TECHNICAL UNIVERSITY OF LIBEREC
Faculty of Mechatronics, Informatics
and Interdisciplinary Studies

Graphene sensors – detection of gases

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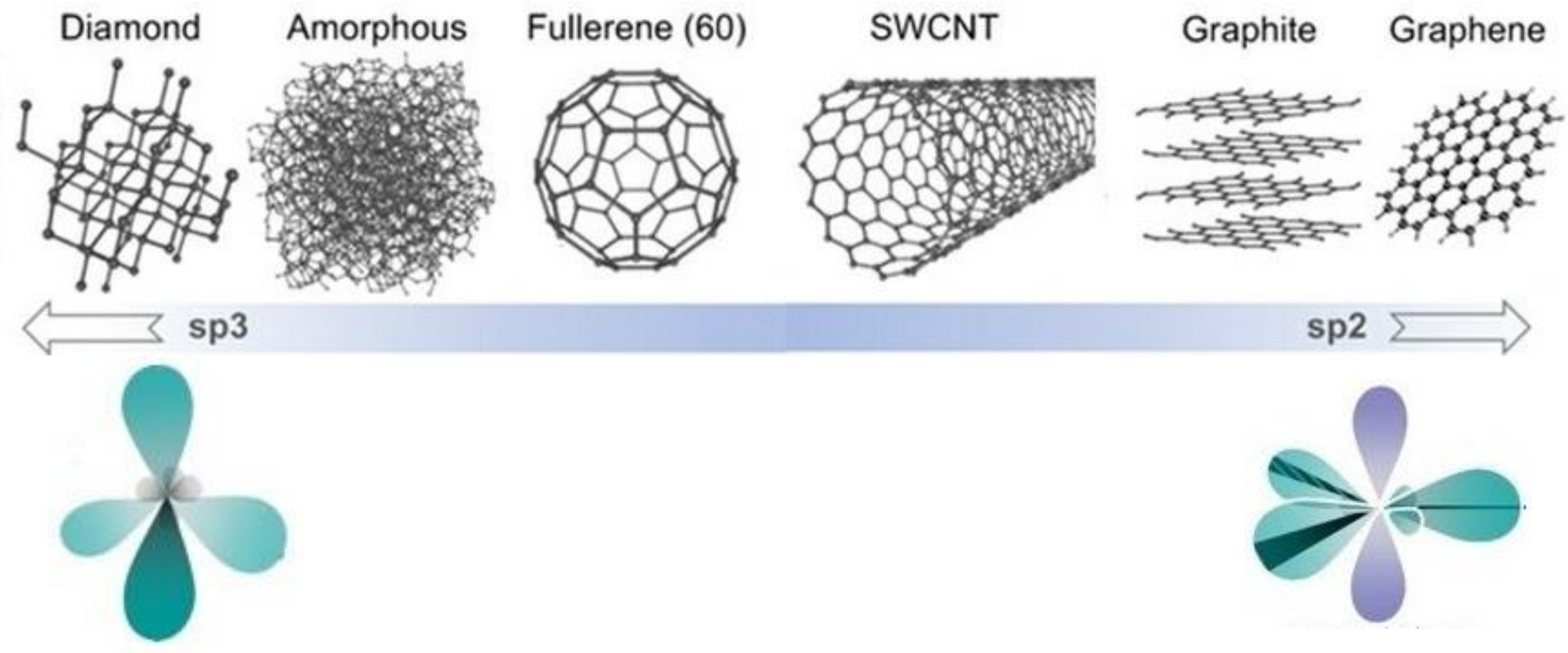
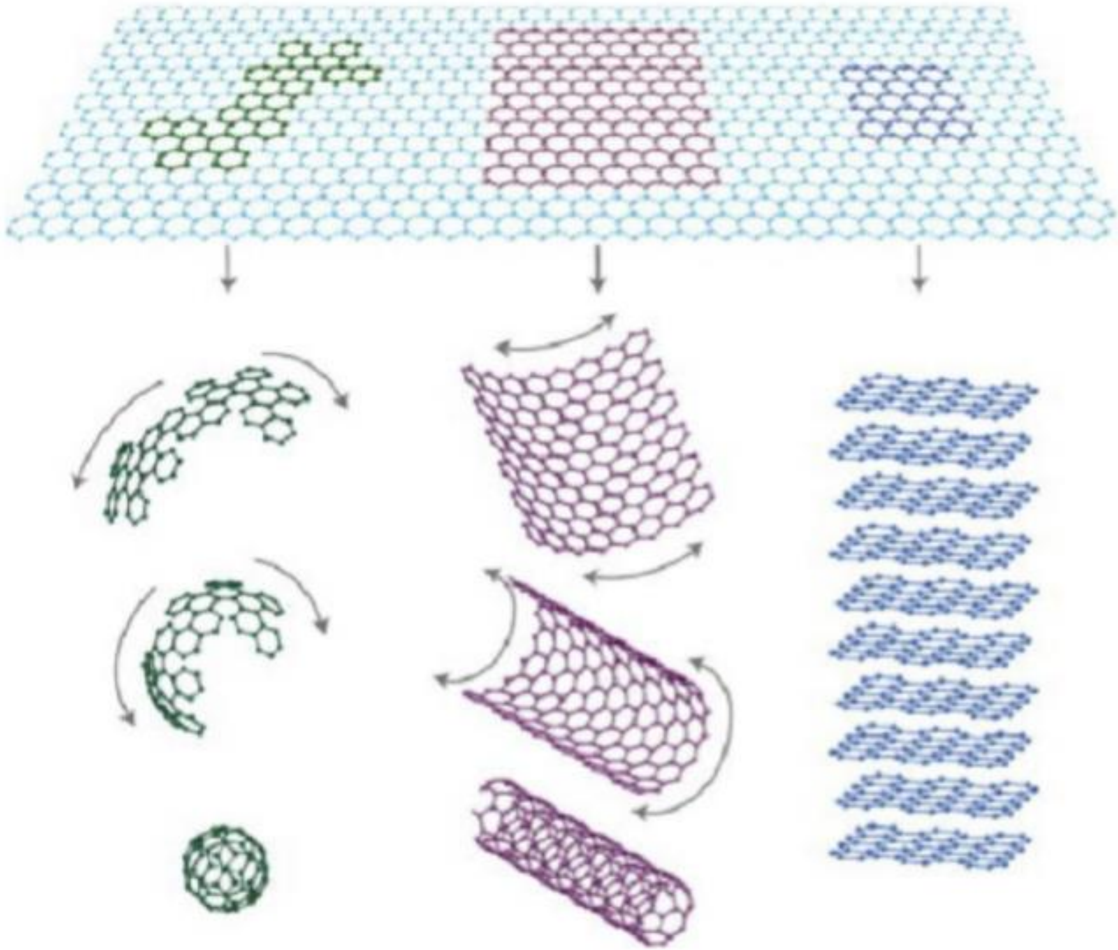
Chapters of Nanostructures
TU Liberec

Allotropes of carbon



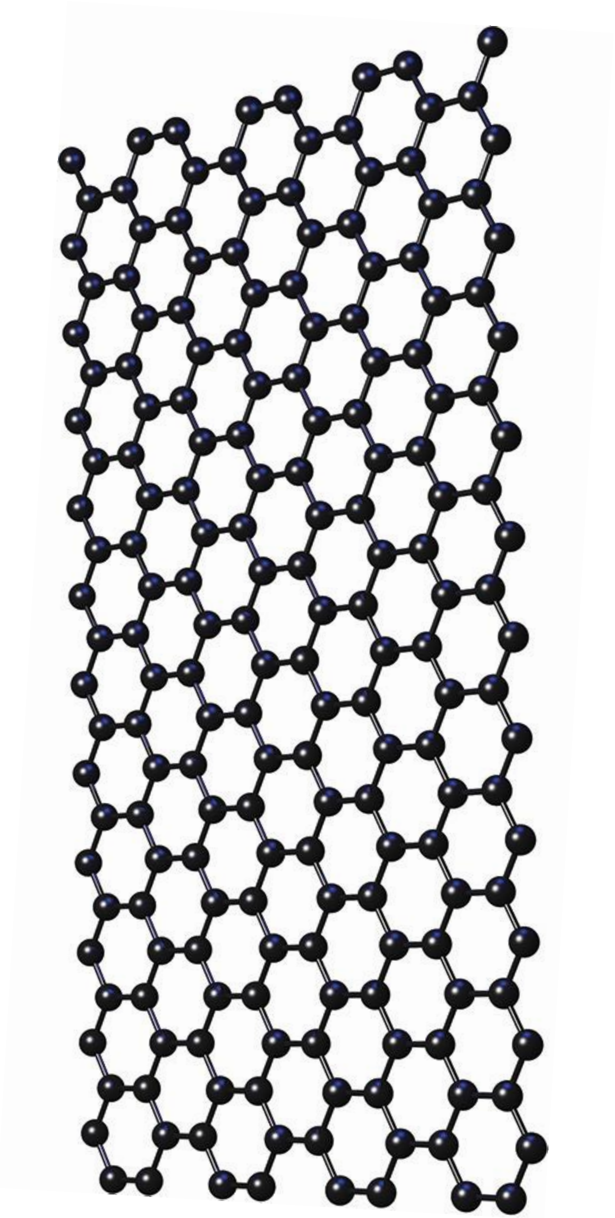
Allotropes of carbon



NAG, Anindya, 2018. *Sensors and Actuators A: Physical.*

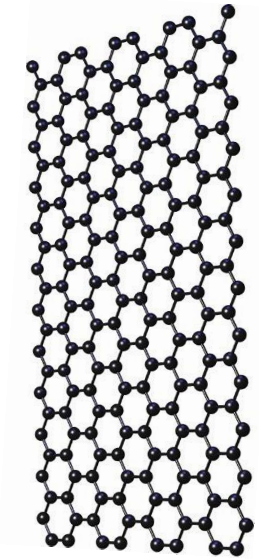
Graphene

- Allotrope of carbon
- Single layer of atoms
- Two-dimensional hexagonal lattice
- Indefinitely large aromatic molecule
- Ultimate case of polycyclic aromatic hydrocarbons
- sp^2



ZHAN, Beibei, 2014. *Small.*

Unique properties of graphene



2 630 $m^2 \cdot g^{-1}$ **nanosilica 1 200 $m^2 \cdot g^{-1}$**

0,76 $mg \cdot m^{-2}$

1,1 TPa

5 000 $W \cdot m^{-1} \cdot K^{-1}$

2,3% absorption

10^8 $S \cdot m^{-1}$

4 510 K

$1{,}6 \cdot 10^9$ $A \cdot cm^{-2}$

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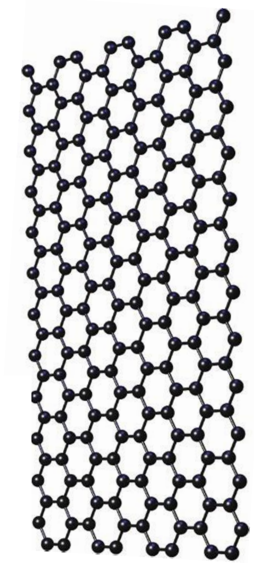

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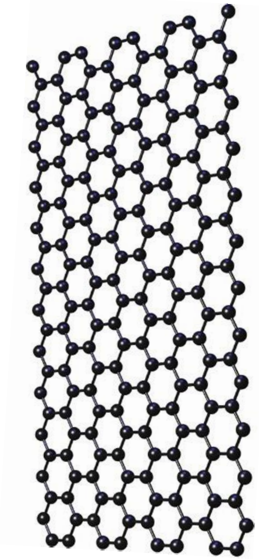

Unique properties of graphene

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0,76 $mg \cdot m^{-2}$	
1,1 TPa	steel 0,2 TPa
5 000 $W \cdot m^{-1} \cdot K^{-1}$	**diamond 1 000 – 2 300**
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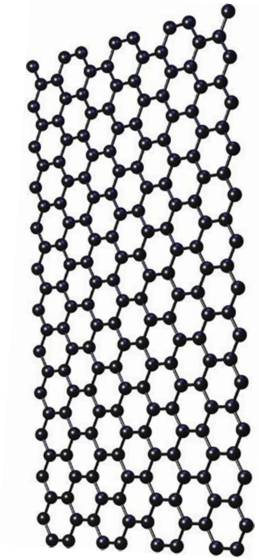

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steel

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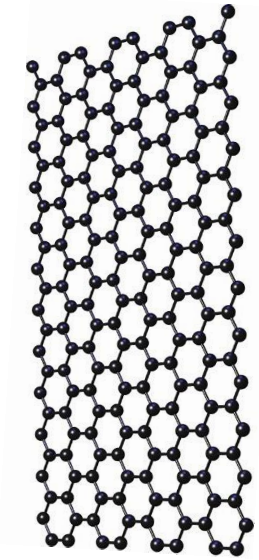

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10^8 $S \cdot m^{-1}$ **silver $6{,}3 \cdot 10^7$ $S \cdot m^{-1}$**

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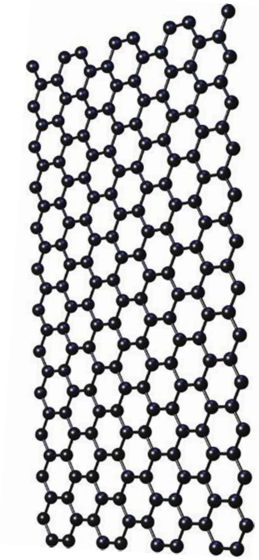

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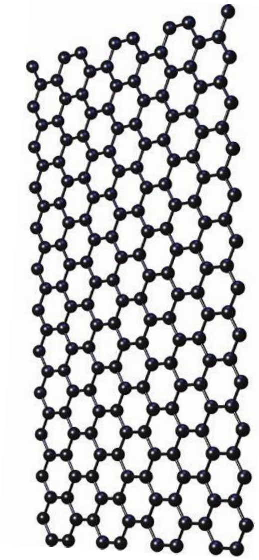

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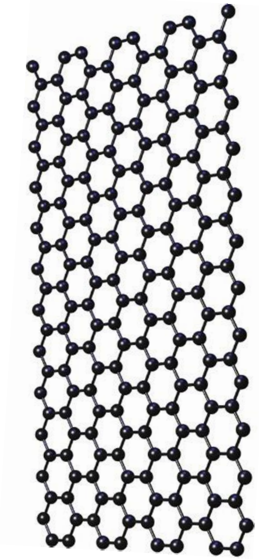
$1{,}6 \cdot 10^9$ $A \cdot cm^{-2}$	**copper 10^5 $A \cdot cm^{-2}$**

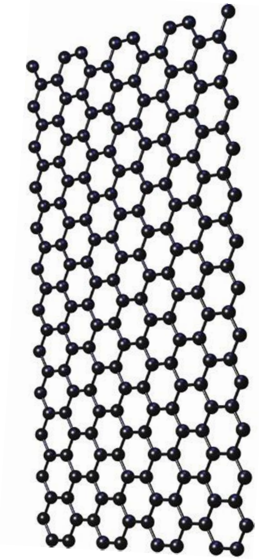


Preparation of graphene

Hummer's method

graphite powder washed in aqua regia, heating, water treatment, drying > 9 H_2SO_4 + 1 H_3PO_4 > slow addition of $KMnO_4$, stirring 6 h > H_2O_2, cooling > washed with HCl + DI water three times > intense heat > sonification > heating > NaH_5O_3 + Na_2 $9H_2O$ + SO_2, stirring > filtration, DI water > freeze drying

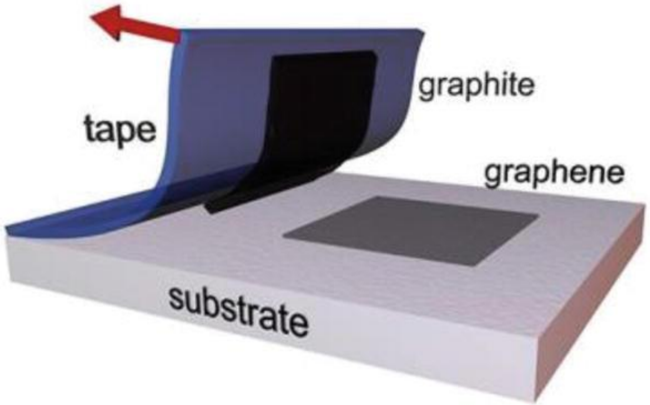
NAG, Anindya, 2018. *Sensors and Actuators A: Physical.*



Preparation of graphene

Mechanical exfoliation

- adhesive tape sticked over graphite crystals or flakes leads to entrapment of graphite layers
- multiple steps, each produces fewer layer
- deposition on silicon wafer
- crystallites larger than 1 mm, visible



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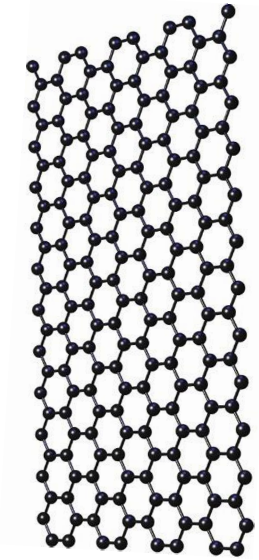
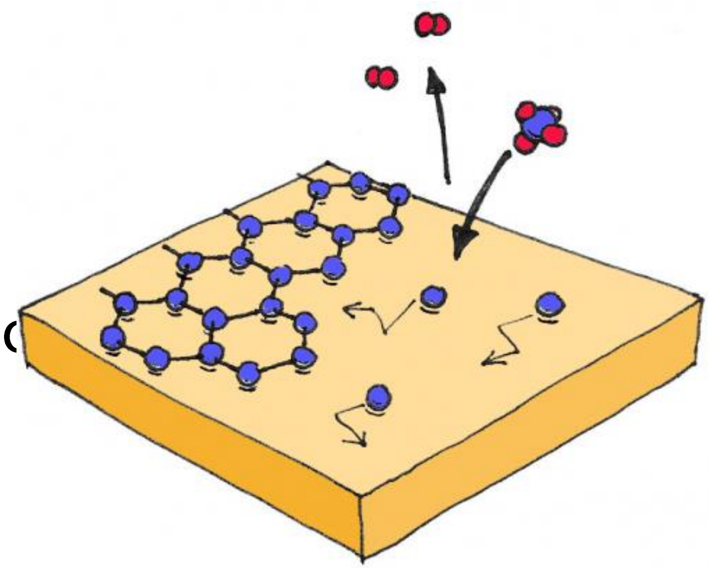


CVD

- quarz furnace with inert evironment is heated
- carbonaceous gases $Ar/H_2/CH_4$
- deposition of carbon on the metal (Ni/Cu/Co/Pt/Ir)
- formation of single long atom-thick mo
of graphene



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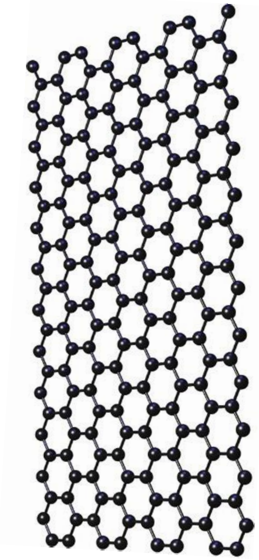
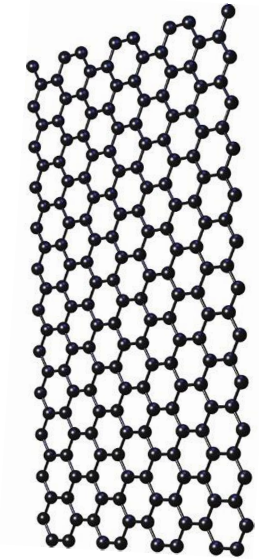


Application of graphene

E V E R Y W H E R E

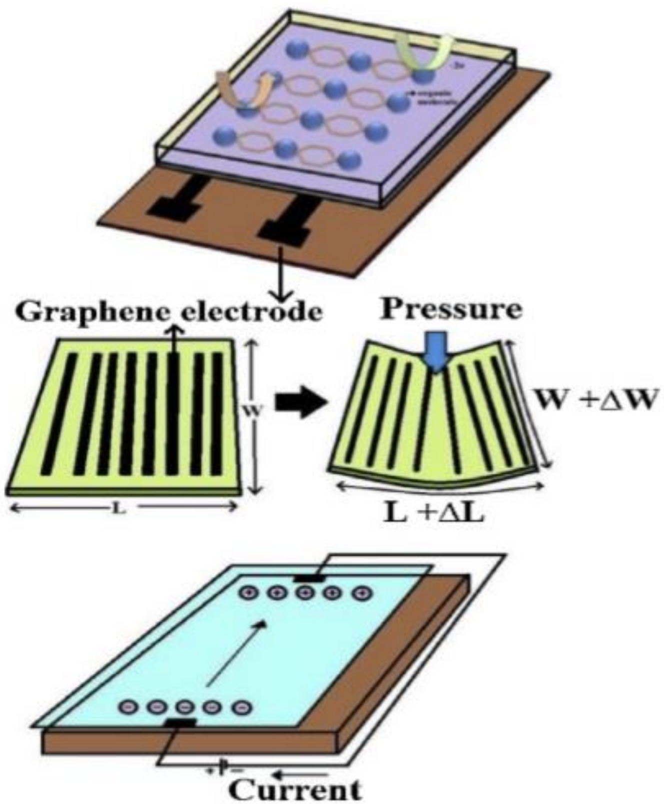
- **Medicine** (contrast agent, drug delivery, ...)
- **Electronics** (transistors, quantum dots, conductive inks, organic electronics, transparent electrodes, ...)
- **Energy** (solar cells, storage)
- **Environmental** (pollution removal, water filtration, ...)
- **Composites**



Graphene-based sensors

Types of sensors

- Electrochemical
- Strain
- Electrical



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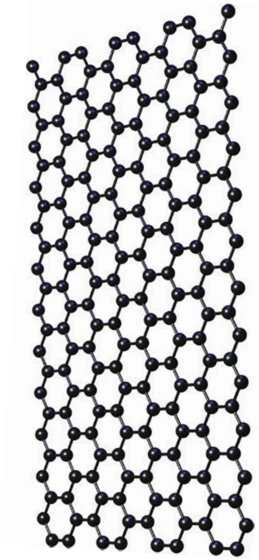


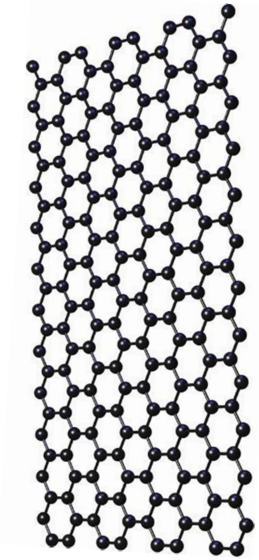
Graphene-based gas sensors

Gas sensors

- electronic device that can qualitatively or quantificationally detect specific gases
- conventionally constructed by semiconductor metal oxides
  → drawbacks: high-temperature operation, large power consumtion, low selectivity

  or conducting polymers
  → degradation

YUAN, Songyang a Shaolin ZHANG, 2019. *Journal of Semiconductors.*

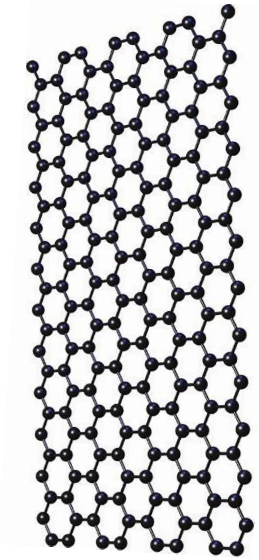


Graphene-based gas sensors

Why?

- all atoms are exposed to surface interactions with gas molecules
- room temperature, strong and flexible
- easy functionalization is able to improve sensing performance

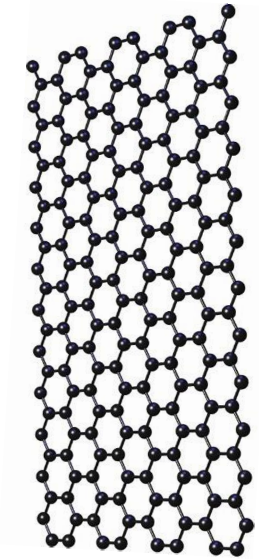
Graphene-based gas sensors



Mechanism

- gaseous adsorbates interact with graphene
- charge transfer processes between gas molecules and graphene surface
  - redistributon of electrons (H_2O)
  - change in electron concentration (NO_2)
  - covalent bonding (H·, HO·)
- leads to conductance changes

YUAN, Songyang a Shaolin ZHANG, 2019. *Journal of Semiconductors.*



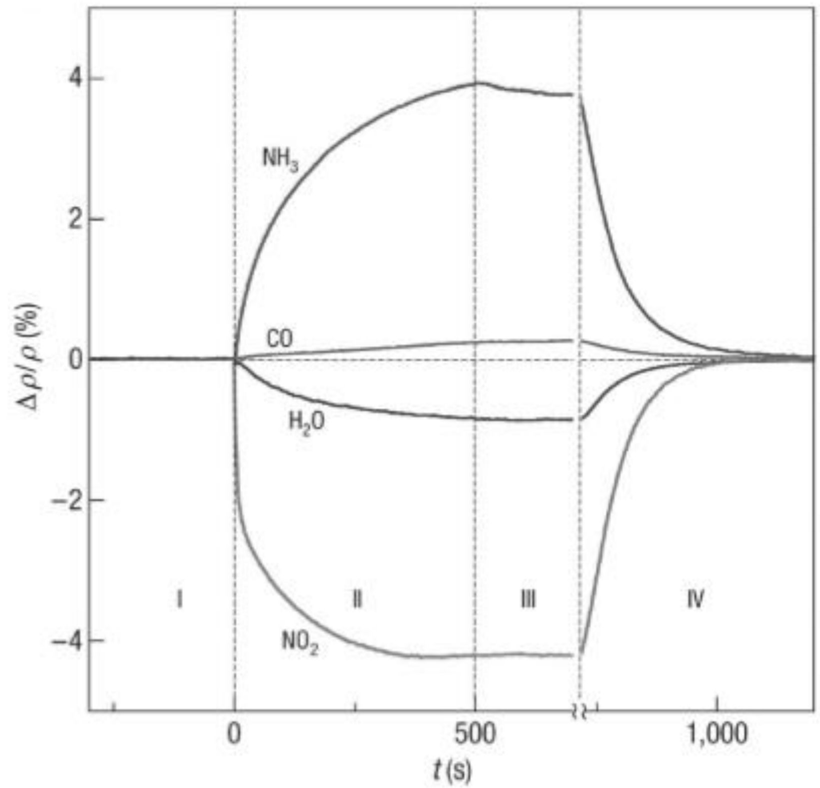
Graphene-based gas sensors

Types

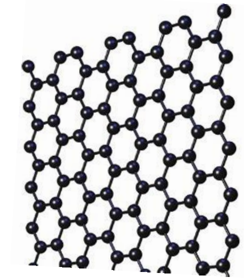
- Chemiresistors – simply, sensitive, stable
  - sensing layer between electrodes
  - resistance/current monitoring
- FET (field effect transistor)
  - source, drain, gate
  - observing output characteristics

Graphene-based gas sensors

- Changes in resistivity
- (II) 5 L of diluted gas
  1 ppm
- (III) evacuation
- (IV) annealing at 150 °C

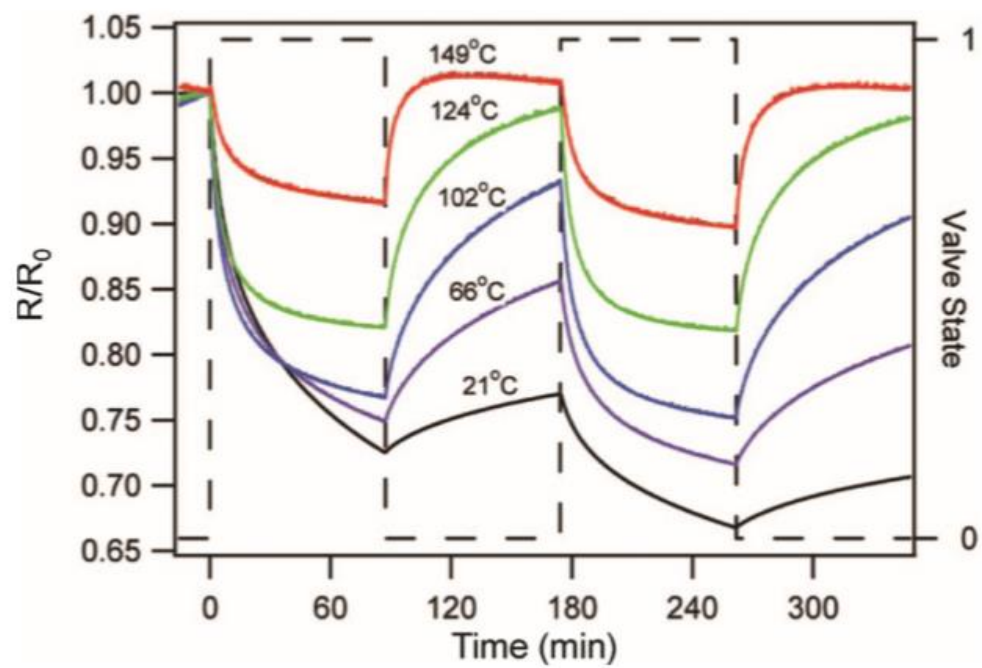


RATINAC, Kyle R. 2010. *Environmental Science & Technology.*



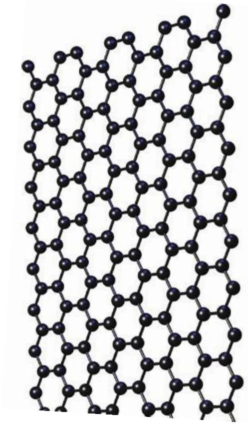
Graphene-based gas sensors

- Changes in resistivity
- Variable temperatures
- 5 ppm of NO_2

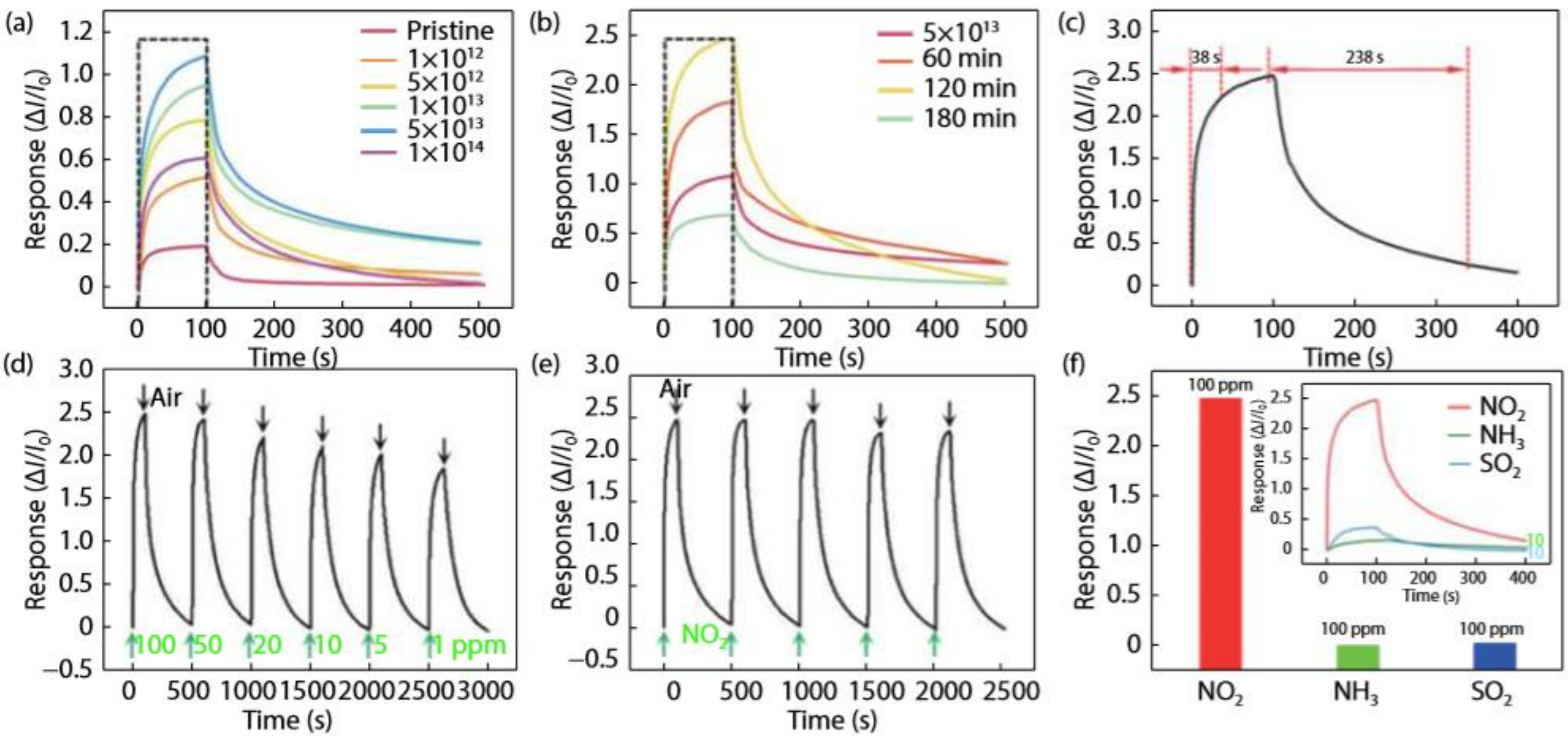


POTYRAILO, Radislav A., 2011. *Chemical Reviews.*

Graphene-based gas sensors



Defective Graphene / Pristine Graphene hybrid layer



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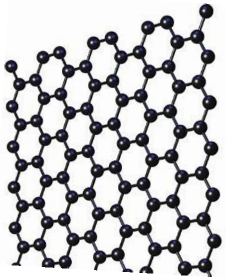

Graphene-based gas sensors

Material	Device type	Synthesis method	Substrate	Analyte	Limit of detection	Working temperature	Response (recovery) time
Graphene + MoS_2	Resistive	CVD + mechanical exfoliation	Polyimide	NO_2	1.2 ppm	150 °C	30 min
Graphene + MoS_2	Resistive	Liquid-phase co-exfoliation	Si/SiO_2	Methanol	10 ppm	–	210 s (220 s)
Graphene + MoS_2	Resistive	GA + ATM	Poly-Si	NO_2	50 ppb	25 °C	21.6 s (< 29.4 s)
Graphene + MoS_2	FET	CVD + mechanical exfoliation	Si/SiO_2	NO_2	1 ppm	RT	–
rGO + MoS_2	Resistive	Microwave-assisted exfoliation	PDMS	NH_3	0.48 mbar	RT	15 s
rGO + MoS_2	Resistive	Soft lithographic patterning	PET	NO_2	0.15 ppm	90 °C	–
rGO + MoS_2	Resistive	Lithography	SiO_2/Si	NO_2	2 ppm	60 °C	30 min
rGO + MoS_2	Resistive	Layer-bylayer self-assembly	SiO_2/Si	Formaldehyde	2.5 ppm	RT	73 s
rGO + MoS_2	Resistive	Self-assembly	PEN	Formaldehyde	2.5 ppm	RT	10 min (13 min)
MoS_2/WS_2	Resistive	Hydrothermal process	–	NO_2	10 ppb	RT	1.6 s (27.7 s)
rGO/WS_2	Resistive	Ball milling and sonication	Si_3N_4	NO_2	1 ppm	RT	22 min (26 min)
Defective graphene/ pristinegraphene	Current	APCVD	Ge	NO_2	1 ppm	RT	28 s (238 s)
rGO-MoS_2-CdS	Resistive	Solvothermal	–	NO_2	0.2 ppm	75 °C	25 s (34 s)
BP/h-BN/MoS_2	FET	Mechanically exfoliated + e-beam lithography	SiO_2/Si	NO_2	3.3 ppb	RT	8 min (8 min)

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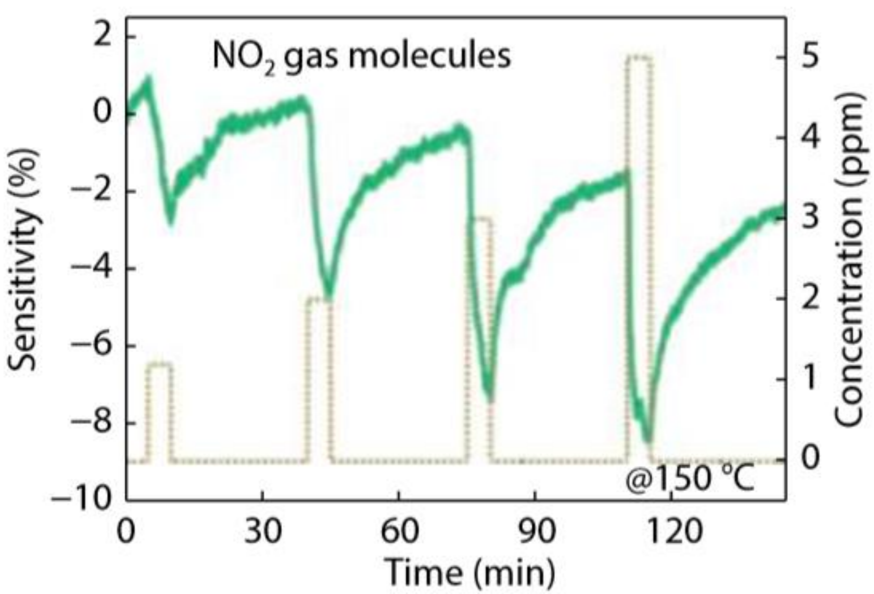
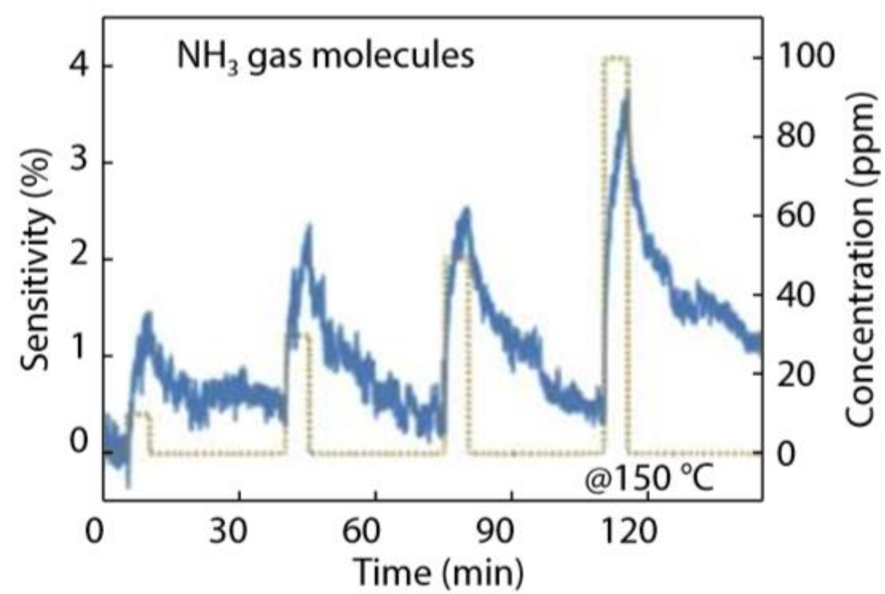
Graphene-based gas sensors

- Graphene + MoS_2
  (conductive layer + analyte acceptor)





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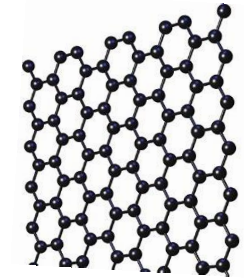

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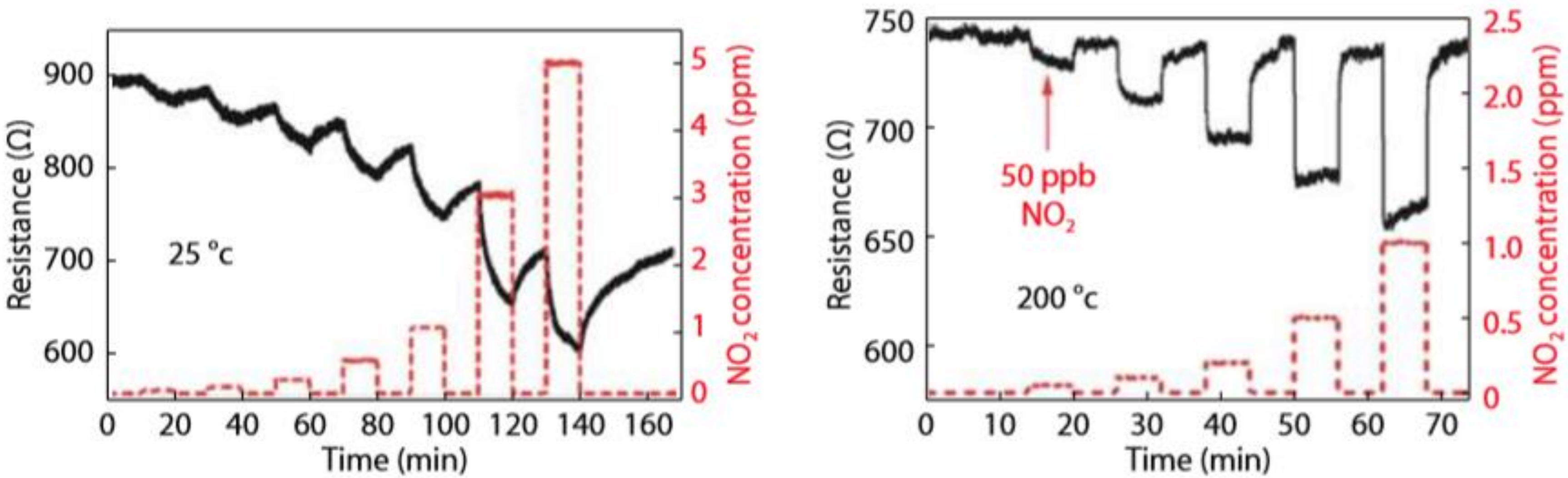
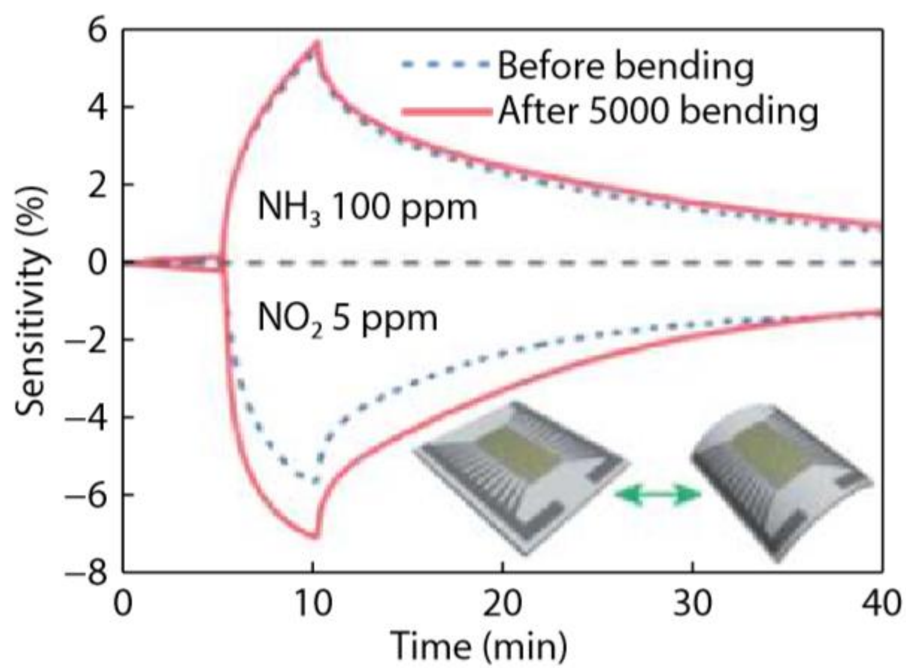


YUAN, Songyang a Shaolin ZHANG, 2019. *Journal of Semiconductors.*

Graphene-based gas sensors

- Graphene + MoS_2
  (conductive layer + analyte acceptor)
- Polyimide substrate
- 5 000 bending cycles



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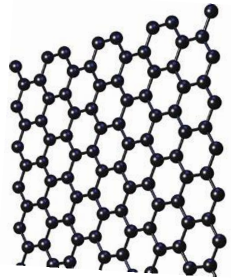
Summary

➢ Sensitivity:	1 ppm, special cases 1 ppb
➢ Selectivity:	DGr/Gr 65x higher response for NO_2
➢ Response/ recovery time:	tens/ houndreds of seconds
➢ Material stability:	temperature, humidity
➢ Reproducibility	



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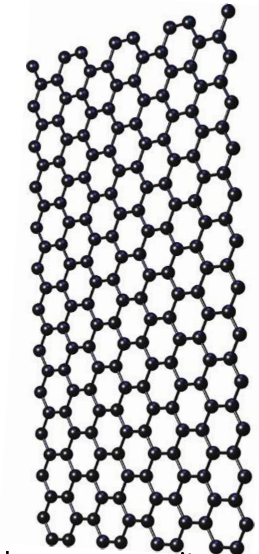

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