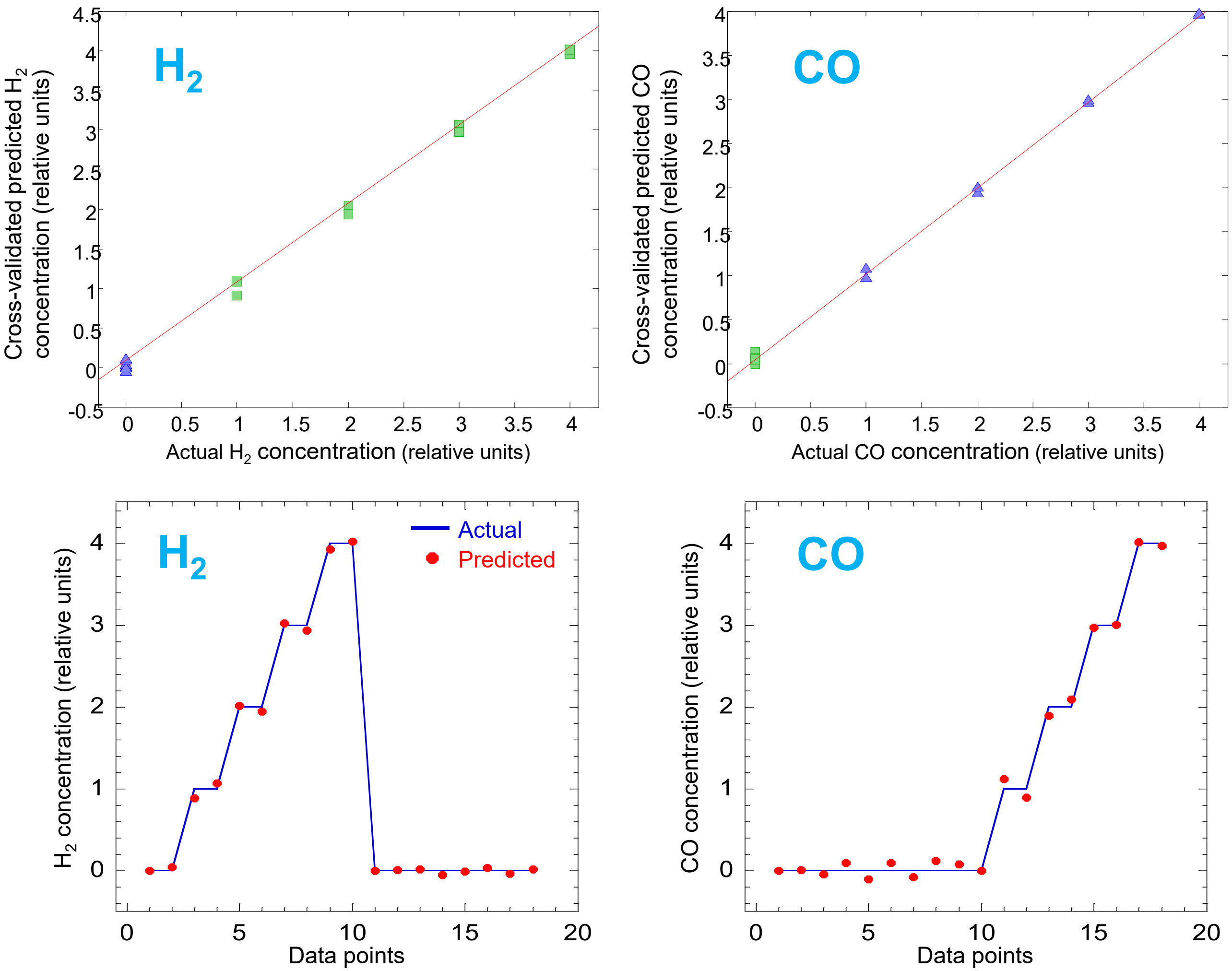
Spectral diversity of responses at different wavelengths allows discrimination of H_2 and CO gases

Dynamic response to H_2 and CO



Discrimination of H_2 and CO based on diversity of responses at different wavelengths:
(1) directions of the response, (2) relative response intensities

Cross validated prediction of H_2 and CO

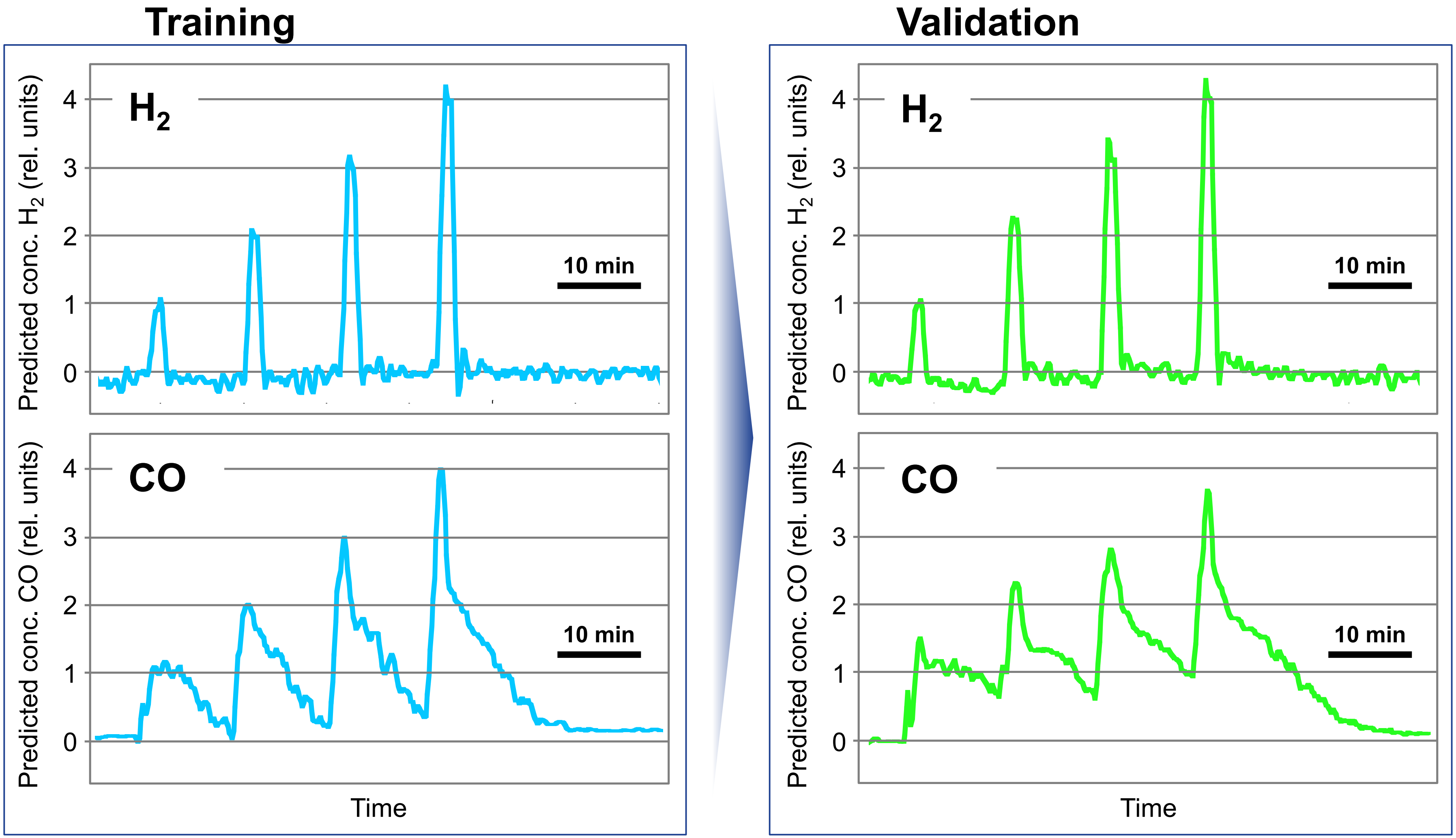


Coded 1 – 4:
H_2 and CO conc:
10, 20, 30, 40 %

Initially tested sensor ability to predict concentrations of H_2 and CO gases

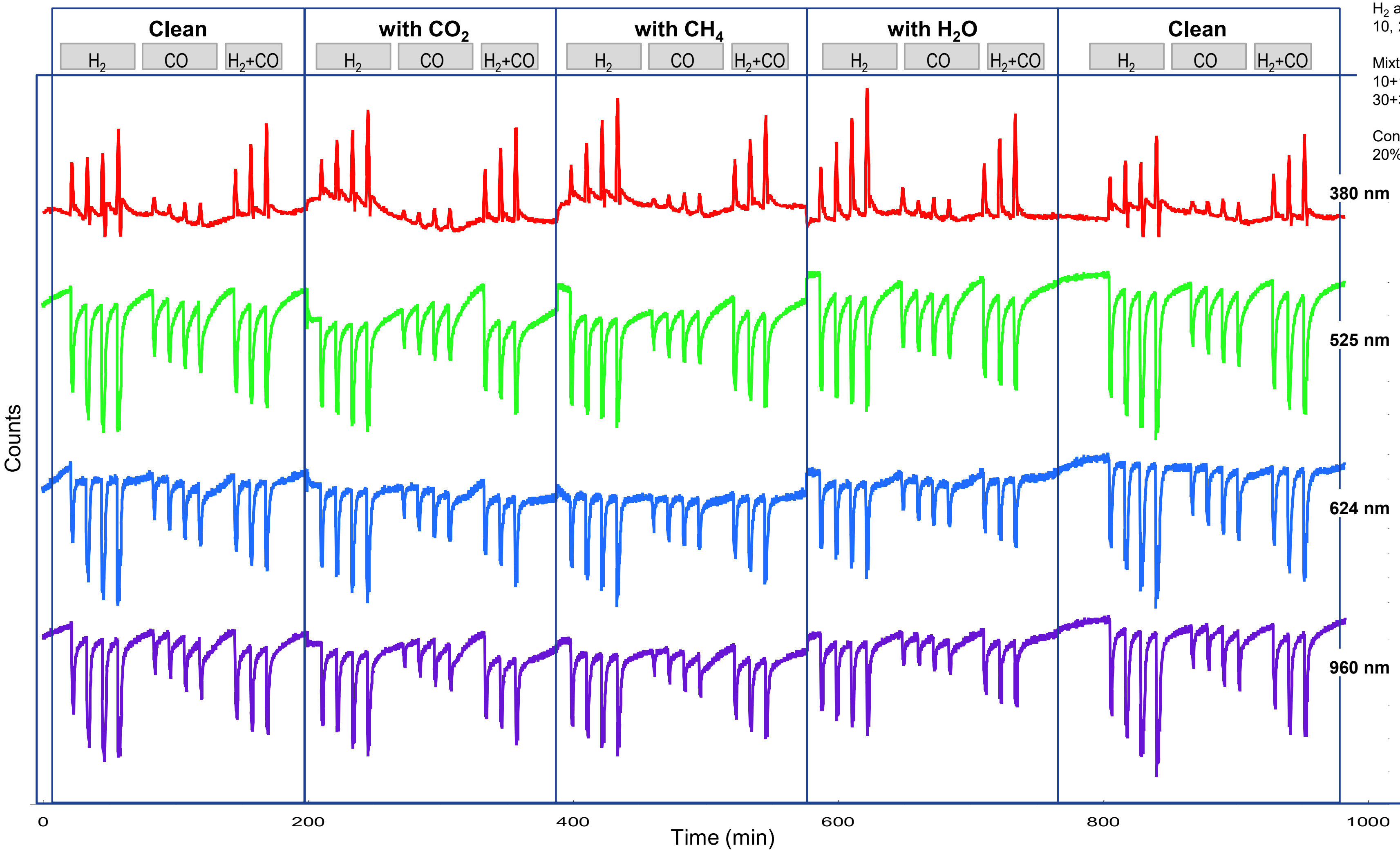
Dynamic prediction of H_2 and CO

Coded 1 – 4:
H_2 and CO conc:
10, 20, 30, 40 %



Initially tested sensor ability to predict concentrations of H_2 and CO gases

Discrimination of H_2 and CO and their mixtures and with interferences CO_2, CH_4, and H_2O



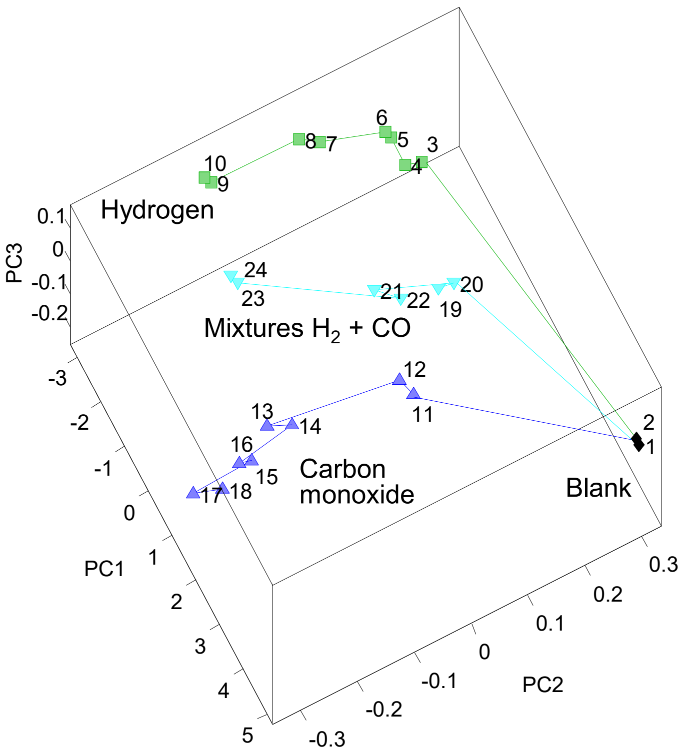
H_2 and CO conc: 10, 20, 30, 40 %

Mixtures: 10+10; 20+20, 30+30%

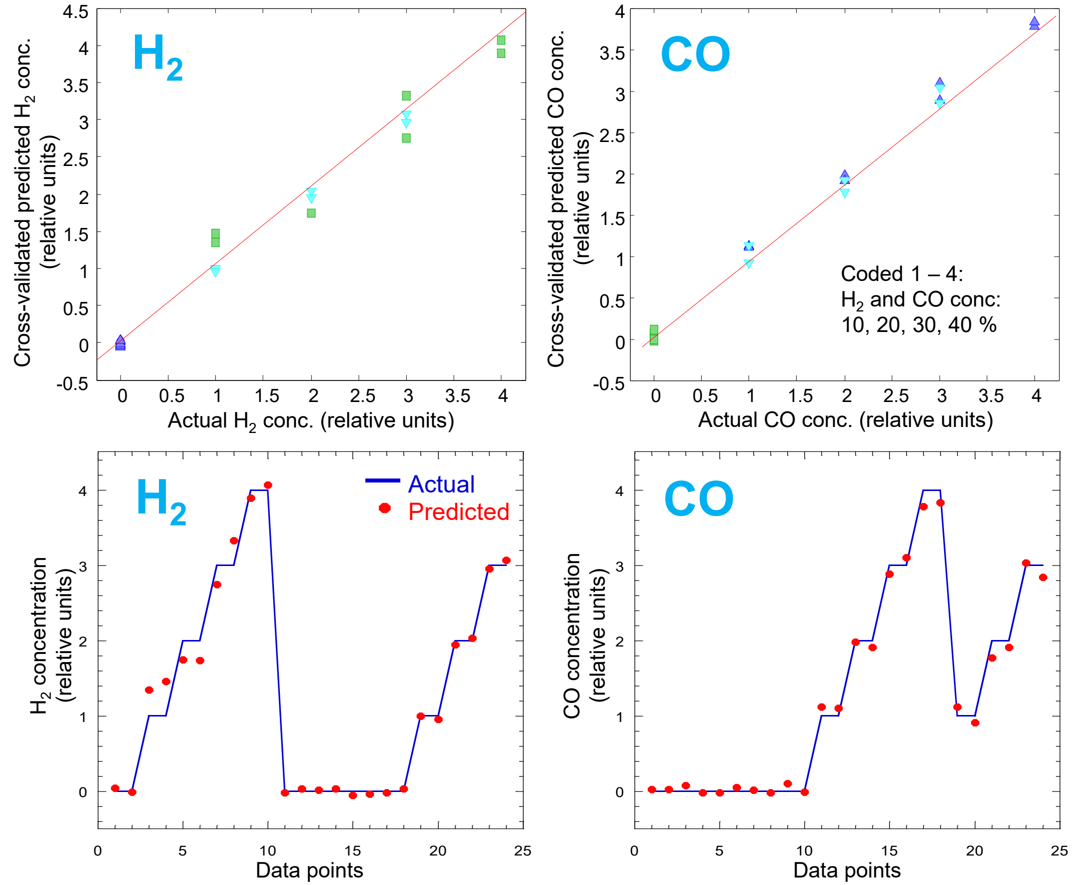
Conc interferences: 20%

Rejection of interferences is a must in sensor performance

Quantitation of H_2 and CO in mixtures

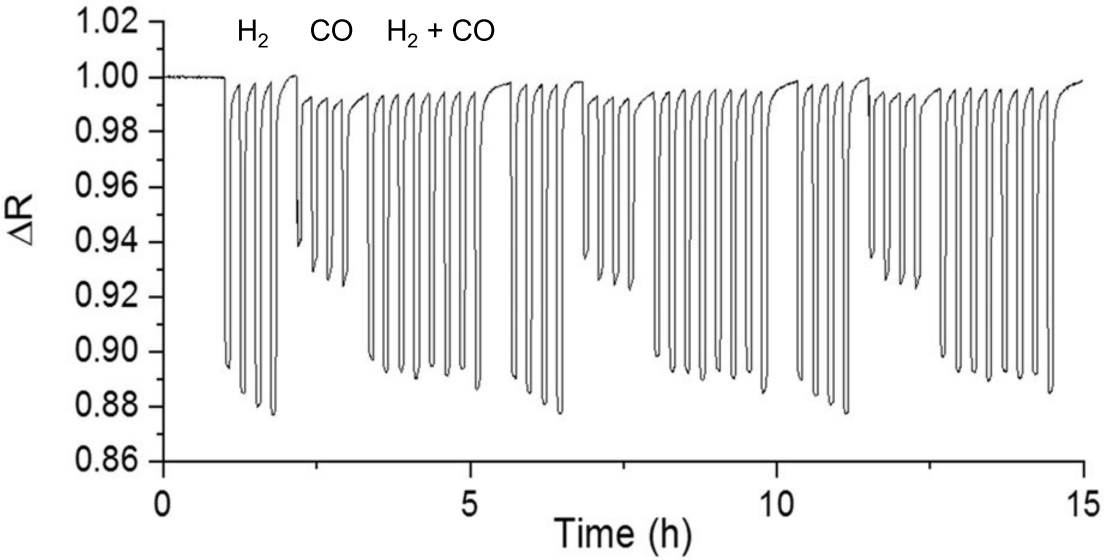


H_2 and CO conc: 10, 20, 30, 40 %
Mixtures: 10+10; 20+20, 30+30%
Conc interferences: 20%

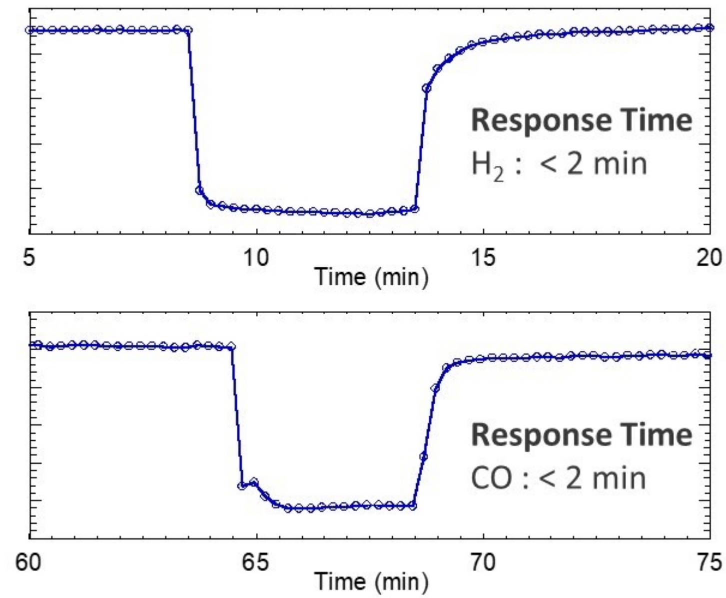


Initially demonstrated discrimination of individual gases and their mixtures
= a must in sensor performance

Example of response stability test



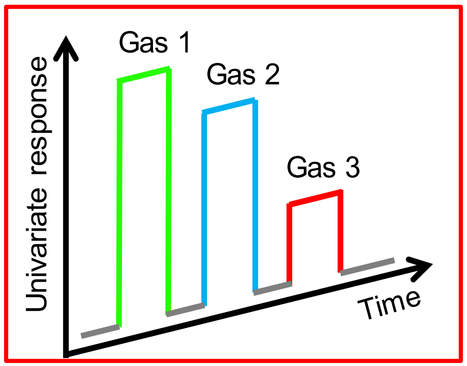
Stability: Baseline drift: <1% full scale over 15 hours

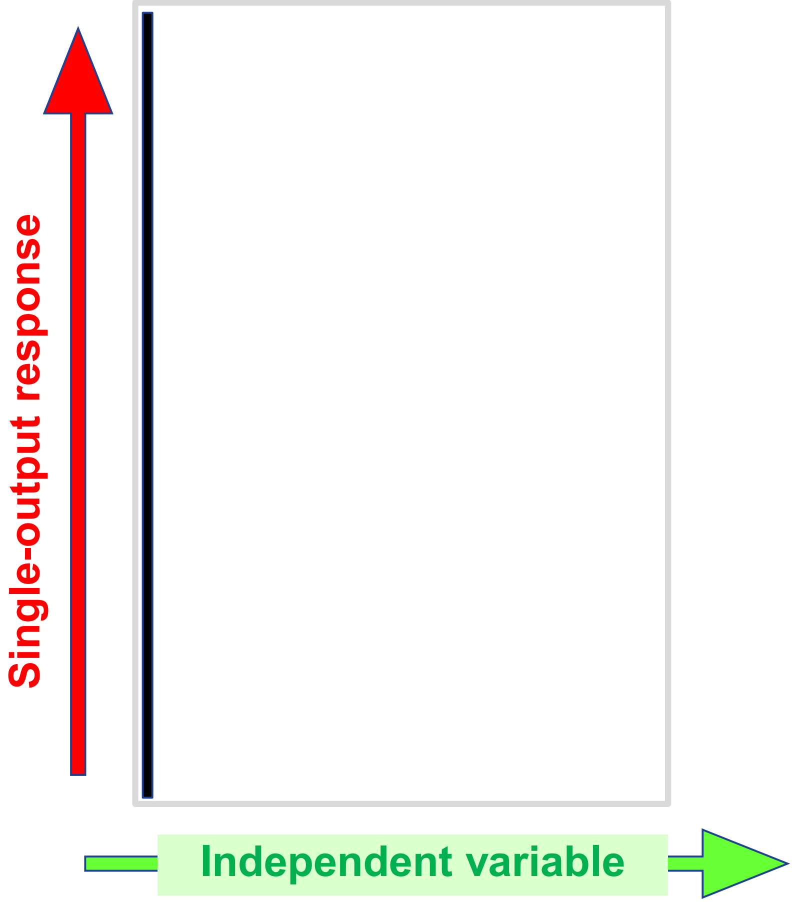


Data: M. Carpenter, SUNY Poly

GE Vision:
Boosting sensor response dimensionality

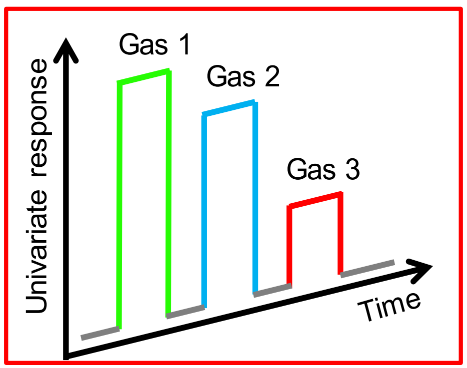
Conventional single-output sensor





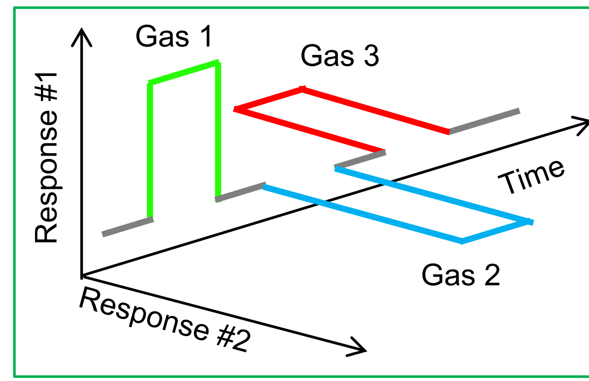
GE Vision:
Boosting sensor response dimensionality

Conventional single-output sensor



Single-output response

Developed multi-output sensor

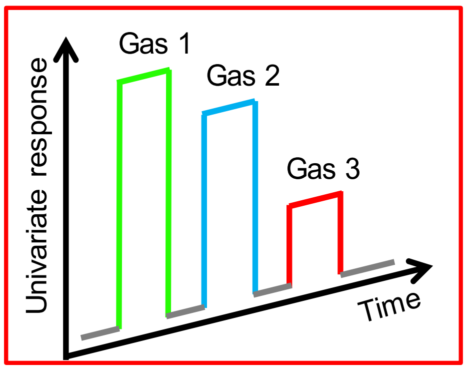


Independent variable

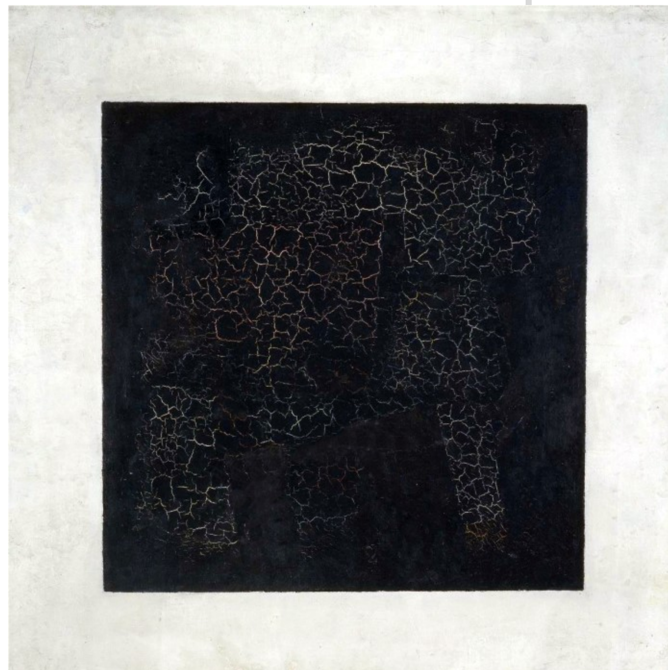
Technology accumulation in diverse areas provide previously untapped opportunities
to build new generation of sensors with complementary capabilities to traditional analytical instruments

Importance of correct independent variables in design of multivariable sensors

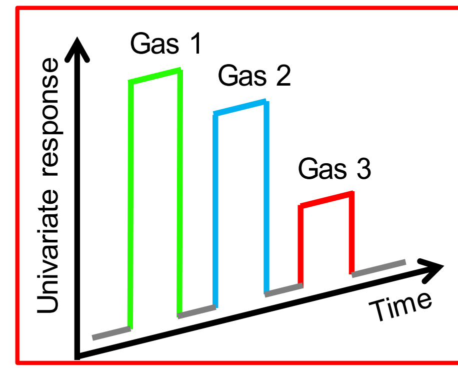
Conventional single-output sensor



Single-output response



Kazimir Malevich, Black Square, 1915, oil on linen
Tretyakov Gallery, Moscow, Russia



Independent variable

Developed design rules of nanostructures
for high temperature gas-sensing applications

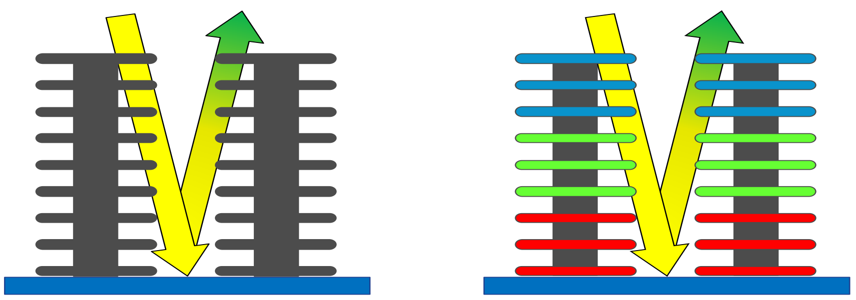
1) Gas-sensitivity:
- Catalytic reactivity of plasmonic nanoparticles incorporated in metal oxide matrix
- Gas responses driven by changes in the refractive index and extinction coefficient

2) Functions of 3D nanostructure:
- High surface area for interactions with ambient gases
- Spectral discrimination of catalytic reactions in different regions of 3D nanostructure

3) Gas-selectivity:
- Diversity of catalytic activity of metal nanoparticles
- Origins of catalytic activity diversity of metal nanoparticles: size, metal type, metal oxide type
- Spatial distribution of catalytically diverse nanoparticles for wavelength-dependent gas response

4) Diverse catalytic activity of metal nanoparticles on 3D nanostructure:
- Nanoparticles of the same noble metal but of different sizes
- Nanoparticles of the different noble metals

5) Rejection of gas interferences:
- Spectral discrimination of response of 3D nanostructure to diverse gases



Acknowledgments

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