東京大学
THE UNIVERSITY OF TOKYO

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Low-energy Integrated Multi-molecular Sensing Systems for Breath-based Health Monitoring

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JST CREST Japan Science and Technology Agency

科研費 KAKENHI

Background: DX and IoT

In order to drive the Digital Transformation (DX), robust sensors that can be used repeatedly over an extremely long period of time are demanded.

Target: Chemical Substances

Chemical Sensor

In our living space,
- Kinds
- Concentrations

of molecules should be monitored

Target: acceleration, motion, strain, temperature

Physical Sensor

Activity Tracker
Fitbit™

Strain Gauge
Resensys SensSpot™

Big Data of Physical Quantity

Performance to be achieved

× Selective Recognition
× Long lifetime
× Low-energy consumption

Open question

Is it possible to realize a chemical sensor (molecular sensor) with molecular discrimination ability which can be repeatedly used for an ultra-long period of time at low energy?

Breath Diagnostics

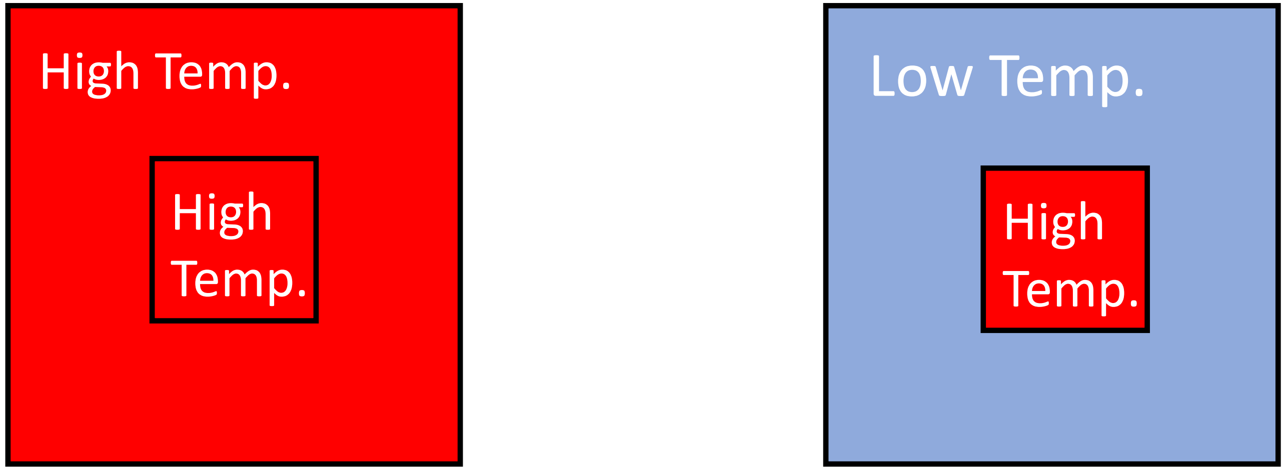
- Human breath contains more than one thousands of compounds.
- Many compounds are by-products of metabolic processes.
- Some compounds are related to diseases and thus detection of these compounds make it possible to realize non-invasive diagnosis.

VOC	Disease
Acetone	Diabetes mellitus
Ammonia	Renal disease
Methane, Hydrogen	Colonic fermentation
Isoprene	Hyperlipidemia
Nonanal etc.	Lung cancer

It is required to detect very small amounts of molecules in real time from exhaled *breath with high relative humidity* ~ 90% (30,000 ppm).

Low-energy Molecular Sensor
By Joule Heating

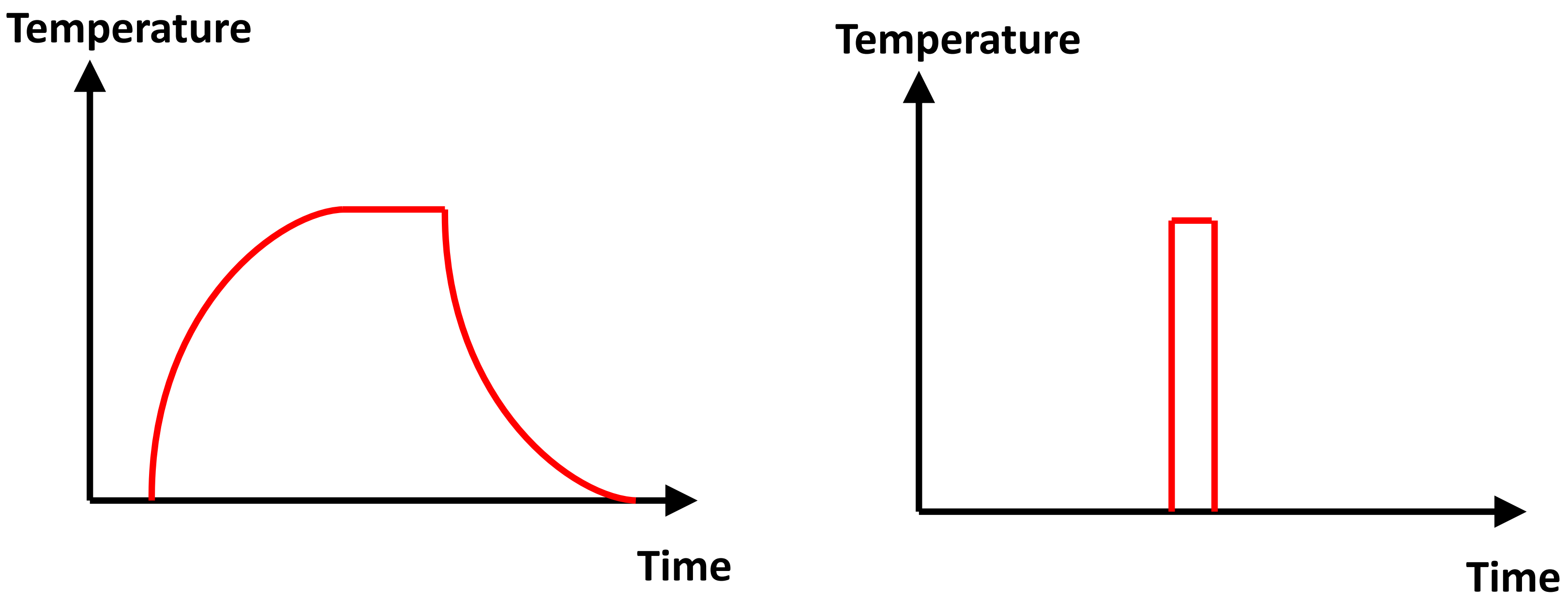
Objective: Localization of heat in space



Increase the temperature only where necessary.

Precisely control the temperature at any location at any time interval.

Objective: Localization of heat in time



Heat up the device during necessary time.

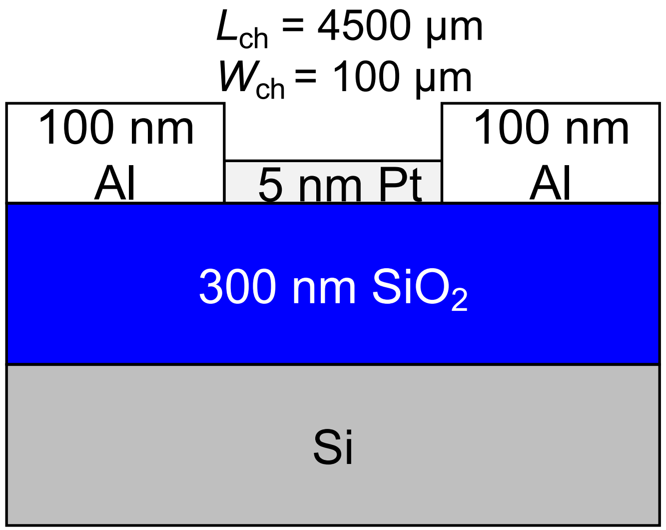
The temperature at any time can be precisely controlled.

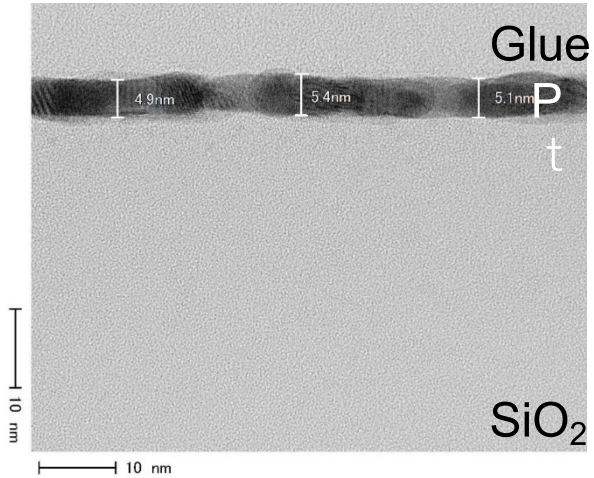
Outline

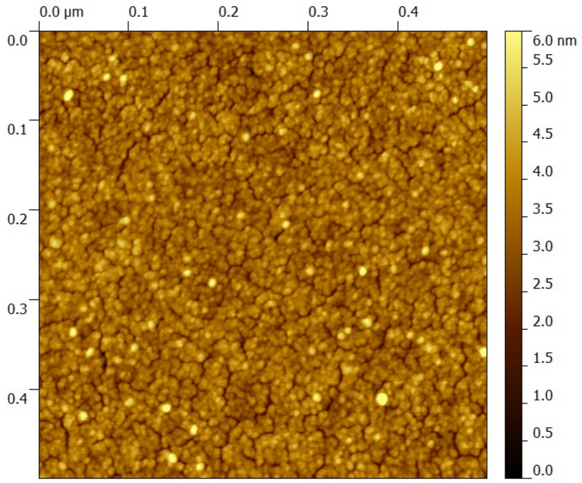
- **Pt Nanosheet: H_2 Sensing in Breath**
- **Integrated Pt & PtRh nanosheets: H_2 & NH_3 Sensing**
- **Graphene Multi-functional Sensor: H_2 & H_2O Sensing**
- **CoOEP-functionalized Graphene Sensor: NH_3 Sensing in Breath**

Pt Nanosheet Hydrogen Sensor

Platinum Nanosheet Sensor: Structure





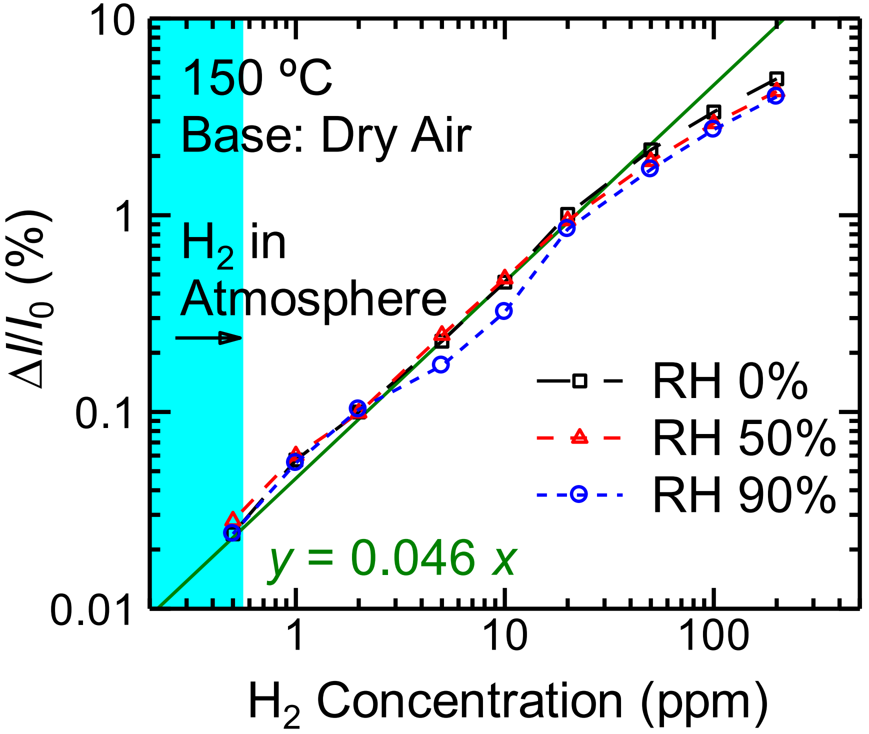


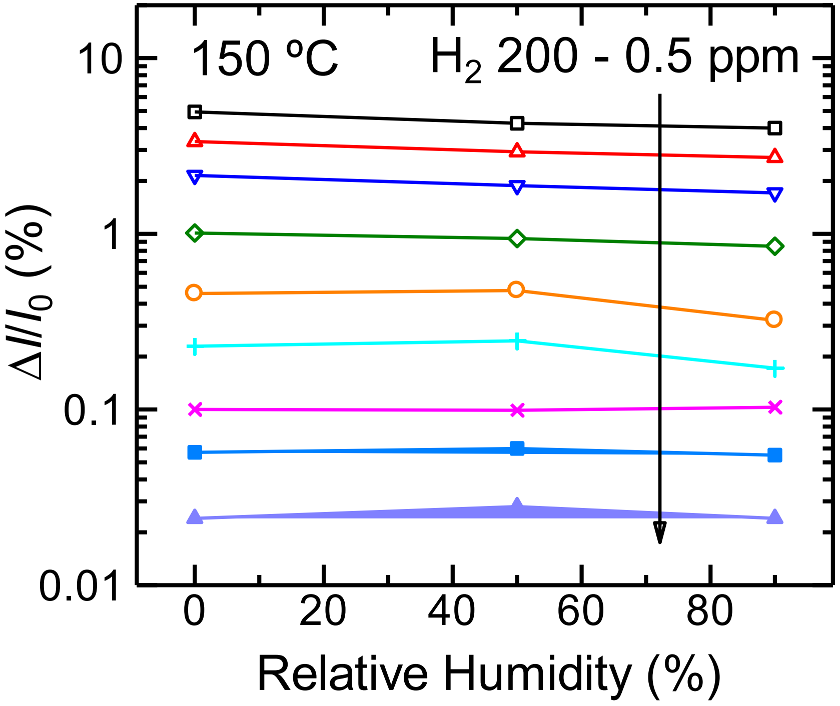
T. Tanaka *et al.*, *Sens. Act. B*, 258, 913-919 (2018).

- 5-nm-thick Platinum (Pt) film with thick Al contact pads.
- The thickness of Pt is relatively uniform.
- There are some cracks. However, not dots but film is formed.

Hydrogen Concentration Dependence

H_2 Conc. and H_2O Conc. (Relative Humidity) Dependence

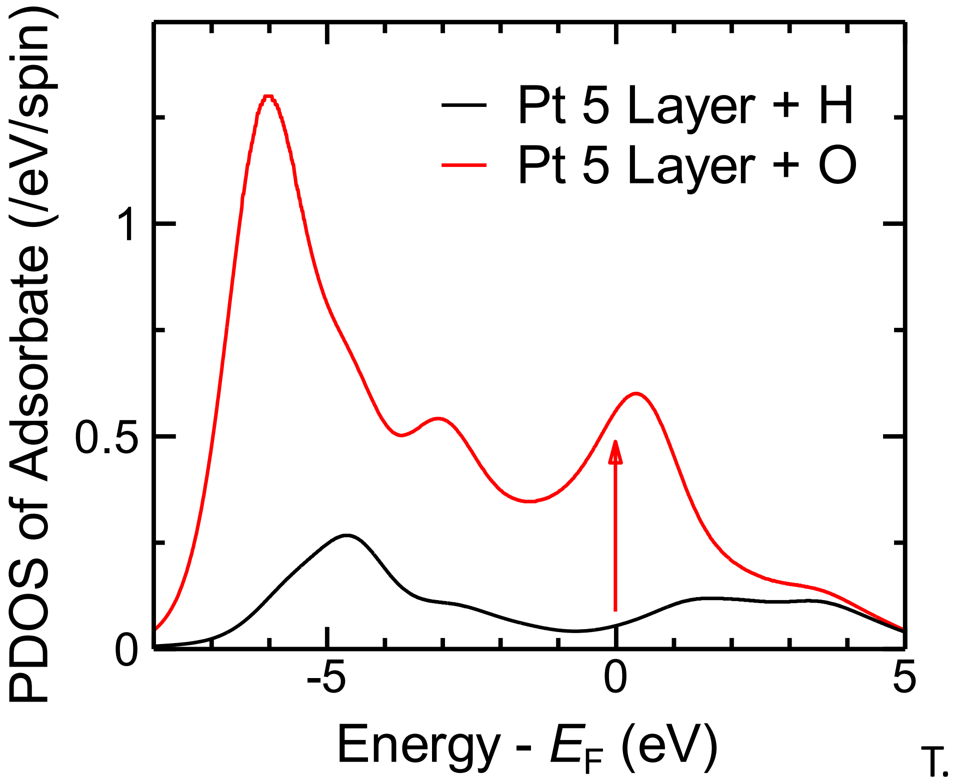


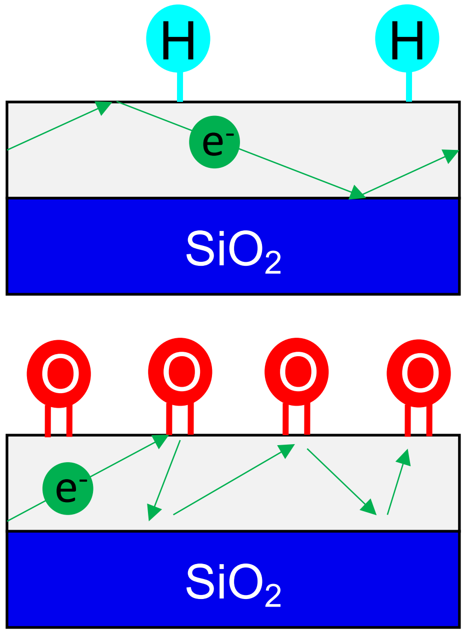


T. Tanaka *et al.*, *Sens. Act. B*, 258, 913-919 (2018).

Pt nano-sheet sensors detect H_2 ranging from 0.5ppm to 100 ppm. The response to H_2 concentration is almost linear and is not affected by the relative humidity.

Mechanisms: Carrier Scattering at Surface

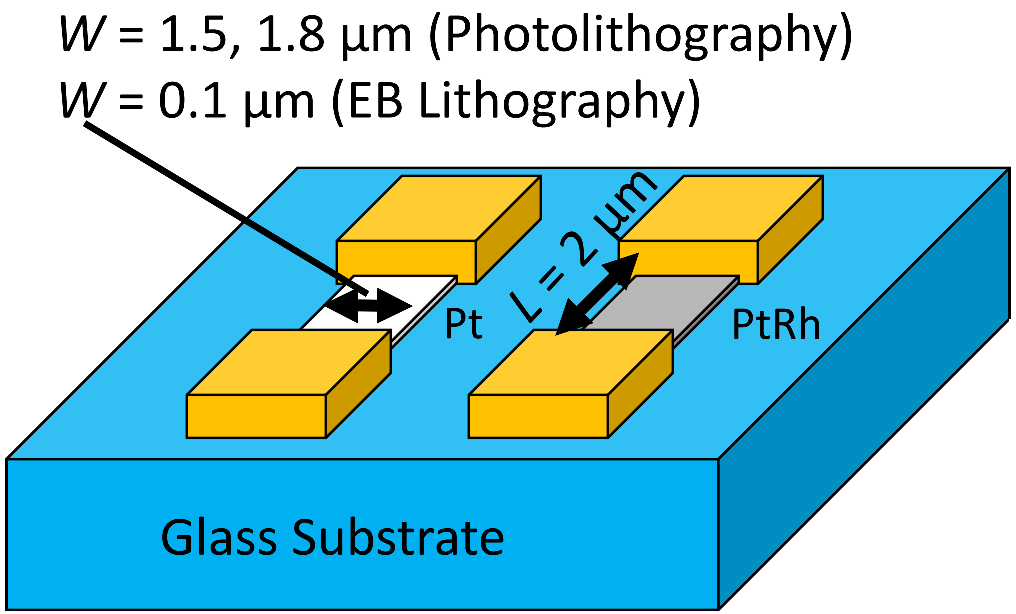




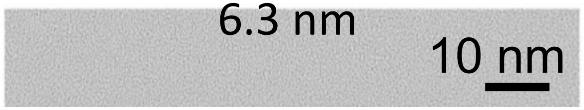
T. Tanaka *et al.*, *Sens. Act. B*, 258, 913-919 (2018).

PDOS is much higher at oxygen-terminated Pt surfaces than at hydrogen terminated surfaces. Larger PDOS results in higher scattering rate of electrons. Thus, the resistivity is higher when the surface is terminated more by oxygens.

Integrated Nanosheet Sensors



Pt Nanosheet

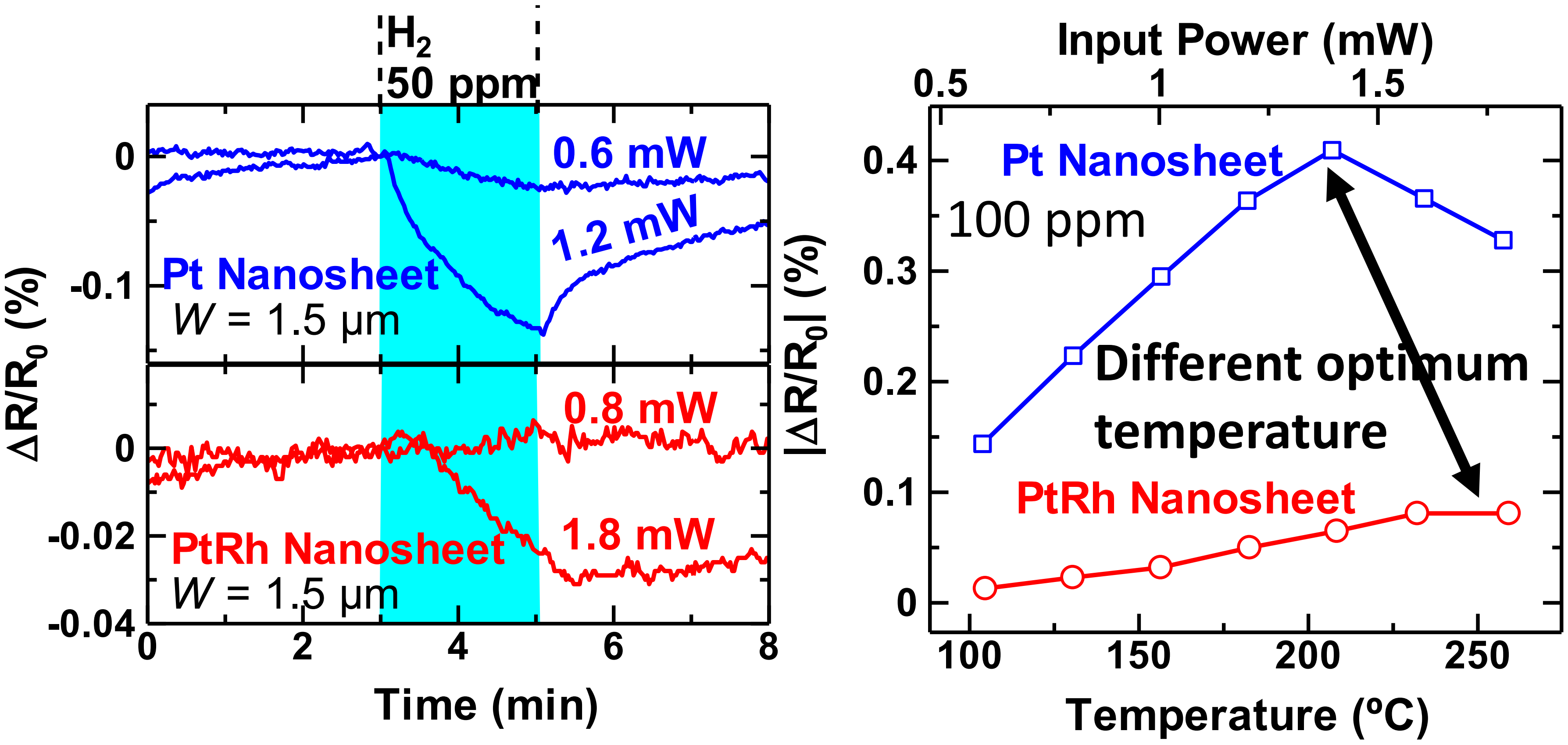


PtRh Nanosheet

Array of polycrystalline metal nanosheets were fabricated.

T. Tanaka et al., *IEEE Trans. Electron Dev.*, **66**, 5393, 2019.

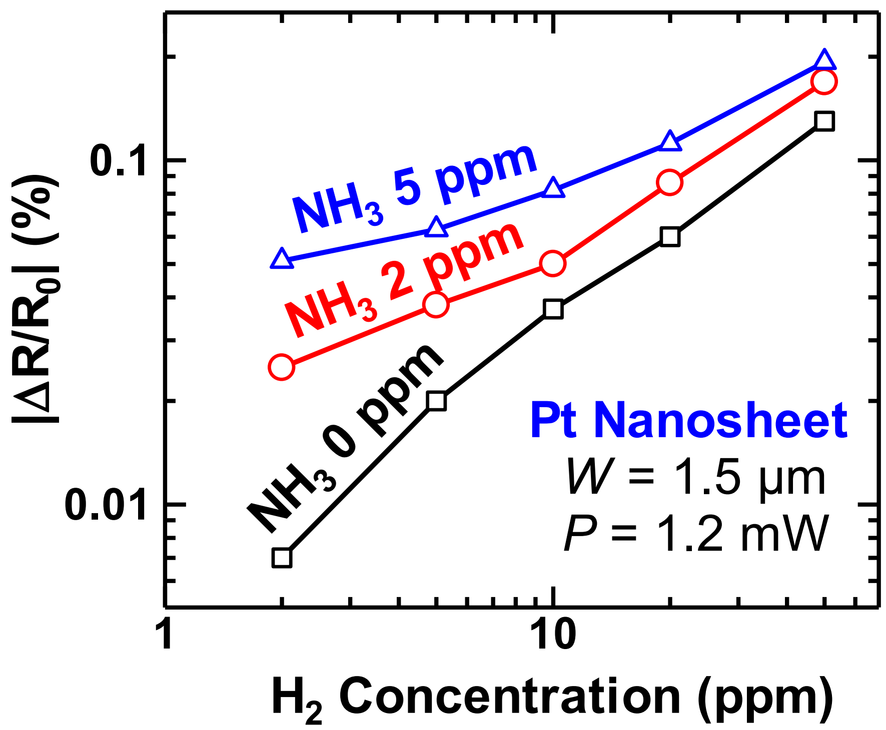
Integration of two kinds of nanosheet sensors

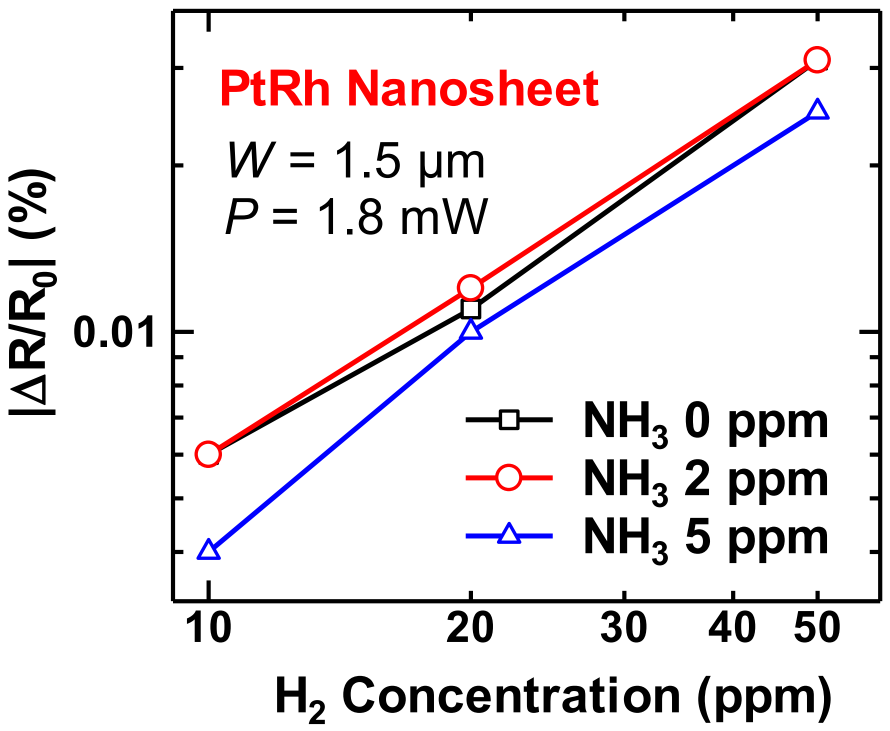


T. Tanaka, *et al.*, IEEE Trans. Electron Devices **66**, 5393 (2019).

The Pt nanosheet and PtRh nanosheet were operated at their respective optimum temperature

Response of each sensor to H_2 and NH_3





T. Tanaka, *et al*., IEEE Trans. Electron Devices **66**, 5393 (2019).

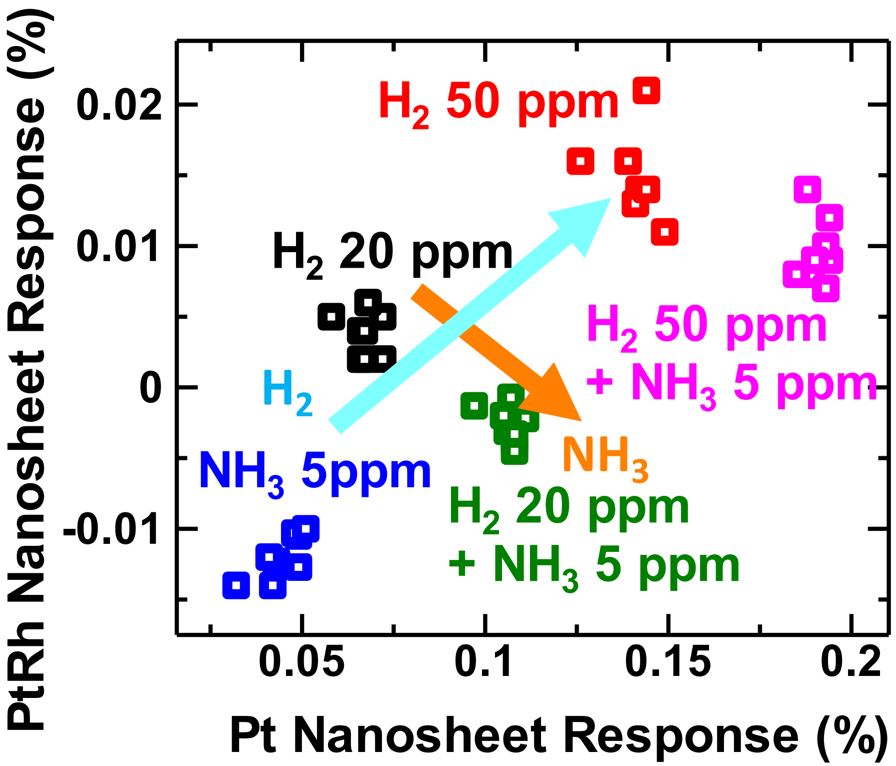
Responds to NH_3

Does not respond to NH_3

Pt nanosheets and PtRh nanosheets respond differently to ammonia

Identification of Concentration of Each Molecular Component in Mixed Gas

Five combinations of H_2 and NH_3 concentrations were tested.

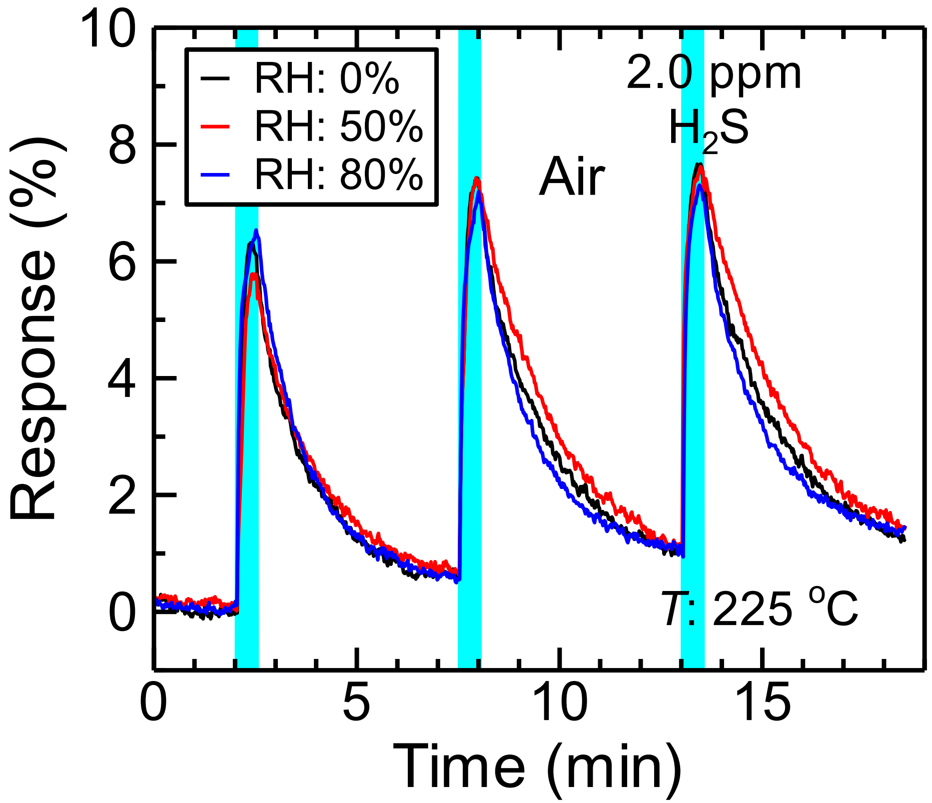


T. Tanaka, *et al.*, IEEE Trans. Electron Devices **66**, 5393 (2019).

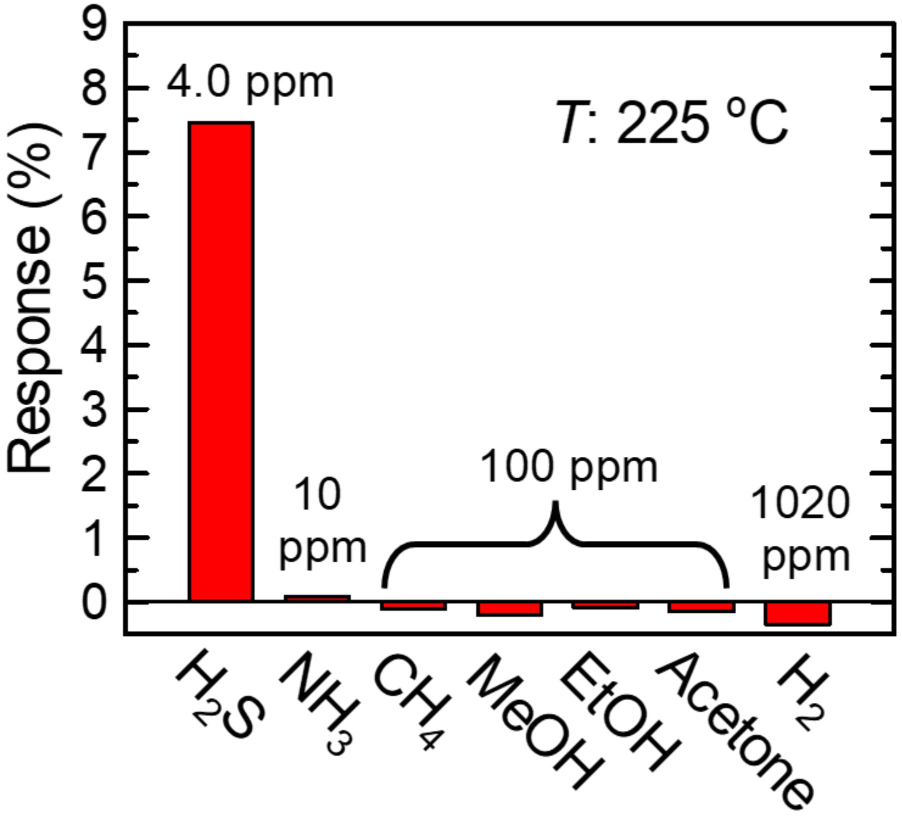
Successfully discriminated H_2 and NH_3 concentrations in gas mixtures

Au Nanosheet H_2S Sensor: Response & Selectivity

Sensor Response to H_2S with various RH's.



Response to various disturbing gas

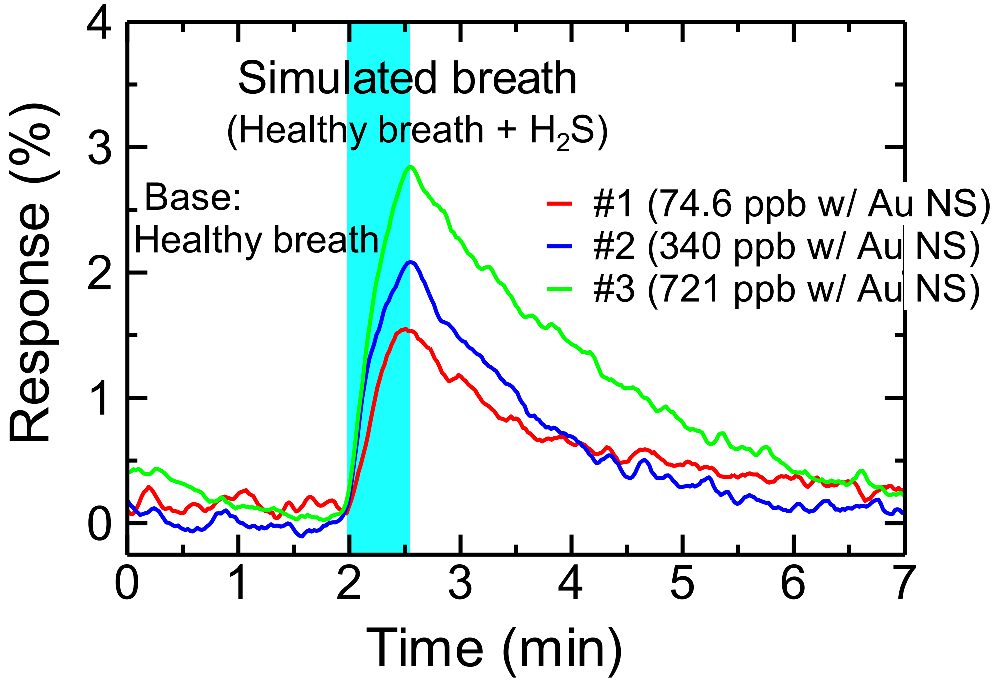


T. Kato *et al.*, *ACS Sens.*, 9, 708–716 (2024).

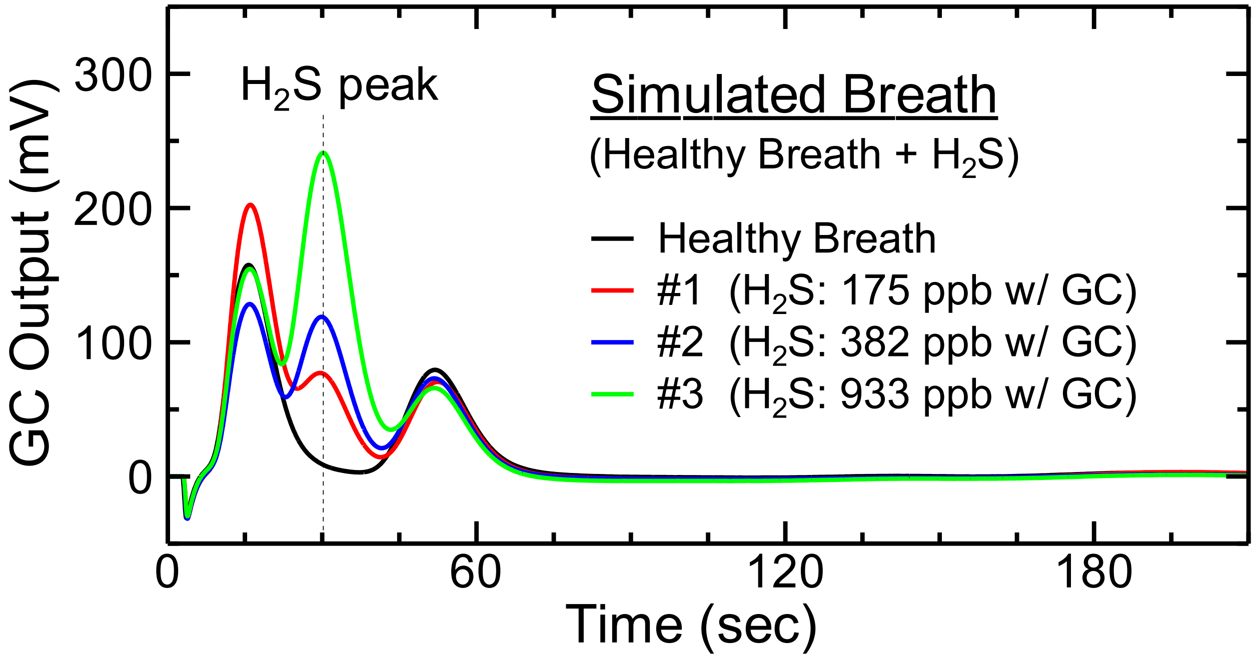
湿度や呼気中に多く含まれる夾雑ガスに対して不感であり，
すなわち選択性が高い．

H_2S Concentration Measurement in Breath

Sensor response to H_2S in breath



Output of gas chromatograph (GC)



Sensitive to hydrogen sulfide in exhaled breath.

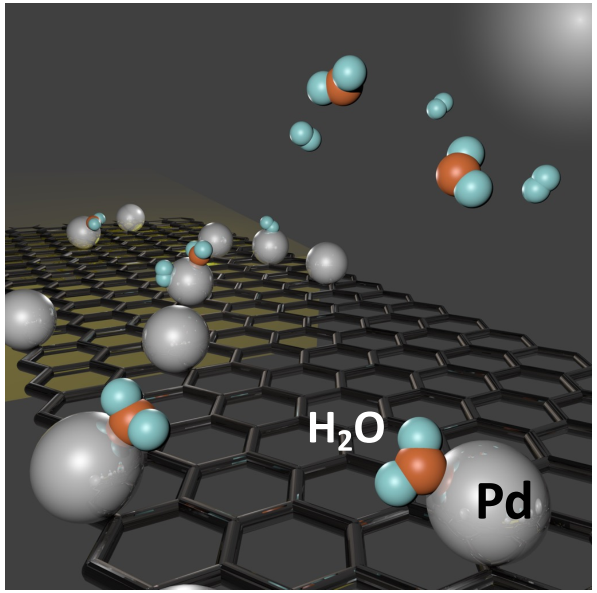
T. Kato *et al., ACS Sens.*, 9, 708–716 (2024).

Sample	Au NS Sensor (ppb)	GC (ppb)	Δ(GC-Au NS)/GC (%)
#1	74.6	175	57.4
#2	340	382	11.0
#3	721	933	22.7

Pd-Functionalized, Suspended Graphene Nanosheet for Fast, Low-Energy Multimolecular Sensors

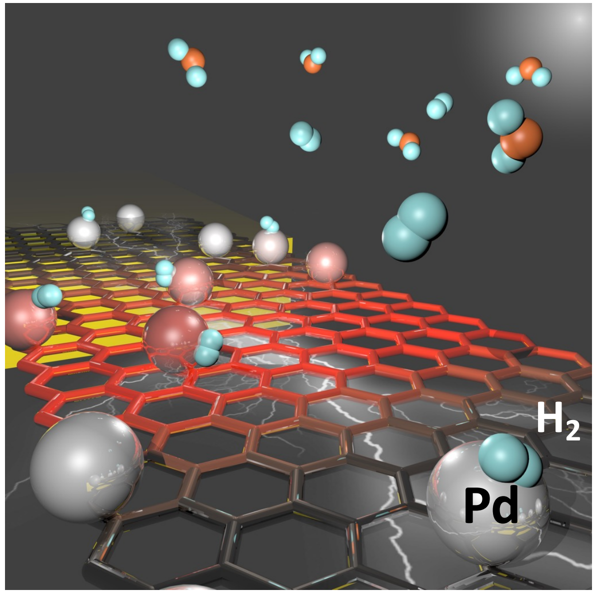
Multi-Functionality by Joule Heating

Low Temperature



Water adsorption on Pd NDs

High Temperature

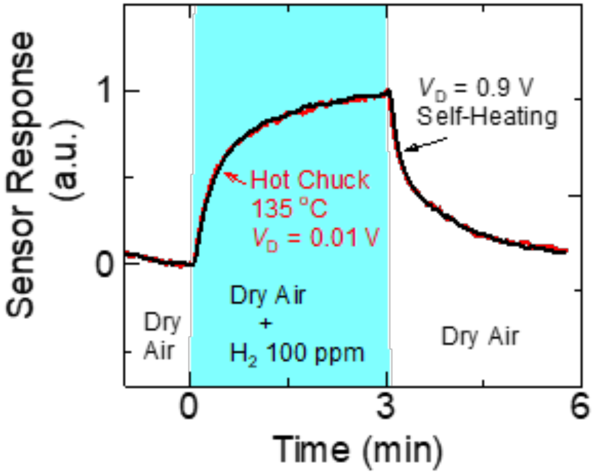


Hydrogen dissociation on Pd NDs

By increasing the temperature by Joule heating, Pd nanodot catalysts are activated.

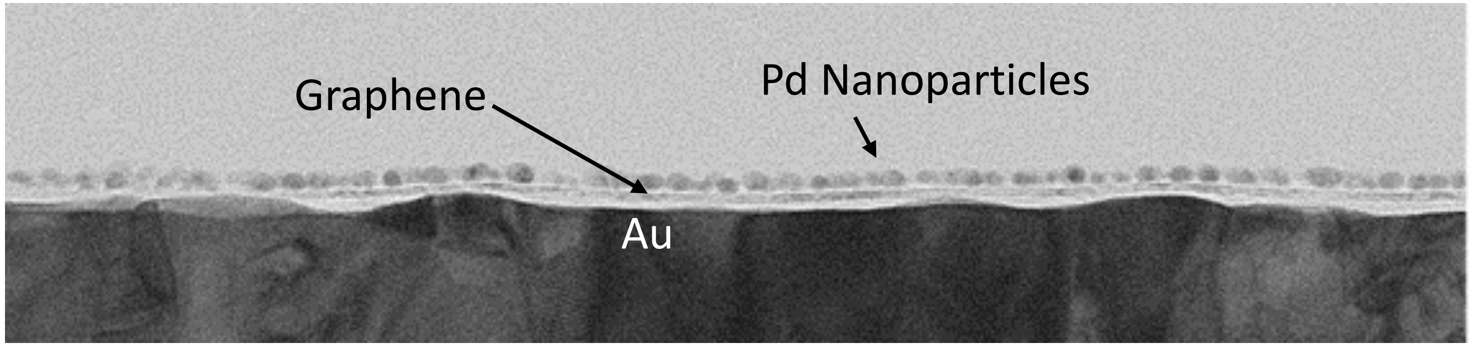
Suspended Graphene: Heater vs Self-Heating

Heater versus Self-Heating



The temperature of graphene should be increased, based on sensing data at different biases and temperatures.

However, because of the cooling effect by Au electrode, much smaller ΔT was estimated from simple model.



Interface between graphene and gold electrode

T. Yokoyama et al., *ACS Appl. Nano Mater.*, **1**, 3886, 2018.

Self-Heating is successfully achieved in suspended graphene.

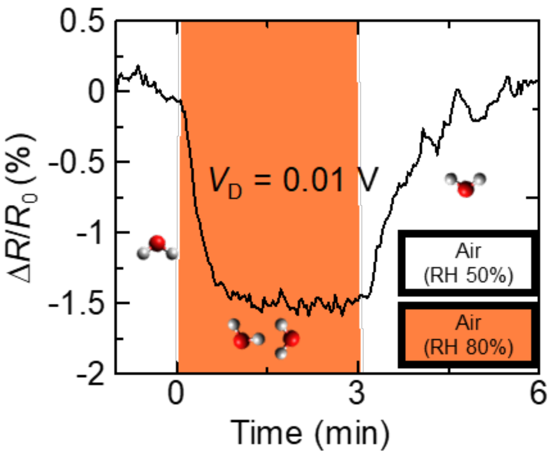
Hydrogen in humid air is detectable with low energy.

Demonstration of Multi-molecular Sensor

10-ppm hydrogen in synthetic breath is detected.

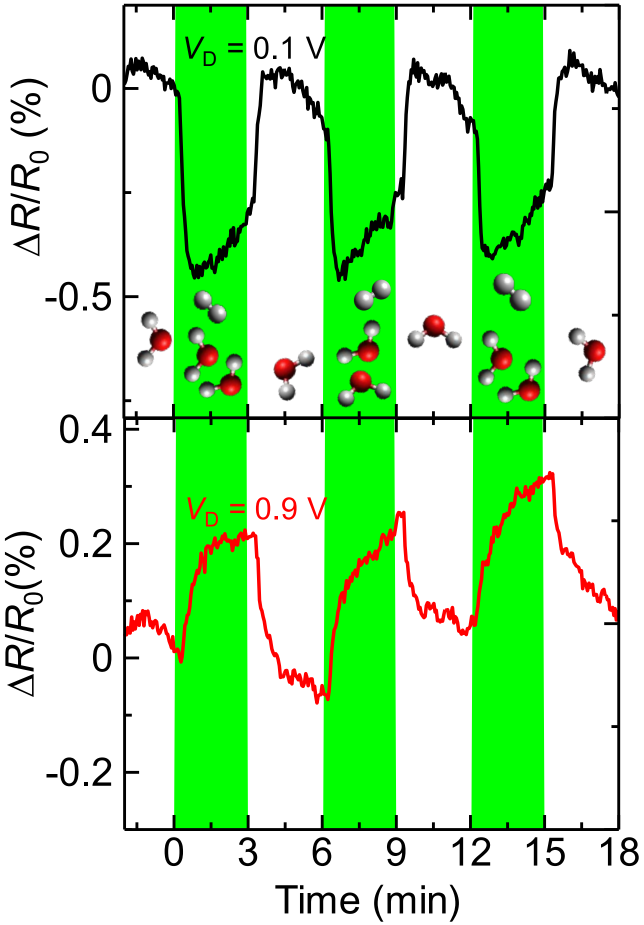
	RH	H_2
Air	50%	0 ppm
Breath	80%	10 ppm

RH50%→RH80%→RH50%



Humidity change is detected.

RH50%→RH80%(H_2 10 ppm)→RH50%



V_D=0.1V

0.019 mW, 26°C

Humidity Sensor

V_D=0.9V

1.55 mW, 135°C

Hydrogen Sensor

T. Yokoyama et al., *ACS Appl. Nano Mater.*, **1**, 3886, 2018.

Single self-heated sensor can detect two types of molecules (Water and hydrogen) by modifying input voltage.

Cooperation is necessary

- **Design Tool for Sensors**
  - **First-principle calculation**
  - **Molecular dynamics**
  - **Thermal properties**
  - **Reliable material parameters**
- **Fabrication Process**
- **Data Analysis**

Summary

- Joule self-heating is effective to realize low-power, highly-sensitive sensors.
- Low-concentration H_2 in wet air & breath are detected by Pt resistive sensor.
- Gas sensors operating at different temperatures were integrated (Pt & PtRh resistive sensors). Low-power and ppm-level H_2 and NH_3 gas sensing was realized.
- Highly selective Au nanosheet H2S sensors were developed.
- By utilizing Joule self heating, multifunctional suspended graphene sensors were realized.

Self-heated nano sensors are promising to drive DX and to realize IoT society.