# Nano-Sensor Technology

## Recent Advances for Smart Intelligent Agriculture

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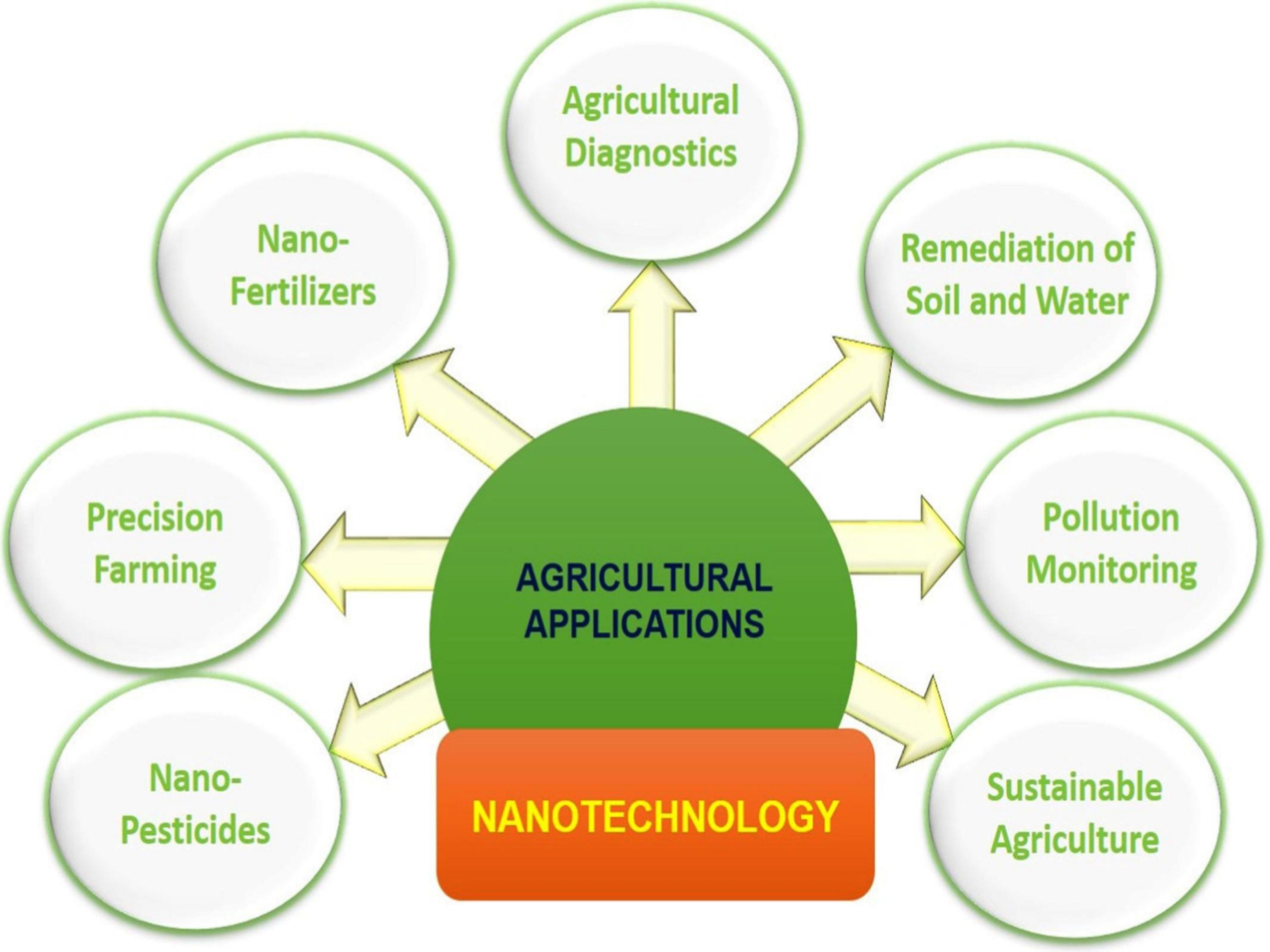
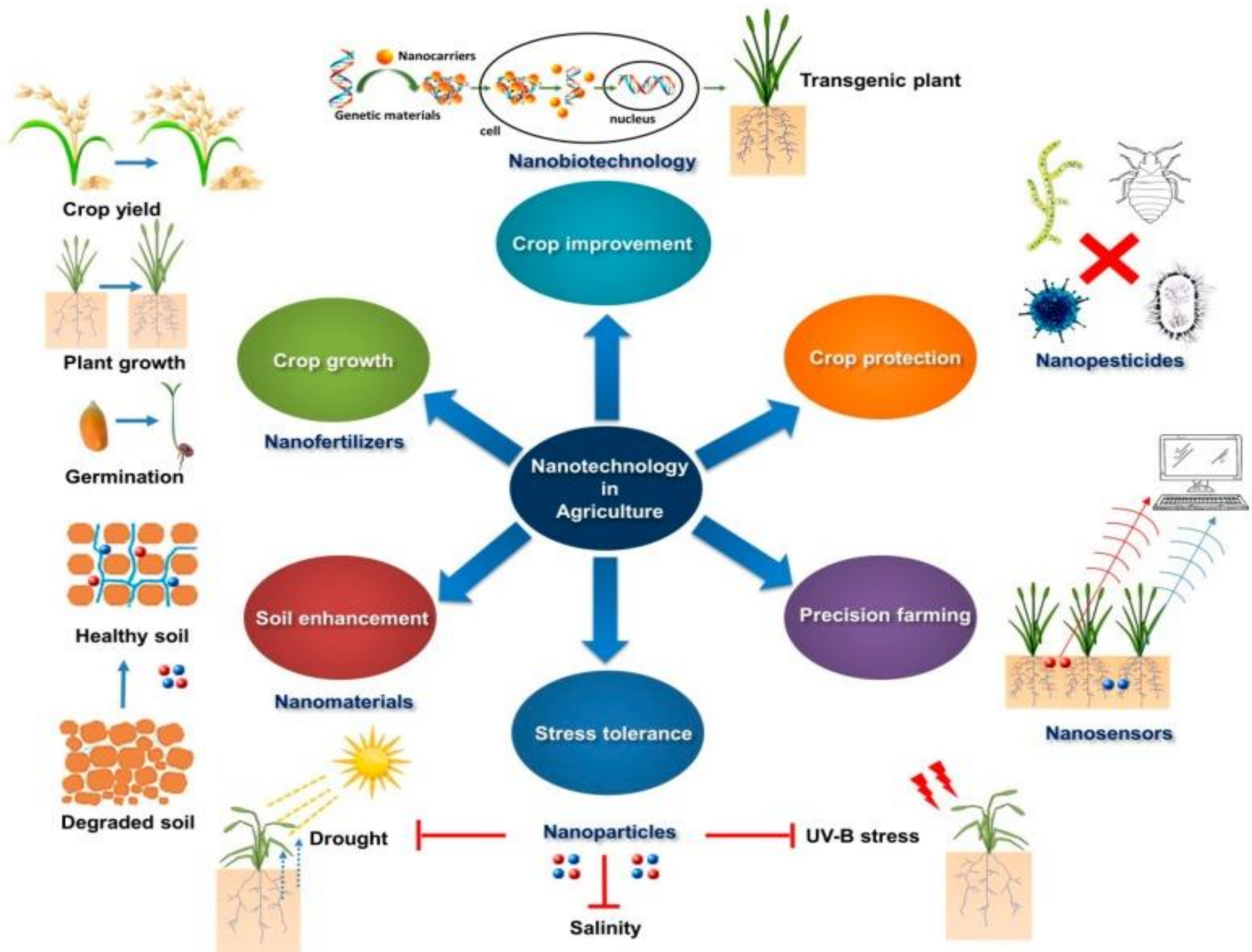
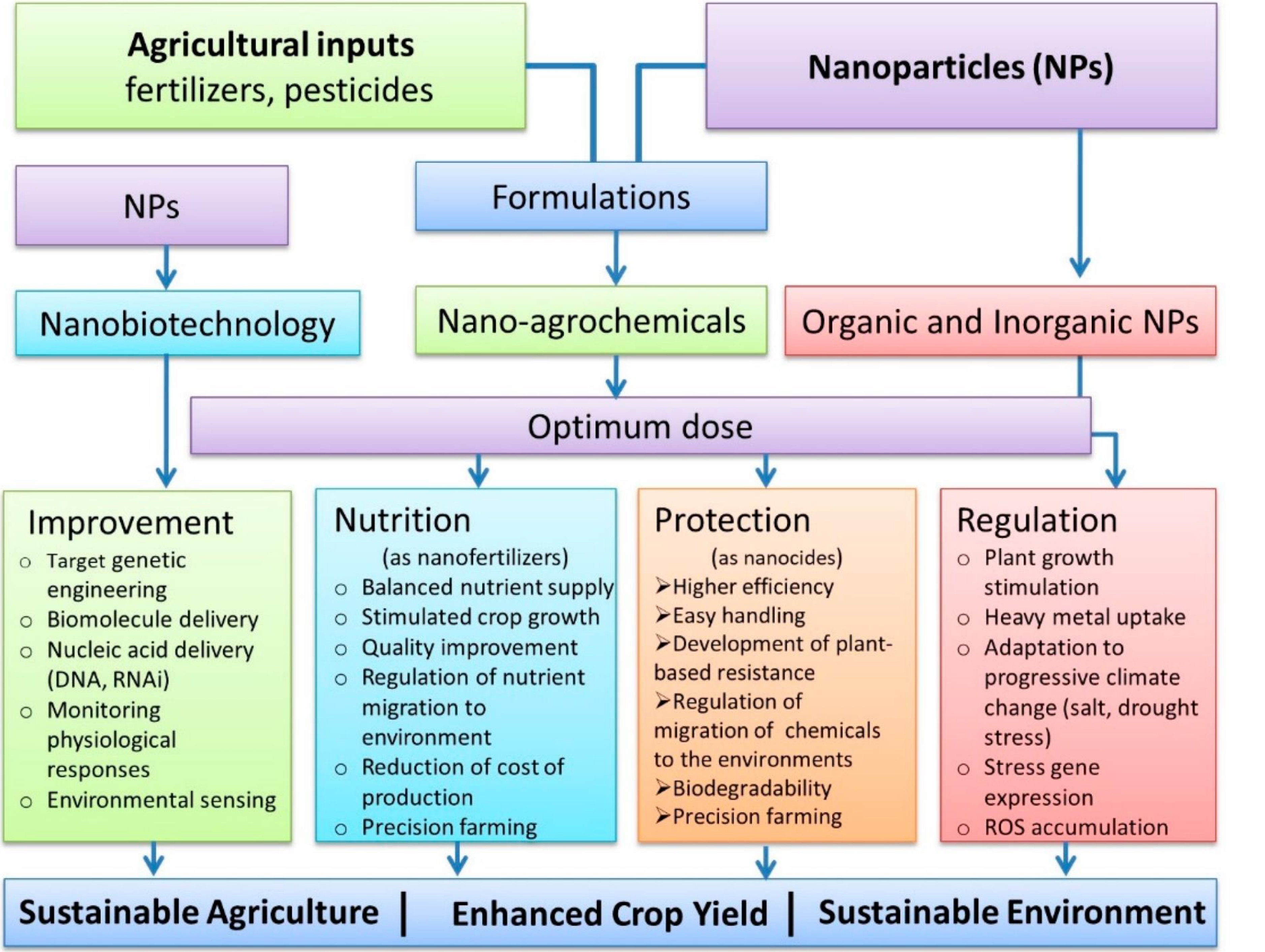
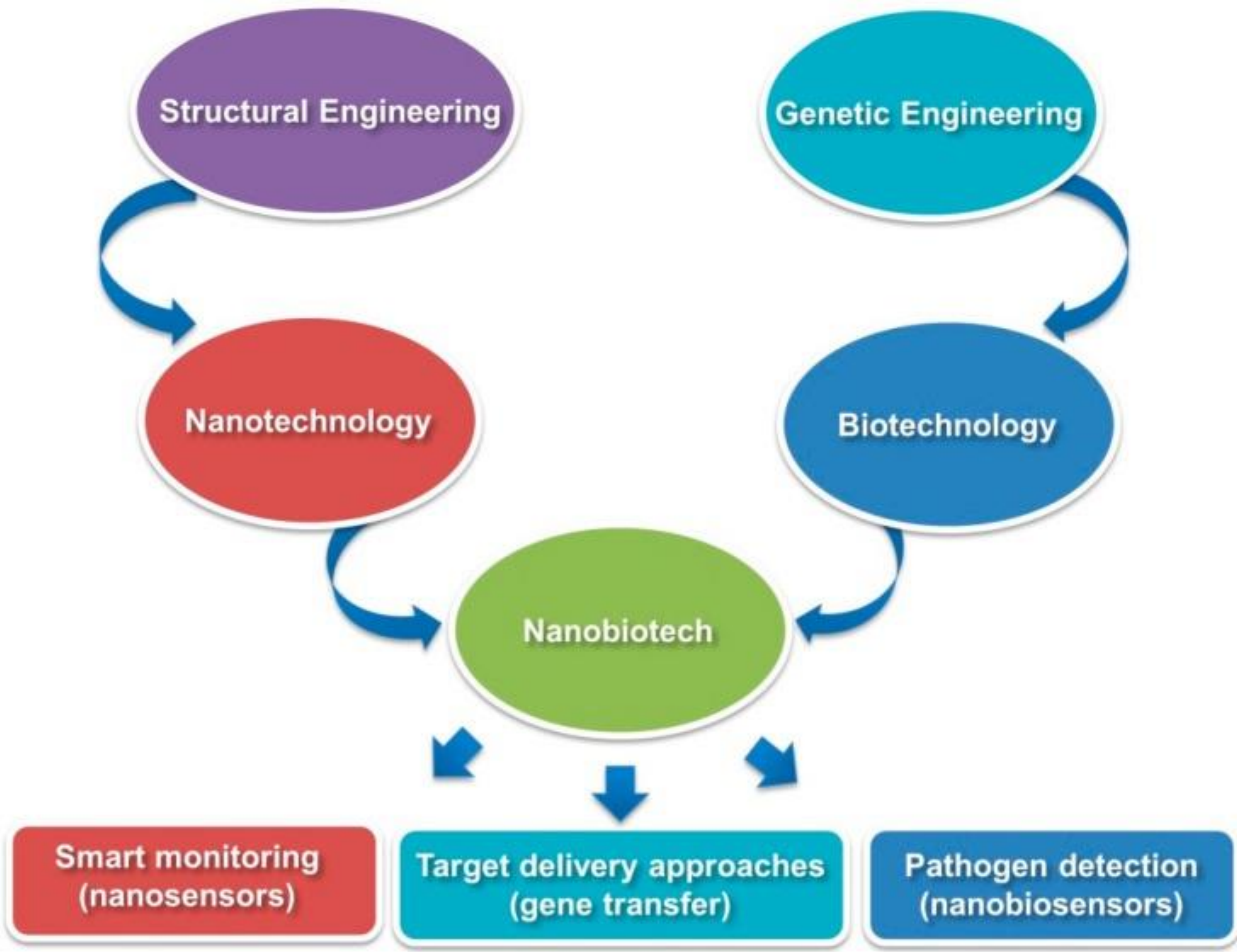
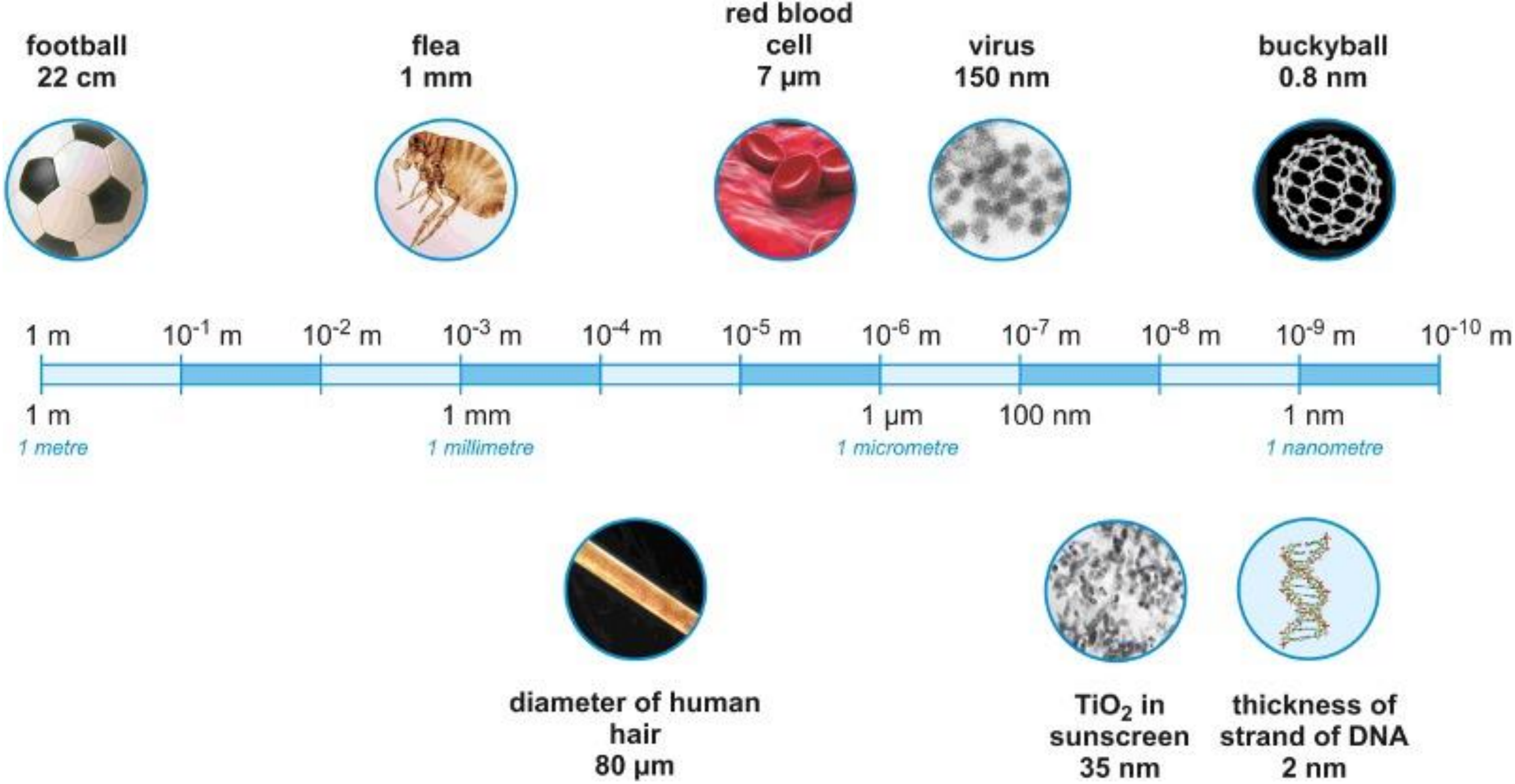


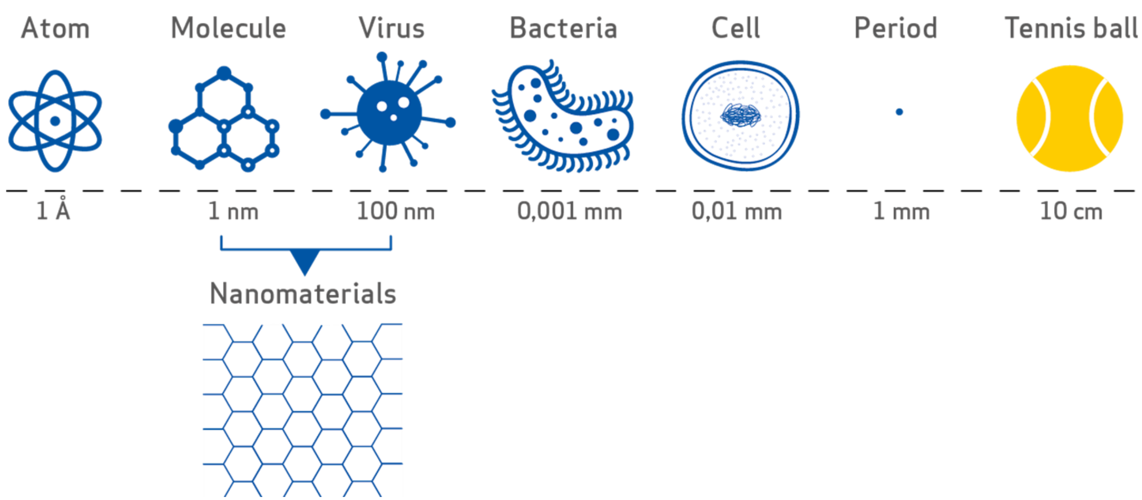
Agricultural Diagnostics
Nano-Fertilizers
Remediation of Soil and Water
Precision Farming
AGRICULTURAL APPLICATIONS
Pollution Monitoring
Nano-Pesticides
NANOTECHNOLOGY
Sustainable Agriculture

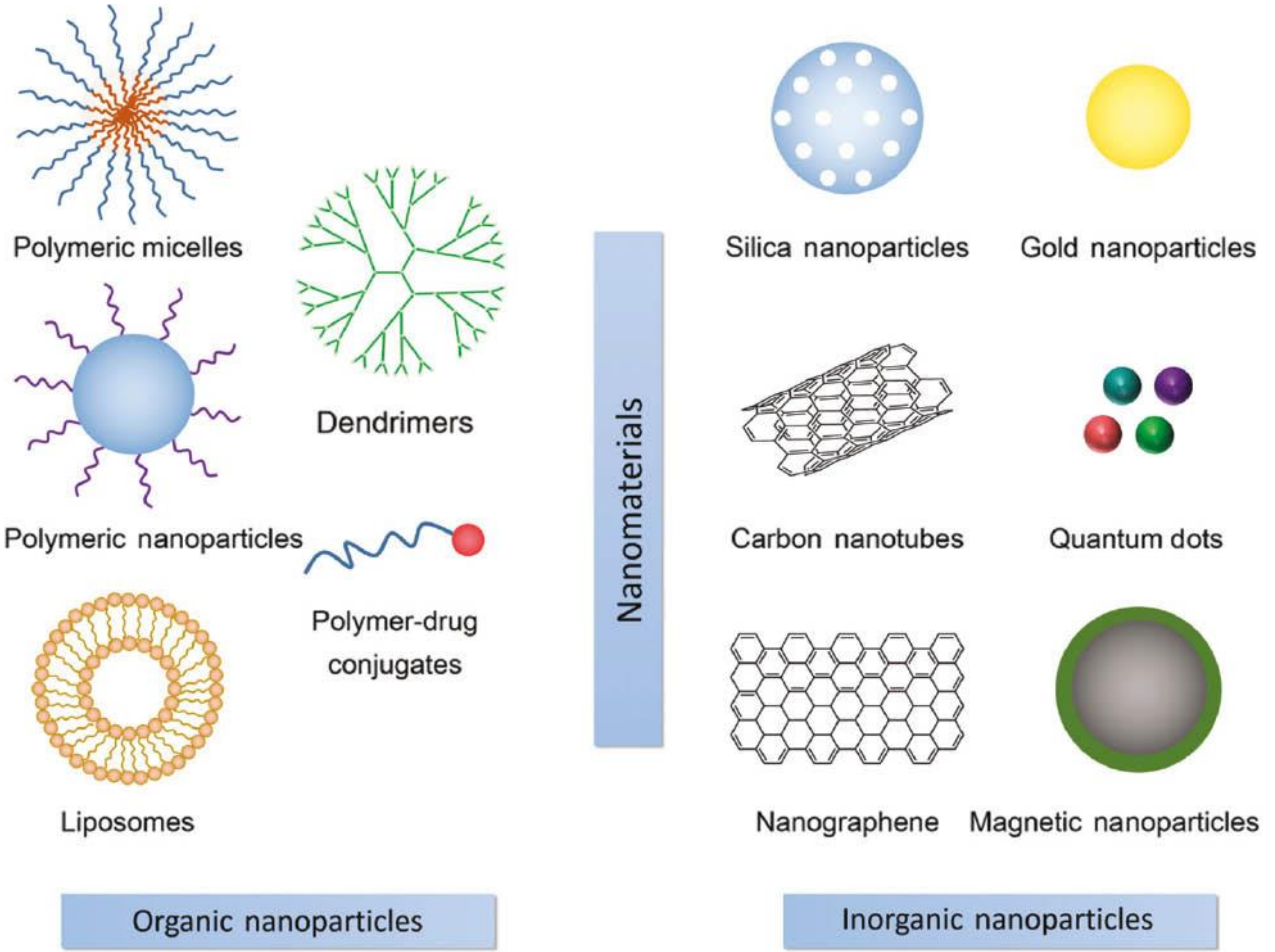

Nanocarriers
Genetic materials
cell
nucleus
Transgenic plant
Nanobiotechnology
Crop yield
Plant growth
Germination
Healthy soil
Degraded soil
Crop improvement
Crop growth
Crop protection
Nanopesticides
Nanofertilizers
Nanotechnology in Agriculture
Soil enhancement
Precision farming
Nanomaterials
Stress tolerance
Nanosensors
Drought
Nanoparticles
UV-B stress
Salinity

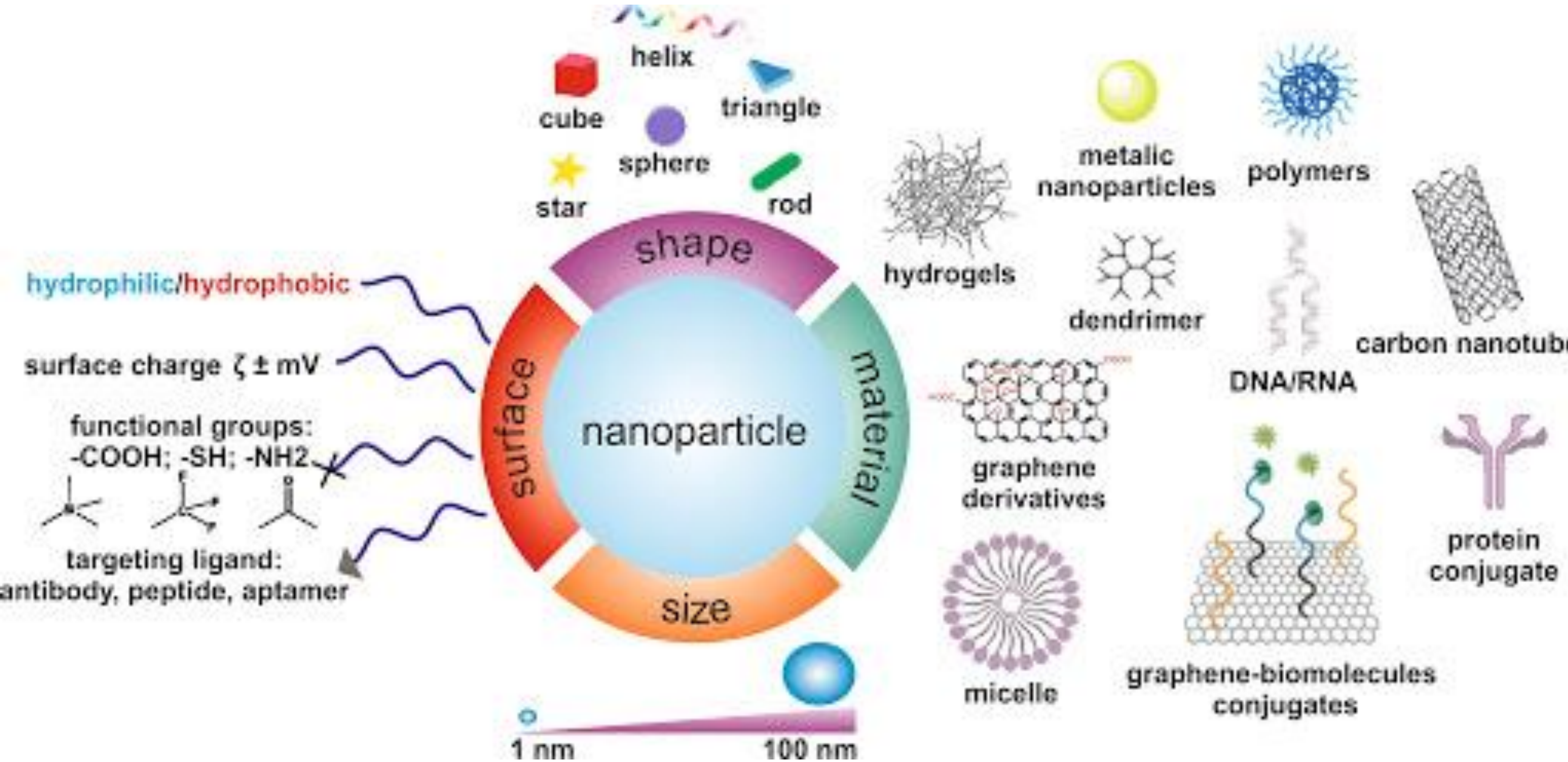

Agricultural inputs
fertilizers, pesticides
Nanoparticles (NPs)
NPs
Formulations
Nanobiotechnology
Nano-agrochemicals
Organic and Inorganic NPs
Optimum dose
Improvement
Target genetic engineering
Biomolecule delivery
Nucleic acid delivery (DNA, RNAi)
Monitoring physiological responses
Environmental sensing
Nutrition
(as nanofertilizers)
Balanced nutrient supply
Stimulated crop growth
Quality improvement
Regulation of nutrient migration to environment
Reduction of cost of production
Precision farming
Protection
(as nanocides)
Higher efficiency
Easy handling
Development of plant-based resistance
Regulation of migration of chemicals to the environments
Biodegradability
Precision farming
Regulation
Plant growth stimulation
Heavy metal uptake
Adaptation to progressive climate change (salt, drought stress)
Stress gene expression
ROS accumulation
Sustainable Agriculture | Enhanced Crop Yield | Sustainable Environment


Structural Engineering
Genetic Engineering
Nanotechnology
Biotechnology
Nanobiotech
Smart monitoring
(nanosensors)
Target delivery approaches
(gene transfer)
Pathogen detection
(nanobiosensors)


football
22 cm
flea
1 mm
red blood
cell
7 µm
virus
150 nm
buckyball
0.8 nm
1 m
10-1 m
10-2 m
10-3 m
10-4 m
10-5 m
10-6 m
10-7 m
10-8 m
10-9 m
10-10 m
1 m
1 metre
1 mm
1 millimetre
1 µm
1 micrometre
100 nm
1 nm
1 nanometre
diameter of human
hair
80 µm
TiO2 in
sunscreen
35 nm
thickness of
strand of DNA
2 nm

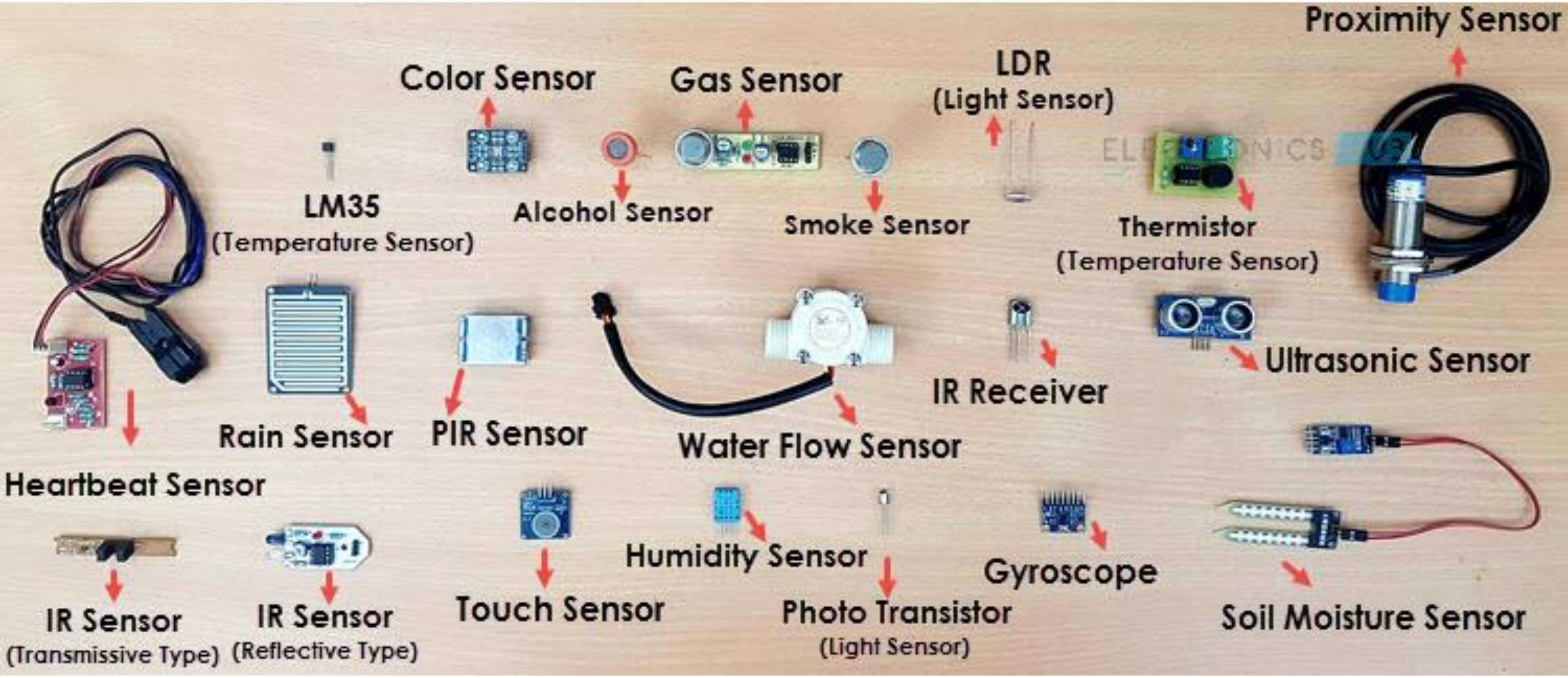

Atom
Molecule
Virus
Bacteria
Cell
Period
Tennis ball
1 Å
1 nm
100 nm
0,001 mm
0,01 mm
1 mm
10 cm
Nanomaterials


Polymeric micelles
Dendrimers
Polymeric nanoparticles
Polymer-drug
conjugates
Liposomes
Nanomaterials
Silica nanoparticles
Gold nanoparticles
Carbon nanotubes
Quantum dots
Nanographene
Magnetic nanoparticles
Organic nanoparticles
Inorganic nanoparticles

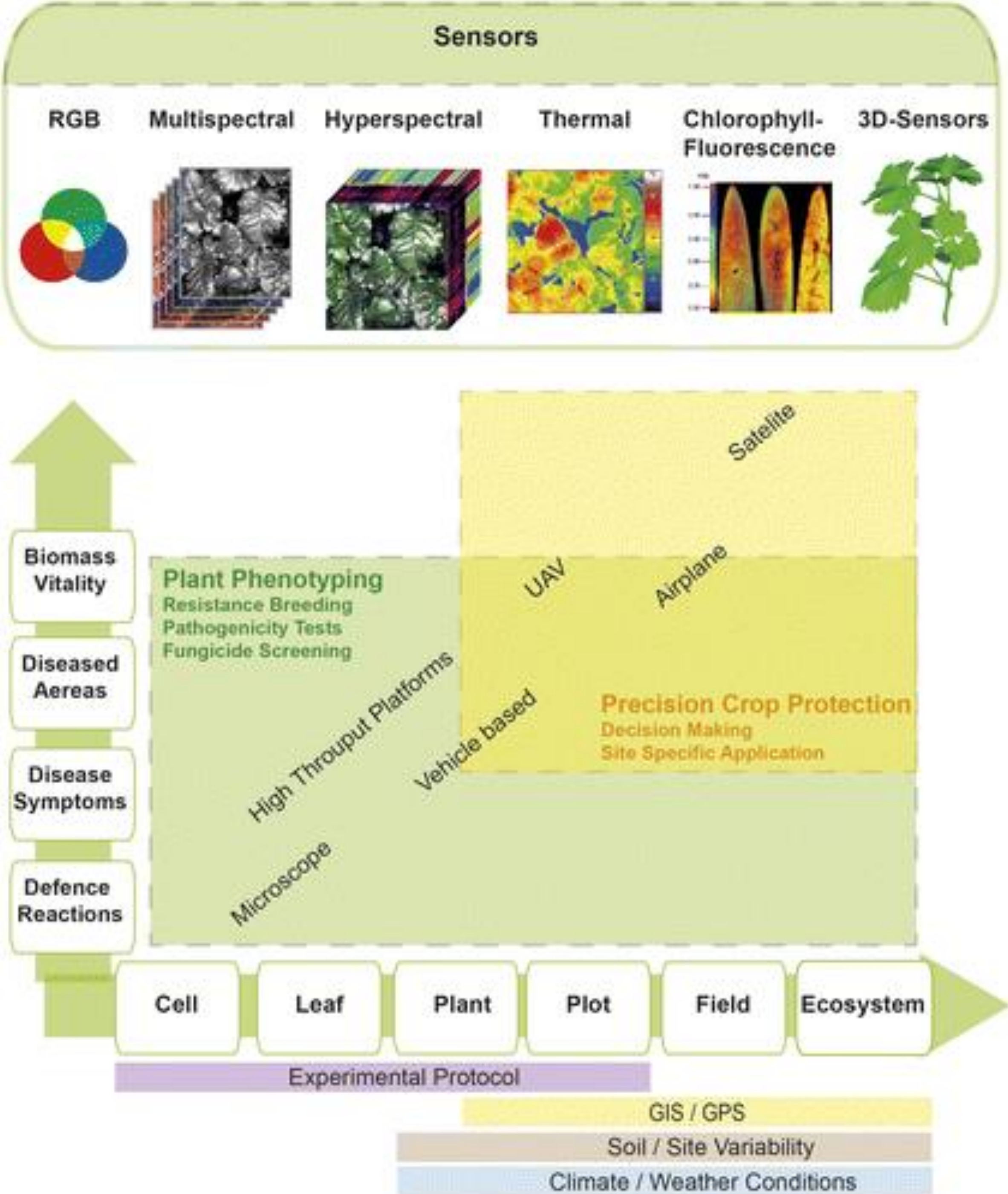

helix
cube
triangle
sphere
star
rod
shape
hydrophilic/hydrophobic
surface charge ζ ± mV
functional groups:
-COOH; -SH; -NH2
targeting ligand:
antibody, peptide, aptamer
surface
nanoparticle
material
size
1 nm
100 nm
hydrogels
metalic
nanoparticles
polymers
dendrimer
DNA/RNA
carbon nanotube
graphene
derivatives
protein
conjugate
micelle
graphene-biomolecules
conjugates

# Enhancing Agricultural Productivity

- Innovative and New Technological Approaches for Managing Crop Stressors
- Delivery of Agrochemicals and Biosensing
- Sensing Materials – Nanomaterials to develop Nanosensors
- Nanosensors as tools for detection and quantification of plant metabolic flux, residual of pesticides in soil and food, and disease diagnosis (viral, bacterial and fungal)

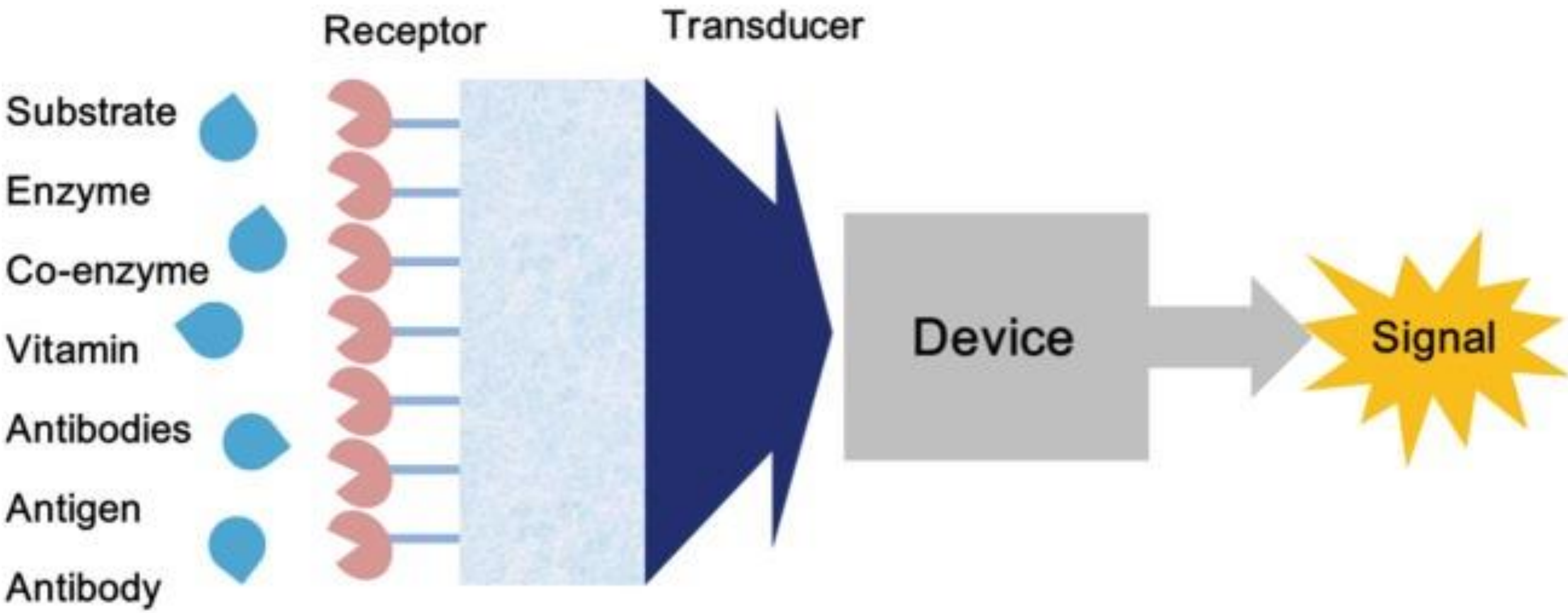


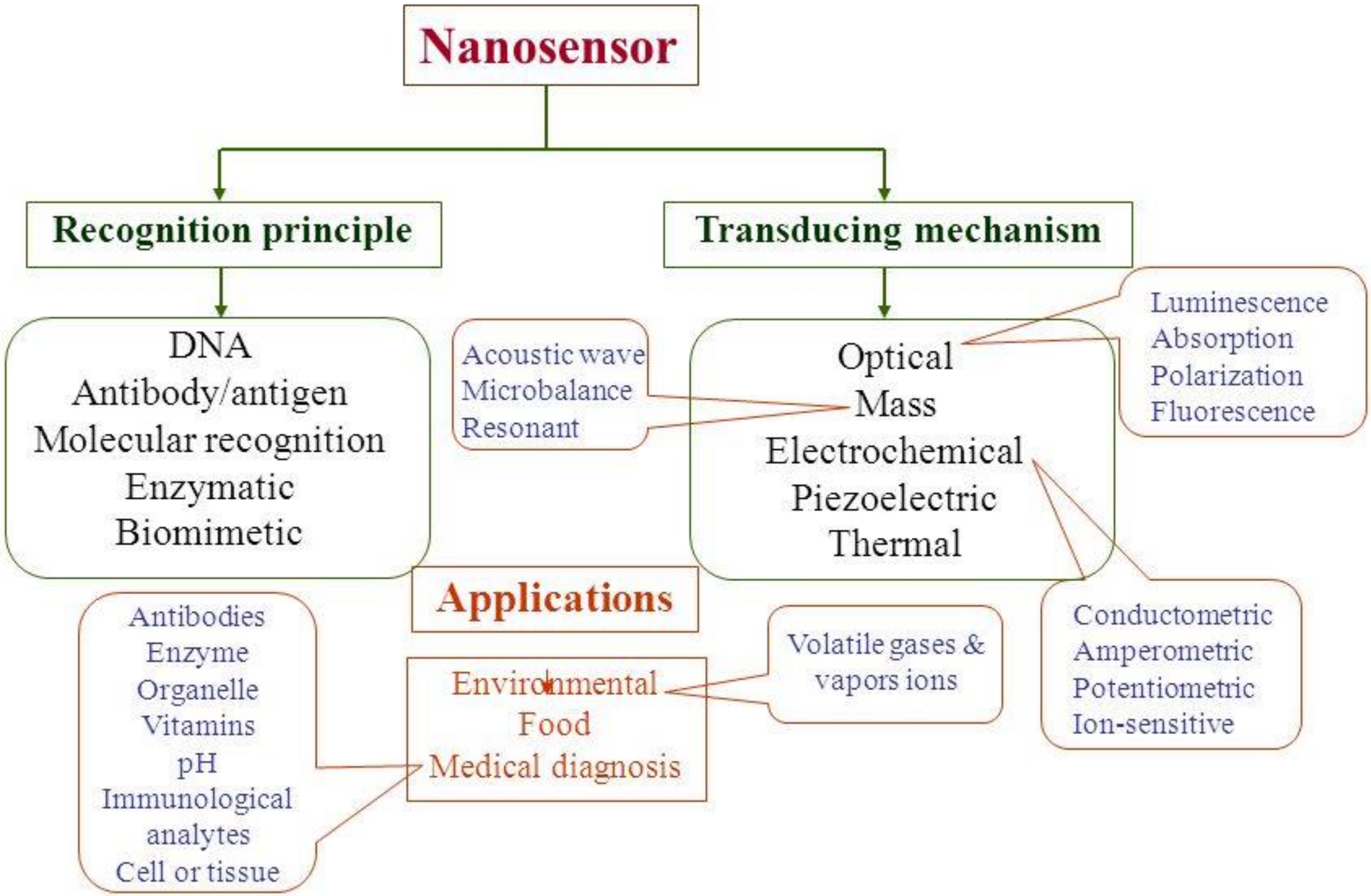
Proximity Sensor
Color Sensor
Gas Sensor
LDR
(Light Sensor)
LM35
(Temperature Sensor)
Alcohol Sensor
Smoke Sensor
Thermistor
(Temperature Sensor)
Ultrasonic Sensor
IR Receiver
Rain Sensor
PIR Sensor
Water Flow Sensor
Heartbeat Sensor
Humidity Sensor
Gyroscope
Touch Sensor
Photo Transistor
(Light Sensor)
Soil Moisture Sensor
IR Sensor
(Transmissive Type)
IR Sensor
(Reflective Type)


Sensors
RGB
Multispectral
Hyperspectral
Thermal
Chlorophyll-Fluorescence
3D-Sensors
Satelite
UAV
Airplane
Plant Phenotyping
Resistance Breeding
Pathogenicity Tests
Fungicide Screening
High Throuput Platforms
Vehicle based
Precision Crop Protection
Decision Making
Site Specific Application
Microscope
Biomass Vitality
Diseased Aereas
Disease Symptoms
Defence Reactions
Cell
Leaf
Plant
Plot
Field
Ecosystem
Experimental Protocol
GIS / GPS
Soil / Site Variability
Climate / Weather Conditions

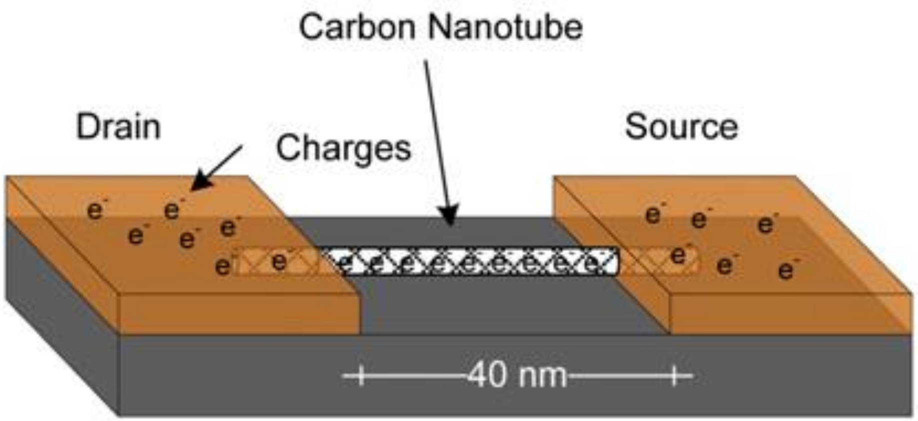
# Nanosensors

- Nanoscale devices that measure physical quantities and convert these to signals that can be detected and analyzed.
- Ways to make nanosensors
  - Top-down Lithography
  - Bottom-up Assembly
  - Molecular Self-assembly

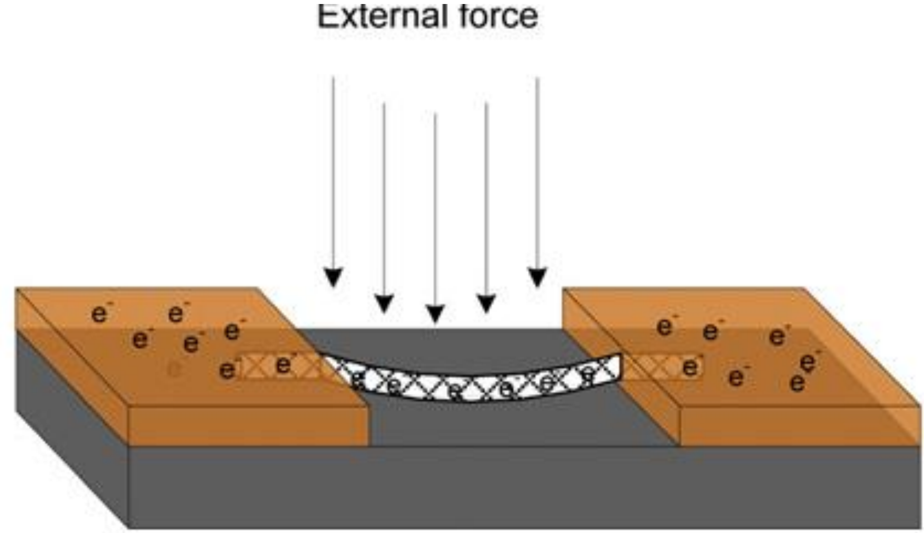

Receptor
Transducer
Substrate
Enzyme
Co-enzyme
Vitamin
Antibodies
Antigen
Antibody
Device
Signal



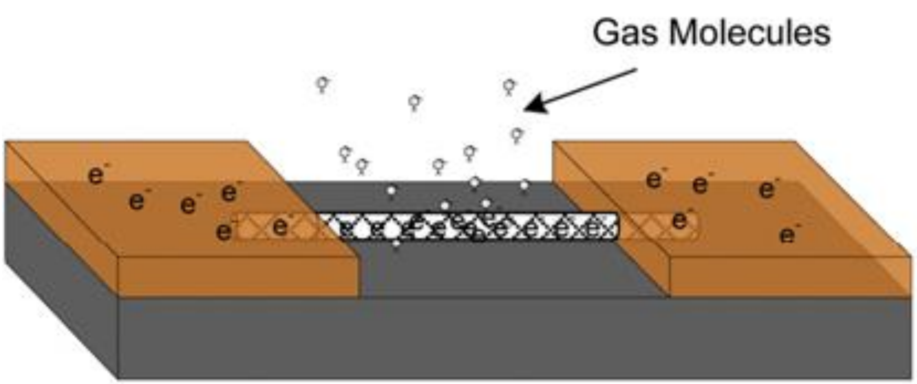

Scheme 1. Representation of recognition process and application of Nanosensor



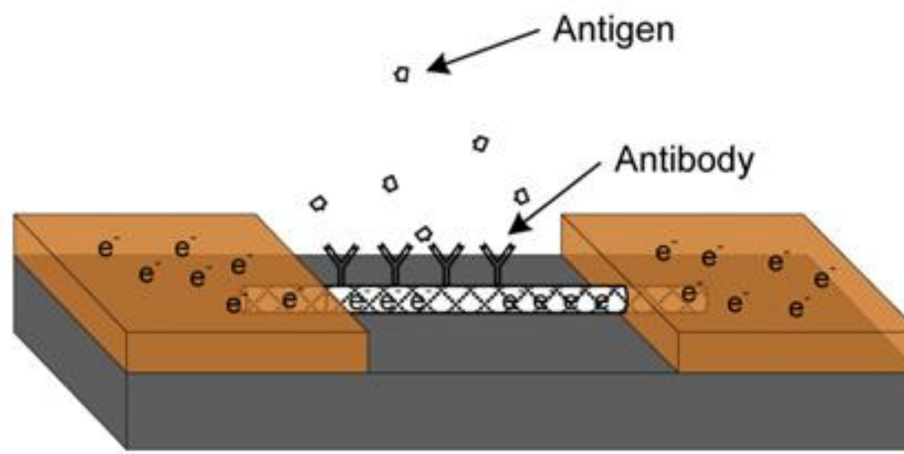

(a) CNT-based FET transistor.



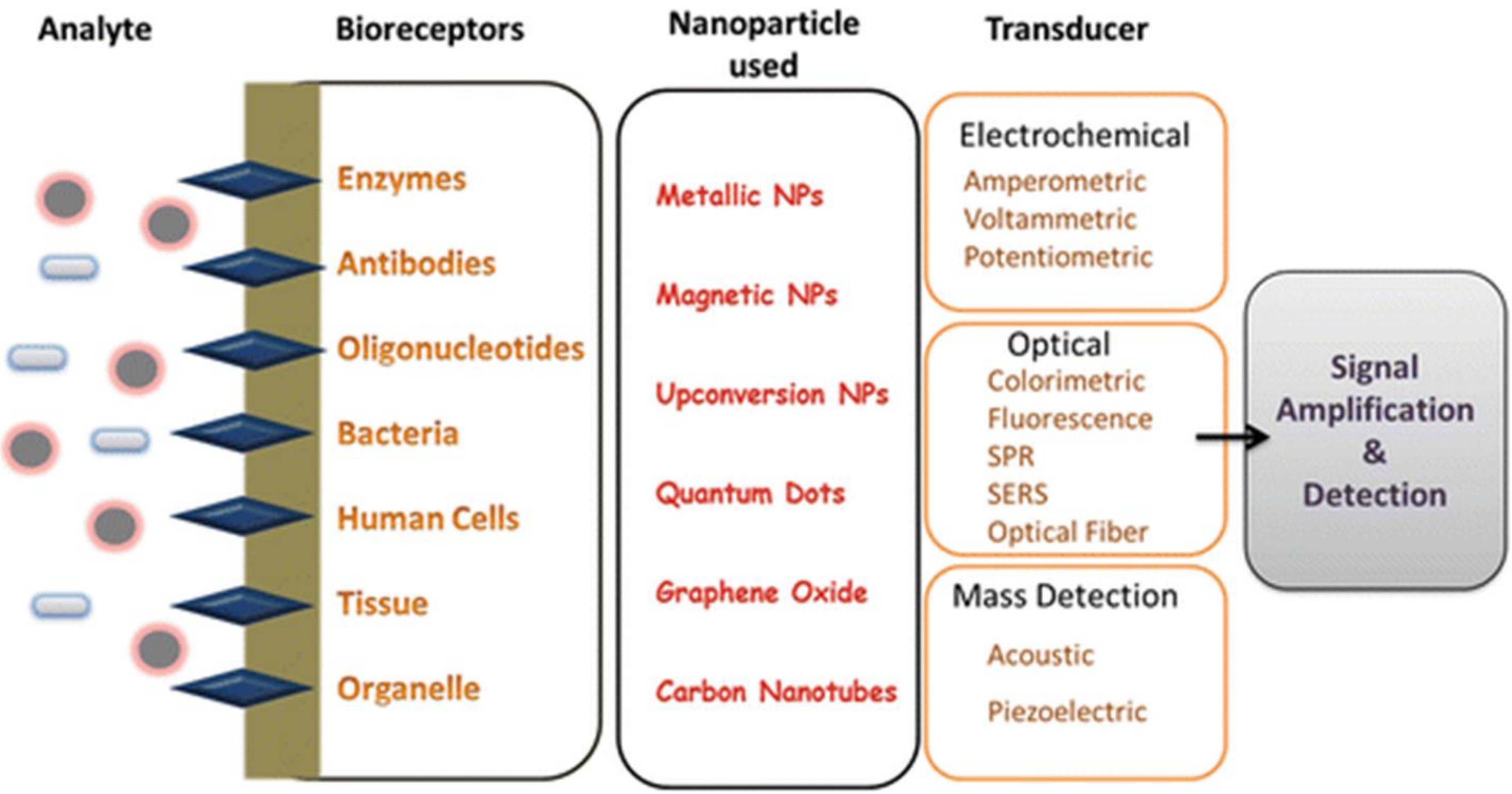

(b) Physical nanosensor.




(c) Chemical nanosensor.



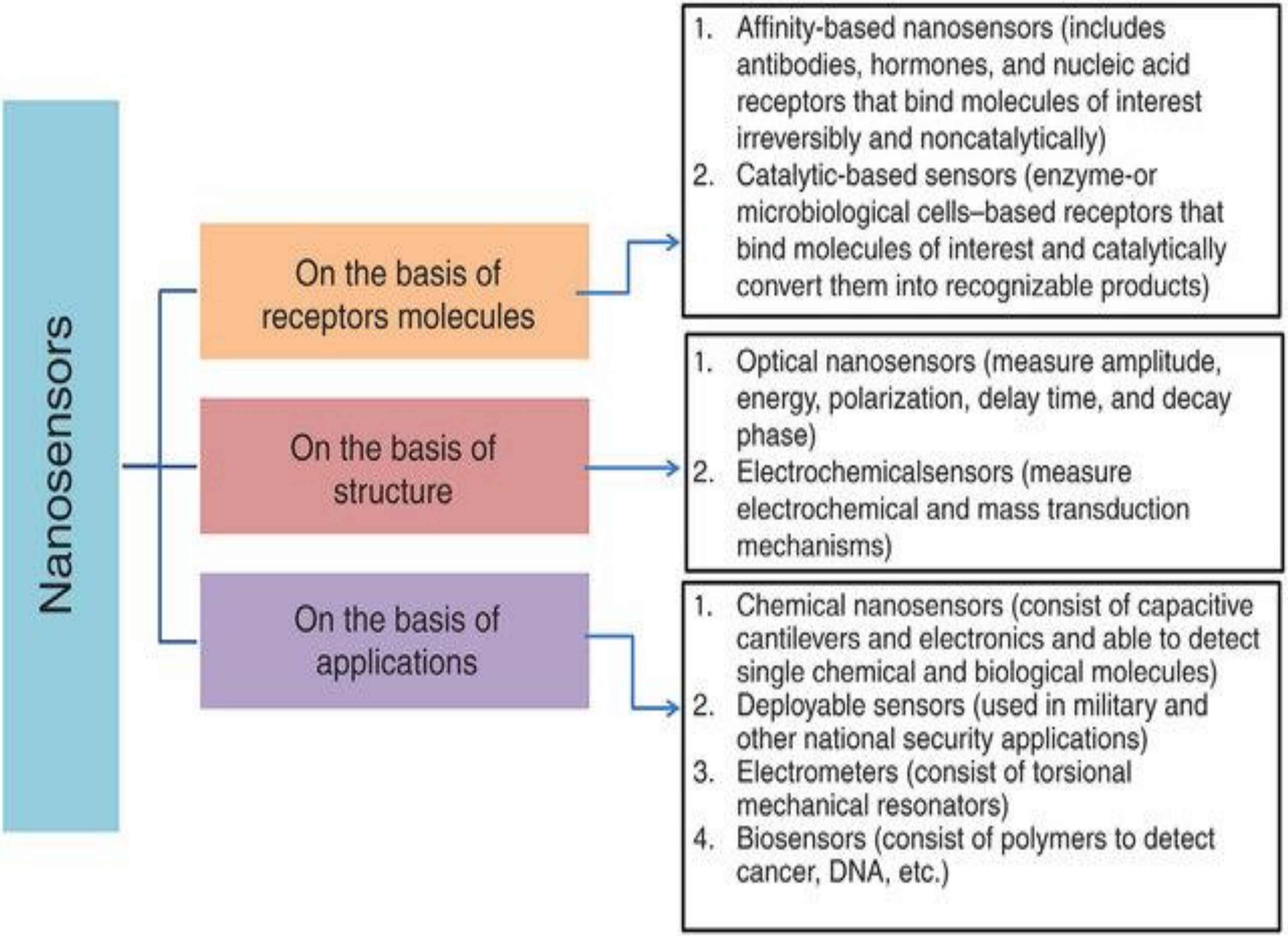

(d) Biological nanosensor.

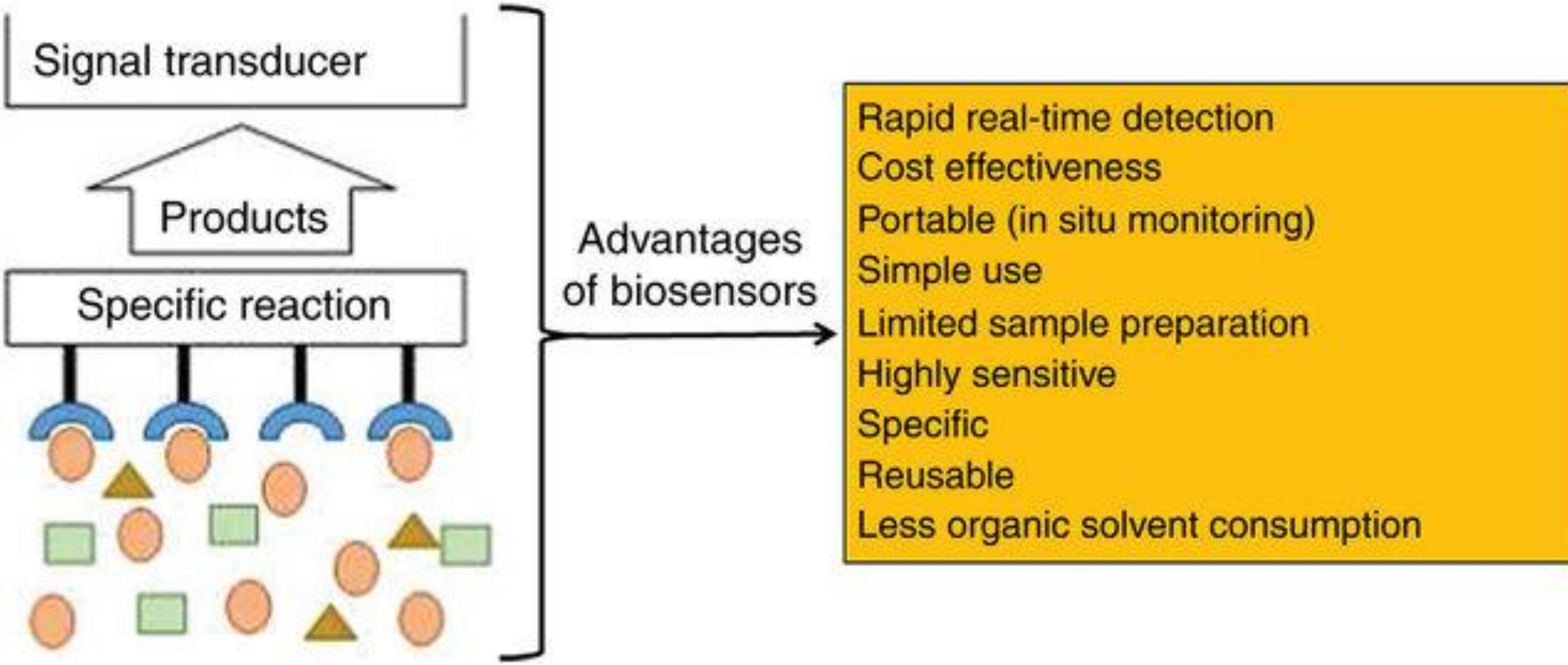

Analyte
Bioreceptors
Nanoparticle used
Transducer
Enzymes
Antibodies
Oligonucleotides
Bacteria
Human Cells
Tissue
Organelle
Metallic NPs
Magnetic NPs
Upconversion NPs
Quantum Dots
Graphene Oxide
Carbon Nanotubes
Electrochemical
Amperometric
Voltammetric
Potentiometric
Optical
Colorimetric
Fluorescence
SPR
SERS
Optical Fiber
Mass Detection
Acoustic
Piezoelectric
Signal Amplification & Detection

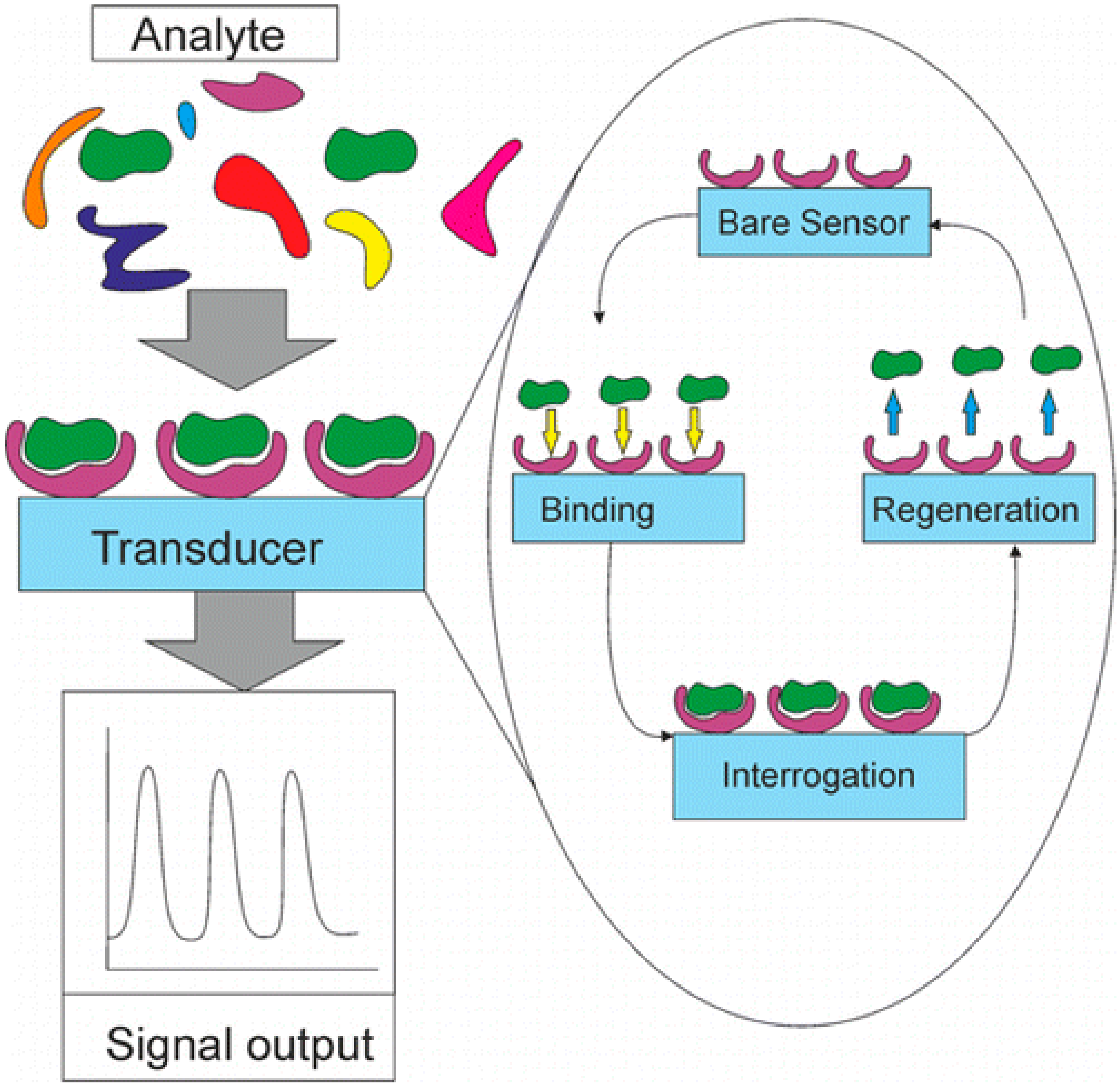
Nanosensors and their types

| Nanosensors | Analytes | Mechanisms | Merits | Demerits |
|---|---|---|---|---|
| Electrochemical | ROS, glucose, VOCs, enzymes, auxin, plant thiols, heavy metals | Consists of a working electrode, counter electrode and reference electrode. Based on the electrochemical response or electrical resistance change of materials caused by reaction with analytes | Simplicity, high sensitivity, low cost, direct data analysis, broad range of analytes | On-site source for the sensor, invasive and destructive, sensitive to pH or temperature |
| Piezoelectric | Mechanical forces in morphogenesis | Converts mechanical vibration into an electric signal | Real-time monitoring of the mechanical environment or plant growth | High cost, no optical readout, labour intensive for fabrication |
| SERS | Adenine dinucleotide, glucose | Enhances Raman signals of analytes adsorbed in the surface of metal nanoparticles | Ultra-high sensitivity, nonphotobleaching, multiplexing | Limited analytes, instrumentation |
| FRET | DNA, ATP, glucose, sucrose, metal ions, phytoestrogens | Consists of a recognition element fused to a reporter element, reports a conformational change in the energy transfer between the fluorophores | High sensitivity, low detection limit, high temporal and spatial resolution | Low stability of expressing FP in plant, photobleaching, low photostability, background signal |
| CoPhMoRe | $H_2O_2$, NO, glucose, dopamine | Turn off or on fluorescence by molecular recognition mediated by | Photostability, non-photobleaching, optical detection *in vivo* | Sensitivity, specificity, stability in vivo rational design of |

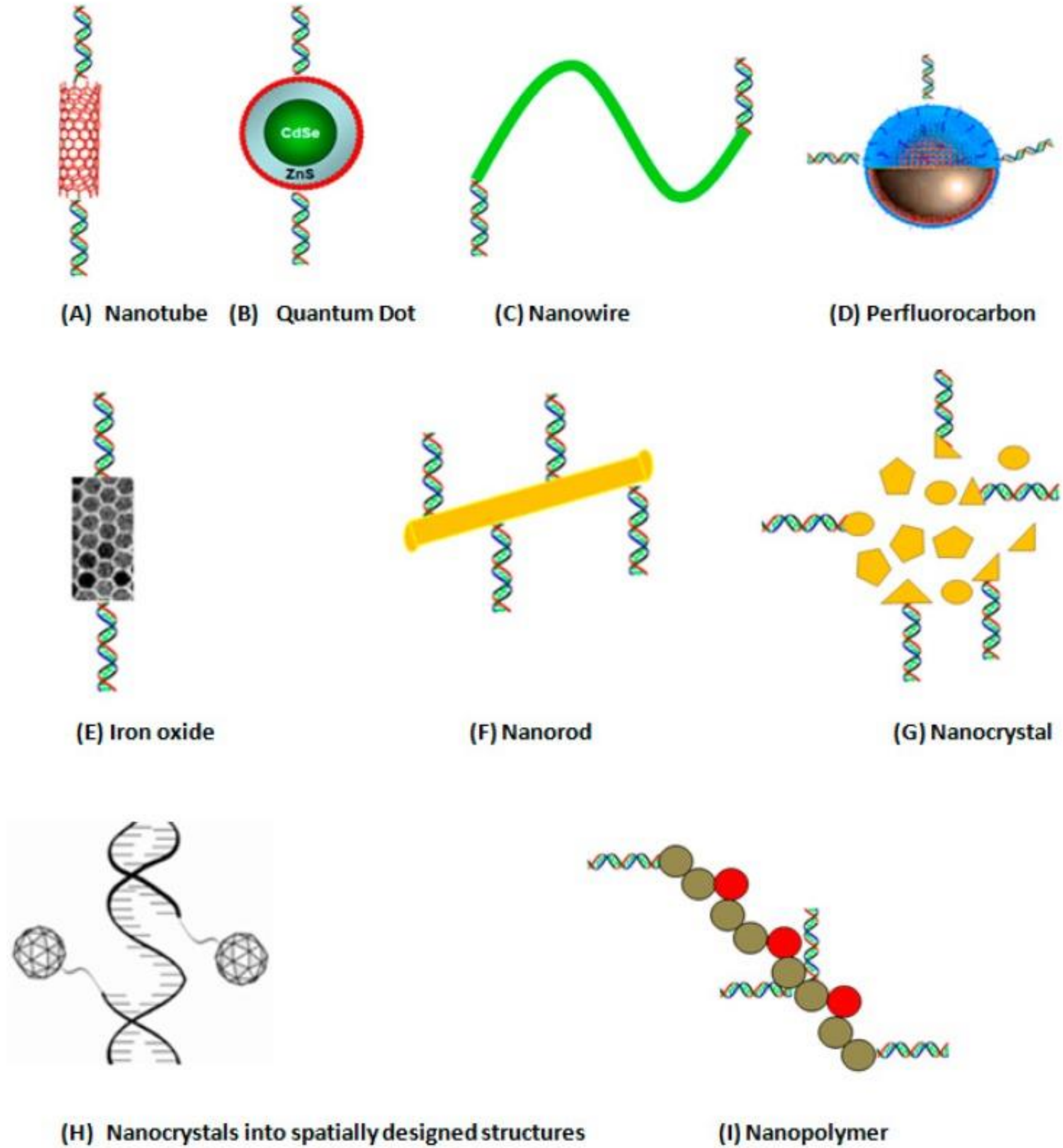
(Source: Kwak et al. 2017)

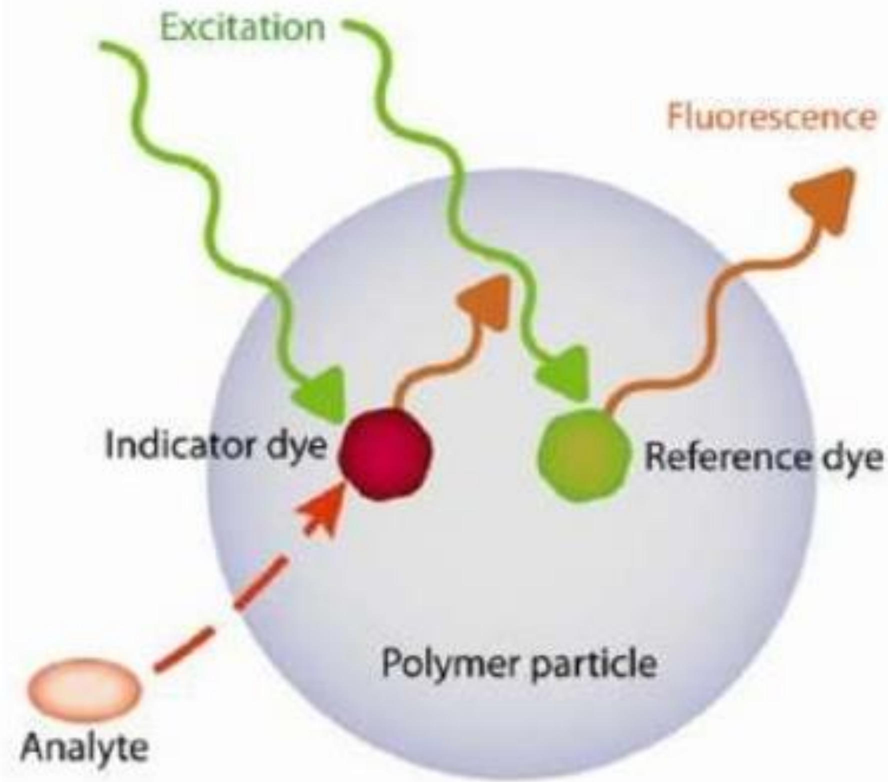

Nanosensors
On the basis of receptors molecules
On the basis of structure
On the basis of applications
1. Affinity-based nanosensors (includes antibodies, hormones, and nucleic acid receptors that bind molecules of interest irreversibly and noncatalytically)
2. Catalytic-based sensors (enzyme-or microbiological cells–based receptors that bind molecules of interest and catalytically convert them into recognizable products)
1. Optical nanosensors (measure amplitude, energy, polarization, delay time, and decay phase)
2. Electrochemicalsensors (measure electrochemical and mass transduction mechanisms)
1. Chemical nanosensors (consist of capacitive cantilevers and electronics and able to detect single chemical and biological molecules)
2. Deployable sensors (used in military and other national security applications)
3. Electrometers (consist of torsional mechanical resonators)
4. Biosensors (consist of polymers to detect cancer, DNA, etc.)


Signal transducer
Products
Specific reaction
Advantages of biosensors
Rapid real-time detection
Cost effectiveness
Portable (in situ monitoring)
Simple use
Limited sample preparation
Highly sensitive
Specific
Reusable
Less organic solvent consumption

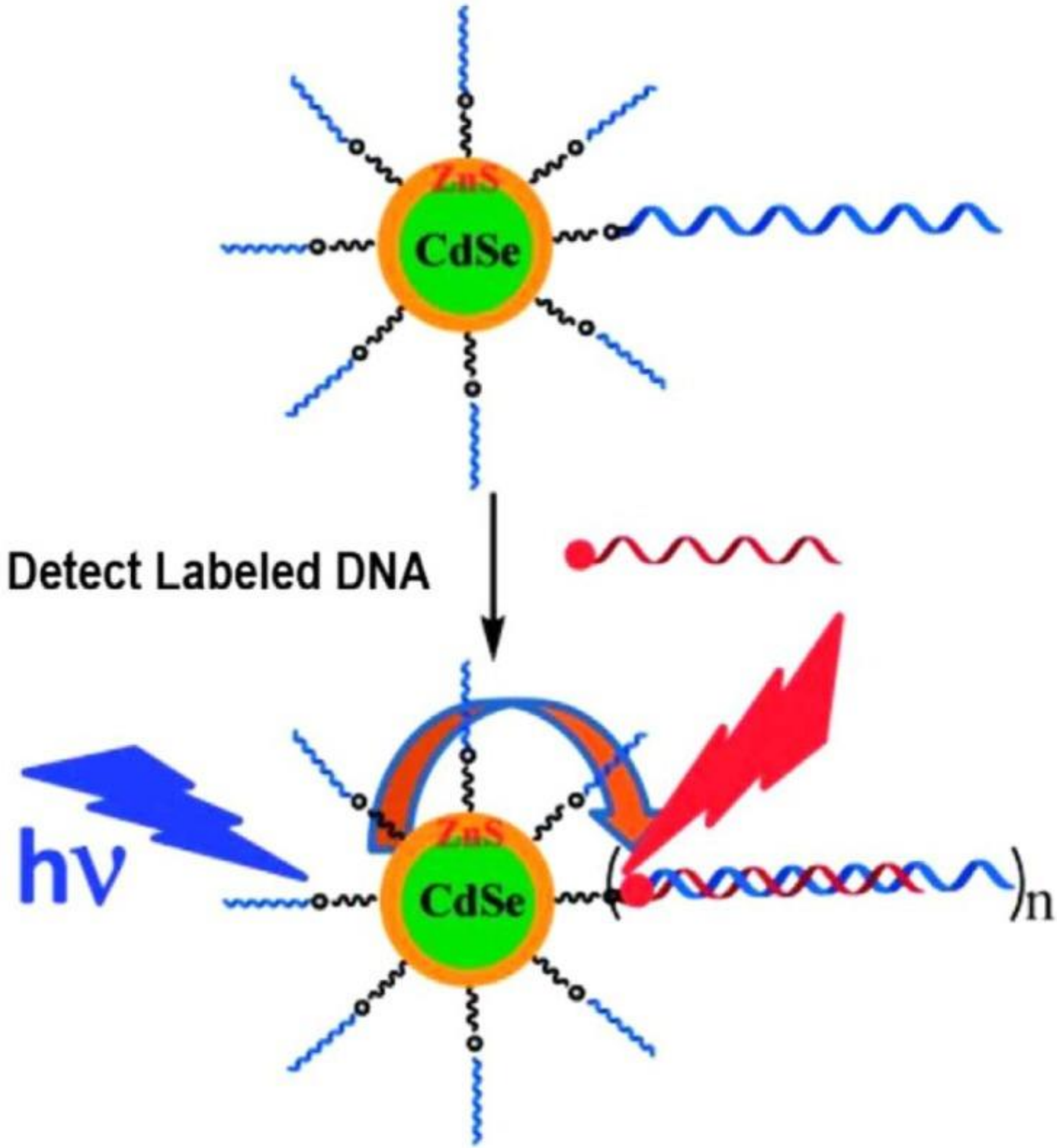


Analyte
Transducer
Signal output
Bare Sensor
Binding
Regeneration
Interrogation


CdSe
ZnS
(A) Nanotube
(B) Quantum Dot
(C) Nanowire
(D) Perfluorocarbon
(E) Iron oxide
(F) Nanorod
(G) Nanocrystal
(H) Nanocrystals into spatially designed structures
(I) Nanopolymer

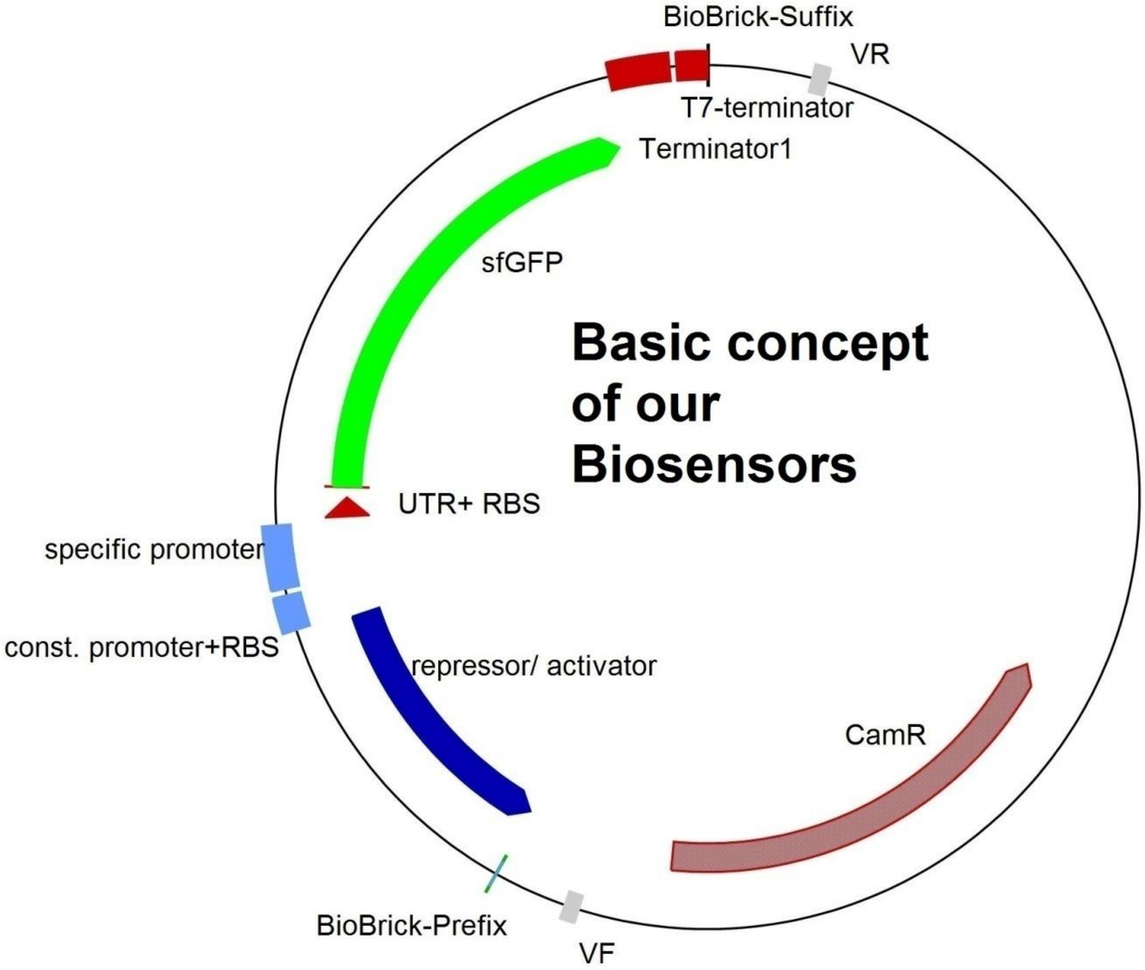


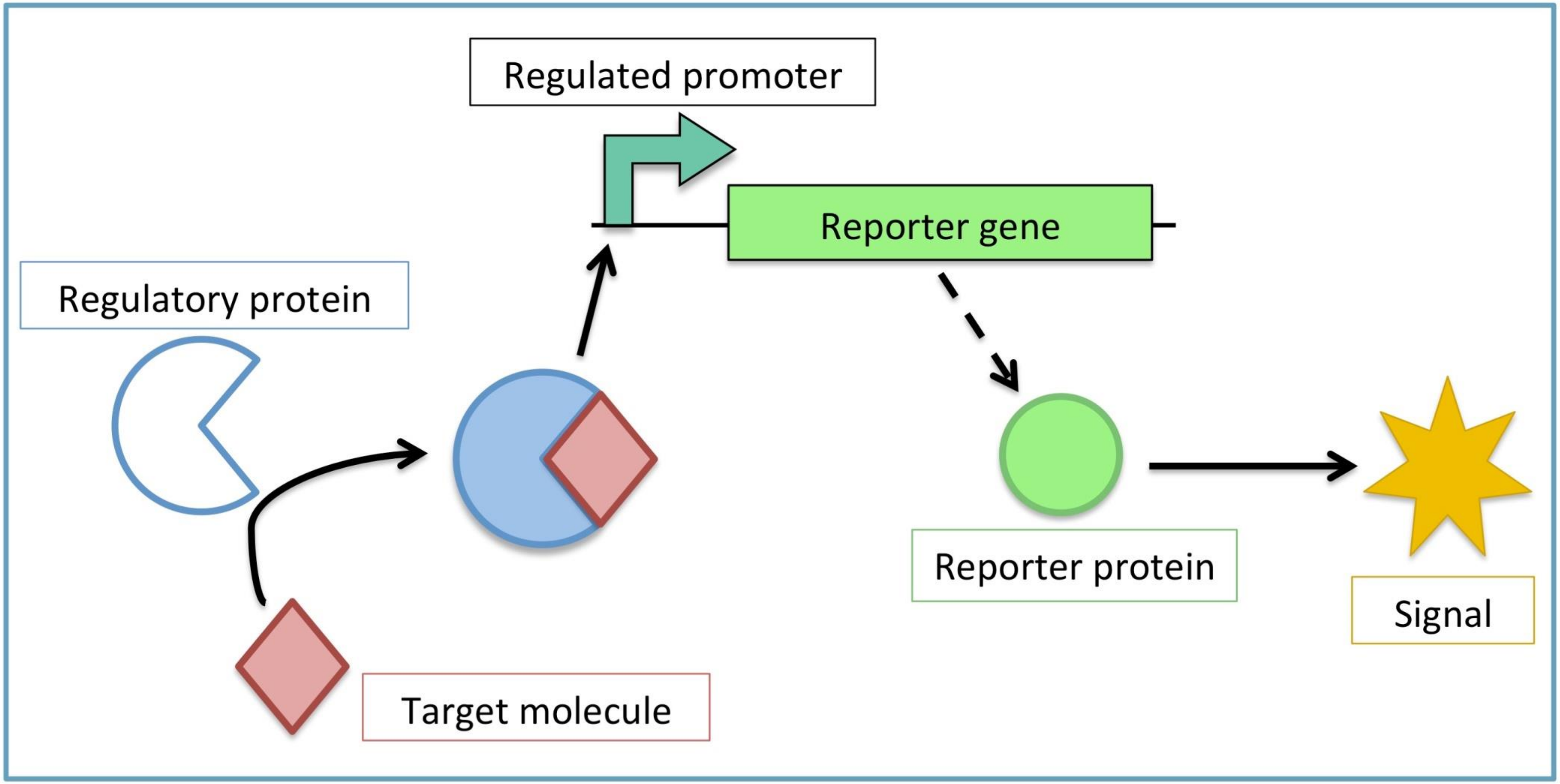
Excitation
Fluorescence
Indicator dye
Reference dye
Polymer particle
Analyte



ZnS
CdSe
Detect Labeled DNA
hν
ZnS
CdSe
n

# Basic concept of our Biosensors





Regulated promoter
Reporter gene
Regulatory protein
Reporter protein
Signal
Target molecule

# Nanosensors in Agriculture

- Important role in Agricultural Revolution
- Next Generation diagnostic tools and technologies
- Nanosensors - electrochemical, optical, nanowires, carbon-based, FRET-based, Plasmonic, antibody, e-nose, e-tongue, nano-barcode
- Reliable, efficient, specific, sensitive, portable, small size and economical

# Nanosensors Technology

- Nanosensors
- Sensing signal molecules
- Monitoring Crop health
- Communication
- Actuation

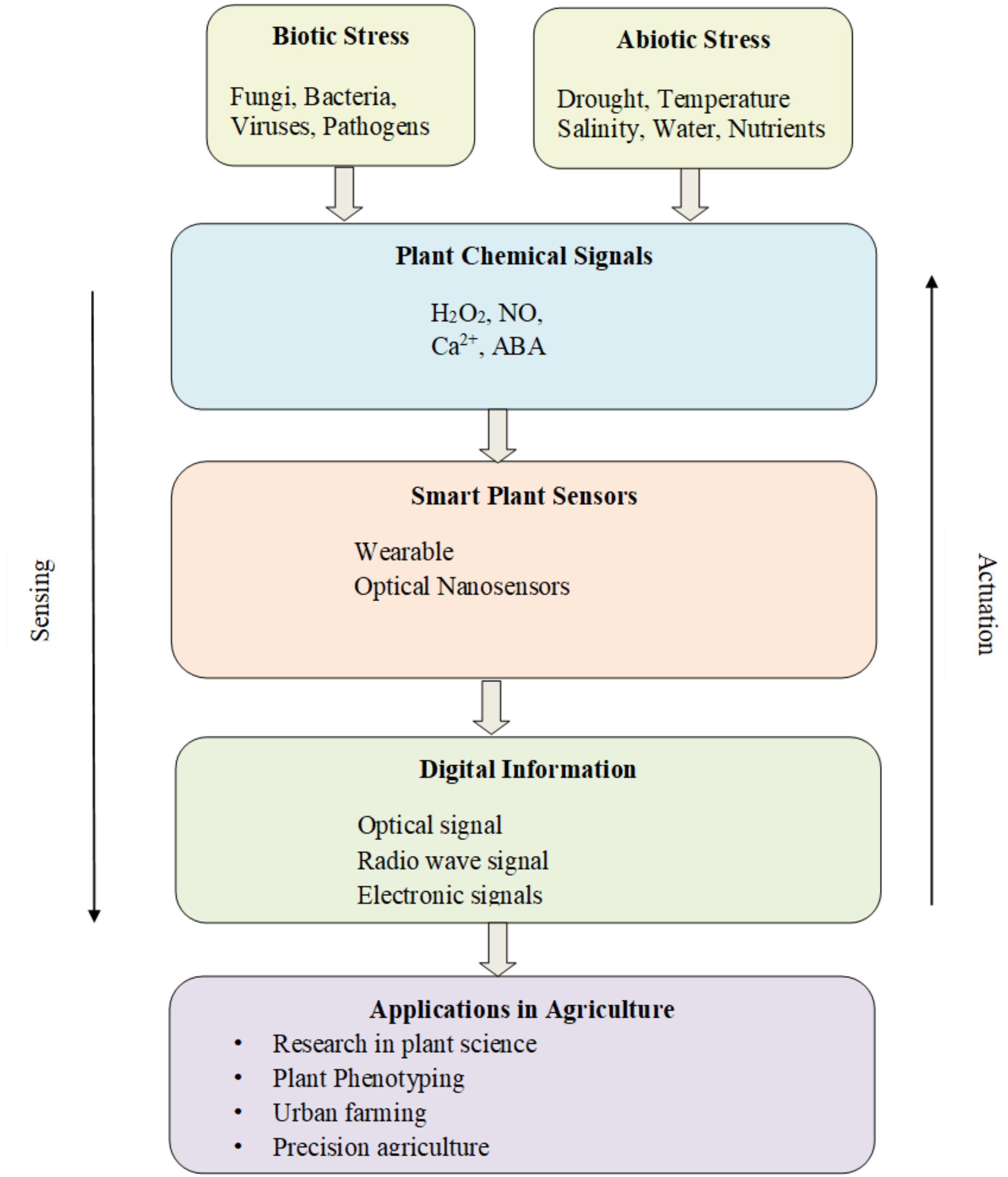
# Plant Signaling Molecules

- $Ca^{2+}$
- $H_2O_2$
- ROS
- NO
- VOC
- ATP
- ABA
- Jasmonic acid
- Methyl Salicylate
- Ethylene

Crop Health Status

# Real-Time Monitoring

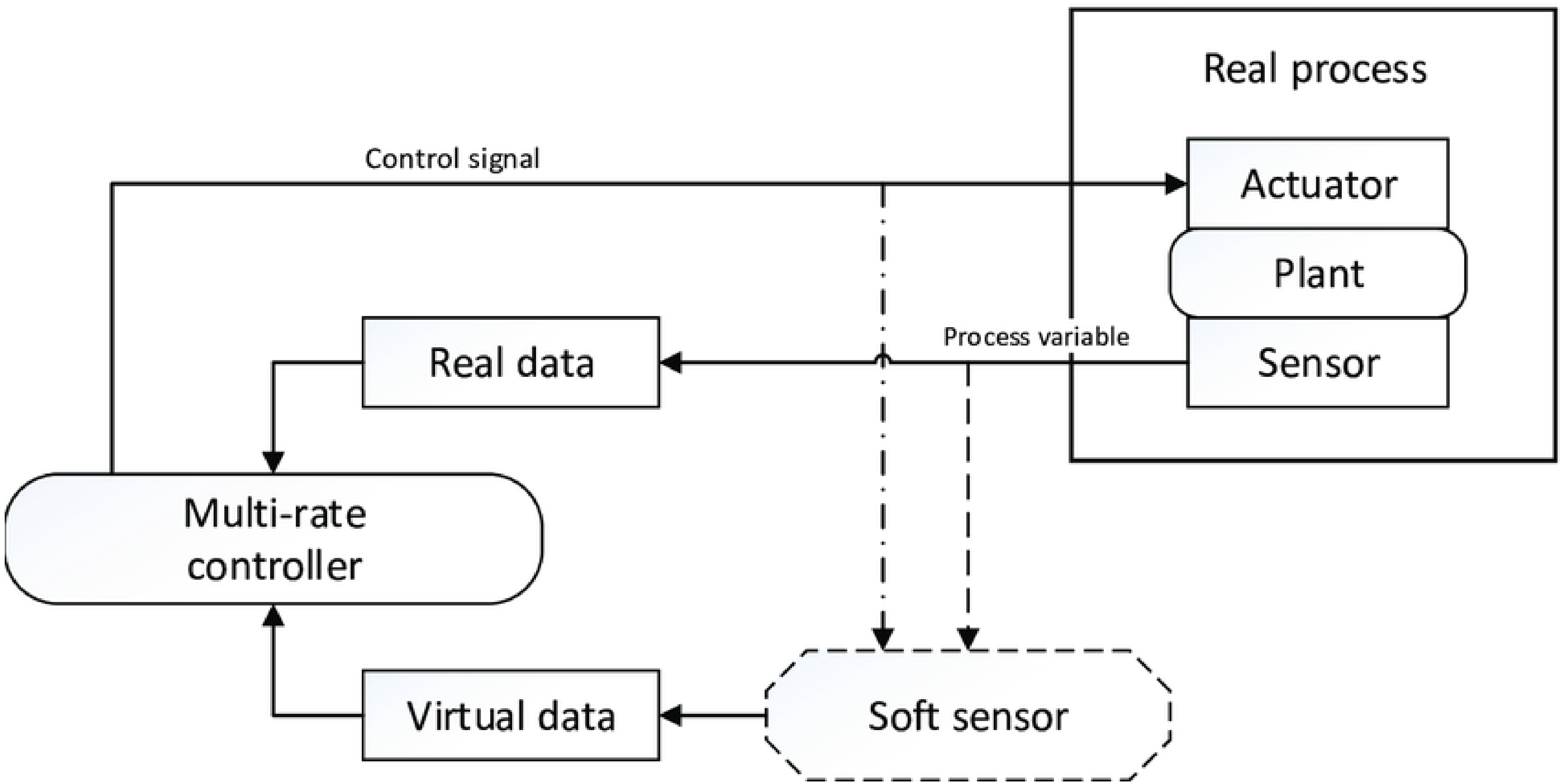
- Engineered nanomaterials embedded in plants
- Monitoring of Signaling Molecules via various communication techniques
- Nanosensors communicate with electronic devices for actuation
- Optimization and automation of water and agrochemical allocation
- Increased Crop Productivity

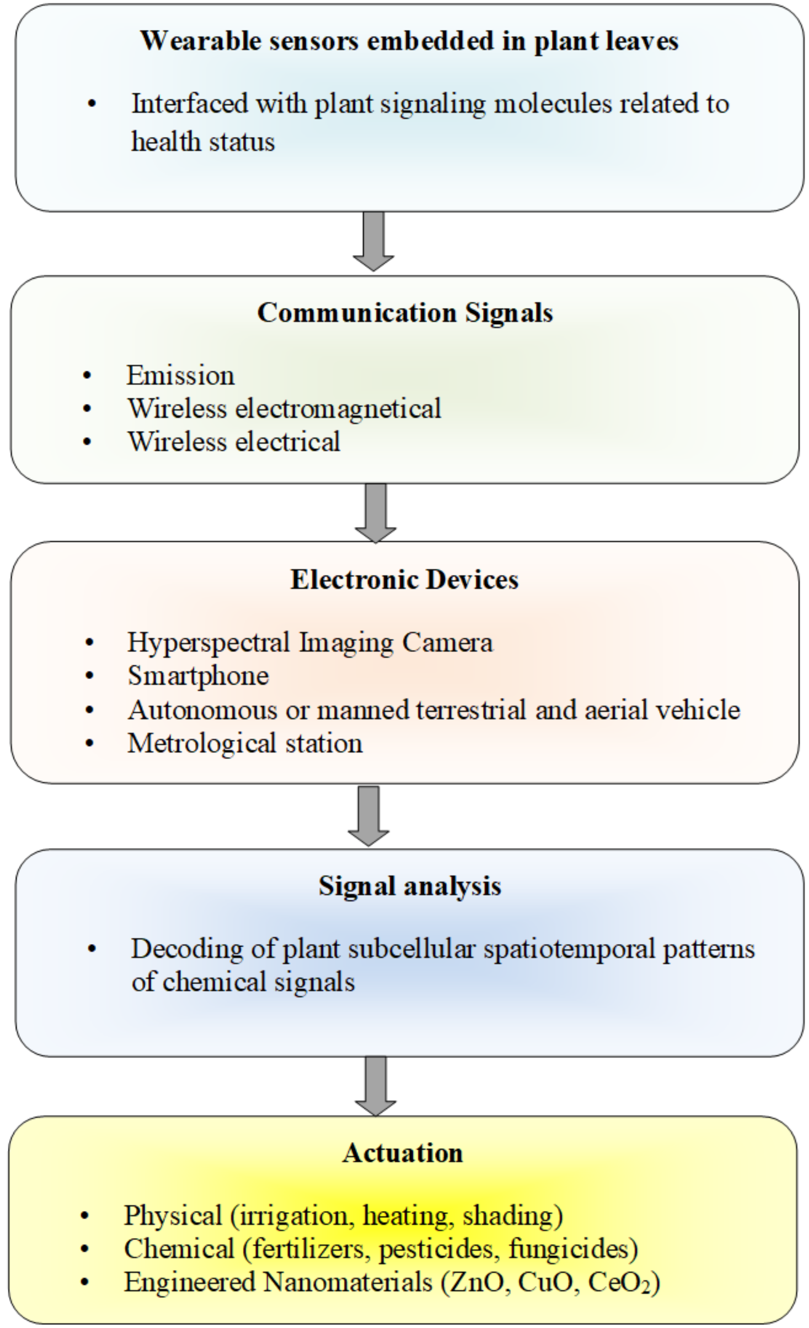

Biotic Stress
Fungi, Bacteria,
Viruses, Pathogens
Abiotic Stress
Drought, Temperature
Salinity, Water, Nutrients
Plant Chemical Signals
$H_2O_2$, NO,
$Ca^{2+}$, ABA
Smart Plant Sensors
Wearable
Optical Nanosensors
Digital Information
Optical signal
Radio wave signal
Electronic signals
Applications in Agriculture
• Research in plant science
• Plant Phenotyping
• Urban farming
• Precision agriculture
Sensing
Actuation

Development of Nanosensor for plant signaling molecules related to health status

| Nanotechnology-based sensor, probe, indicator, reporter | Plant molecular targets |
|---|---|
| SWCNT<br><br>HyPer, roGFP-Orp1 | $H_2O_2$ |
| SWCNT, GCaMP3, YC3.6, R-GECO1 | $Ca^{2+}$ |
| SWCNT | NO |
| SWCNT, FLIPglu-2µVΔ13, FLIPglu-600µΔ13, BA-QD | Glucose |
| FLIPsuc-90µΔ1 | Sucrose |
| SWCNT | Ethylene |
| Ag NPs | Methyl salicylate |
| Jas9-VENUS | Jasmonic acid |
| ABAleon2.1, ABACUS1 | Abscisic acid |
| GFP H148D | $H^+$ gradient (pH) |

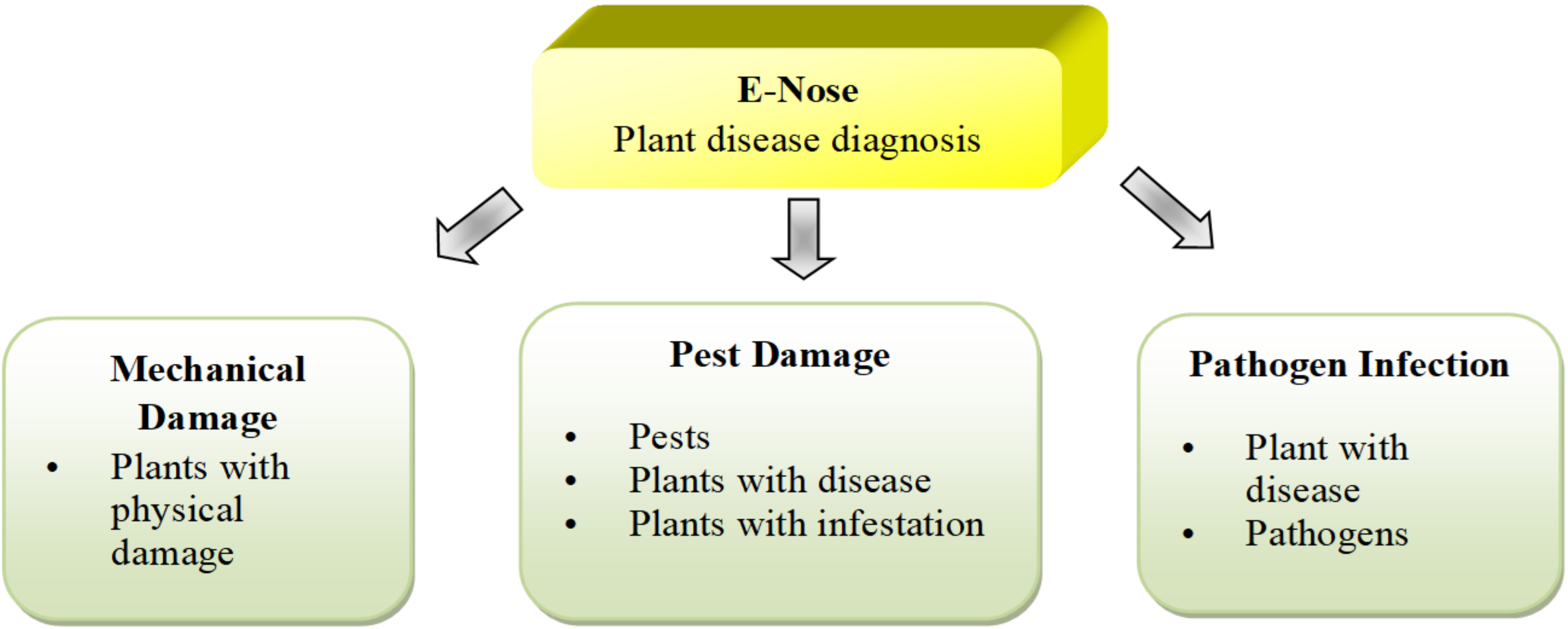
(Source: Adapted from Giraldo et al. 2019)


Real process
Control signal
Actuator
Plant
Process variable
Real data
Sensor
Multi-rate
controller
Virtual data
Soft sensor


Wearable sensors embedded in plant leaves
• Interfaced with plant signaling molecules related to health status
Communication Signals
• Emission
• Wireless electromagnetical
• Wireless electrical
Electronic Devices
• Hyperspectral Imaging Camera
• Smartphone
• Autonomous or manned terrestrial and aerial vehicle
• Metrological station
Signal analysis
• Decoding of plant subcellular spatiotemporal patterns of chemical signals
Actuation
• Physical (irrigation, heating, shading)
• Chemical (fertilizers, pesticides, fungicides)
• Engineered Nanomaterials (ZnO, CuO, $CeO_2$)


VOCs
Gas sensor array
Signal transducers
Pattern recognition algorithms
Discrimination & classification

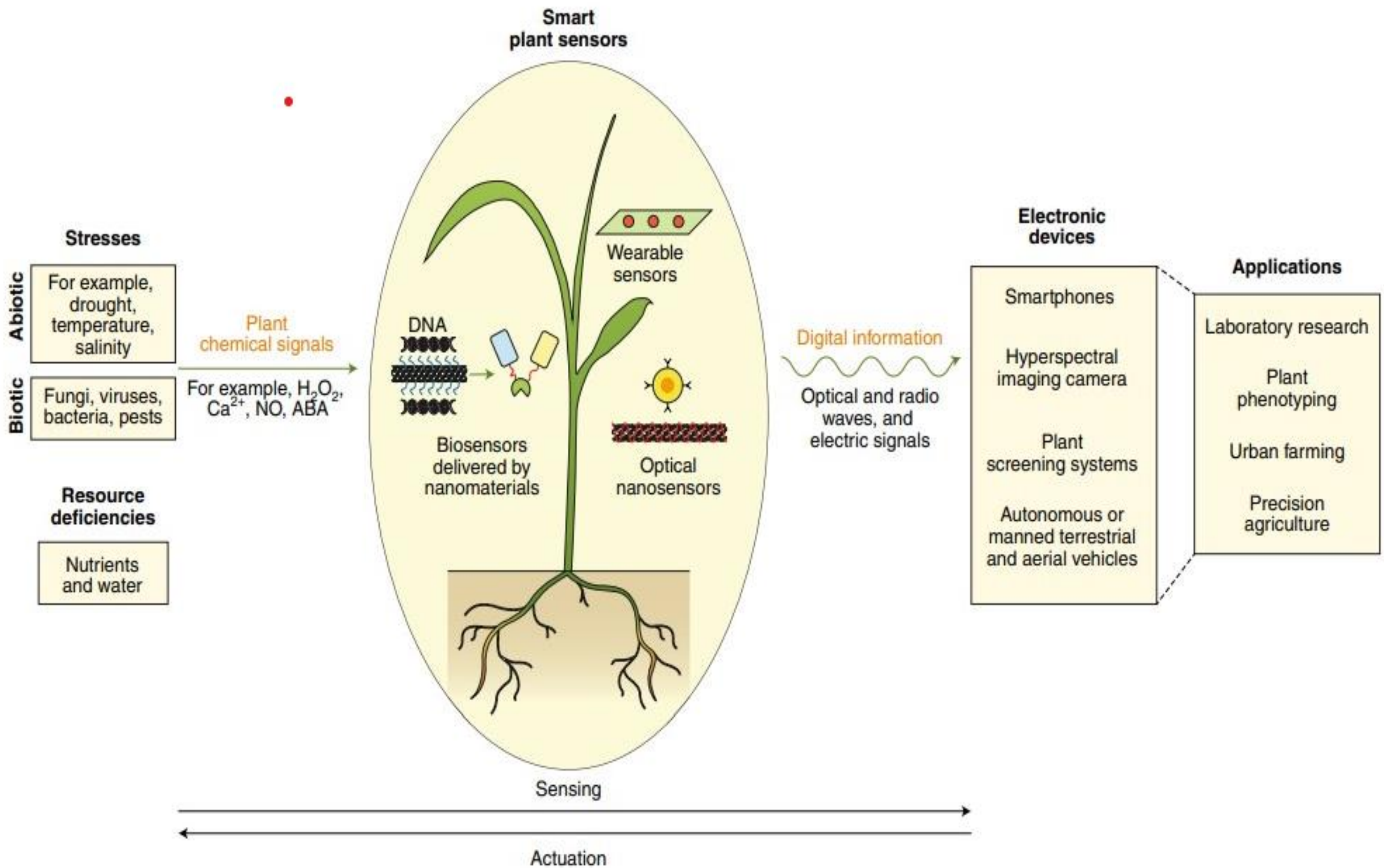
a.


E-Nose
Plant disease diagnosis
Mechanical Damage
Plants with physical damage
Pest Damage
Pests
Plants with disease
Plants with infestation
Pathogen Infection
Plant with disease
Pathogens

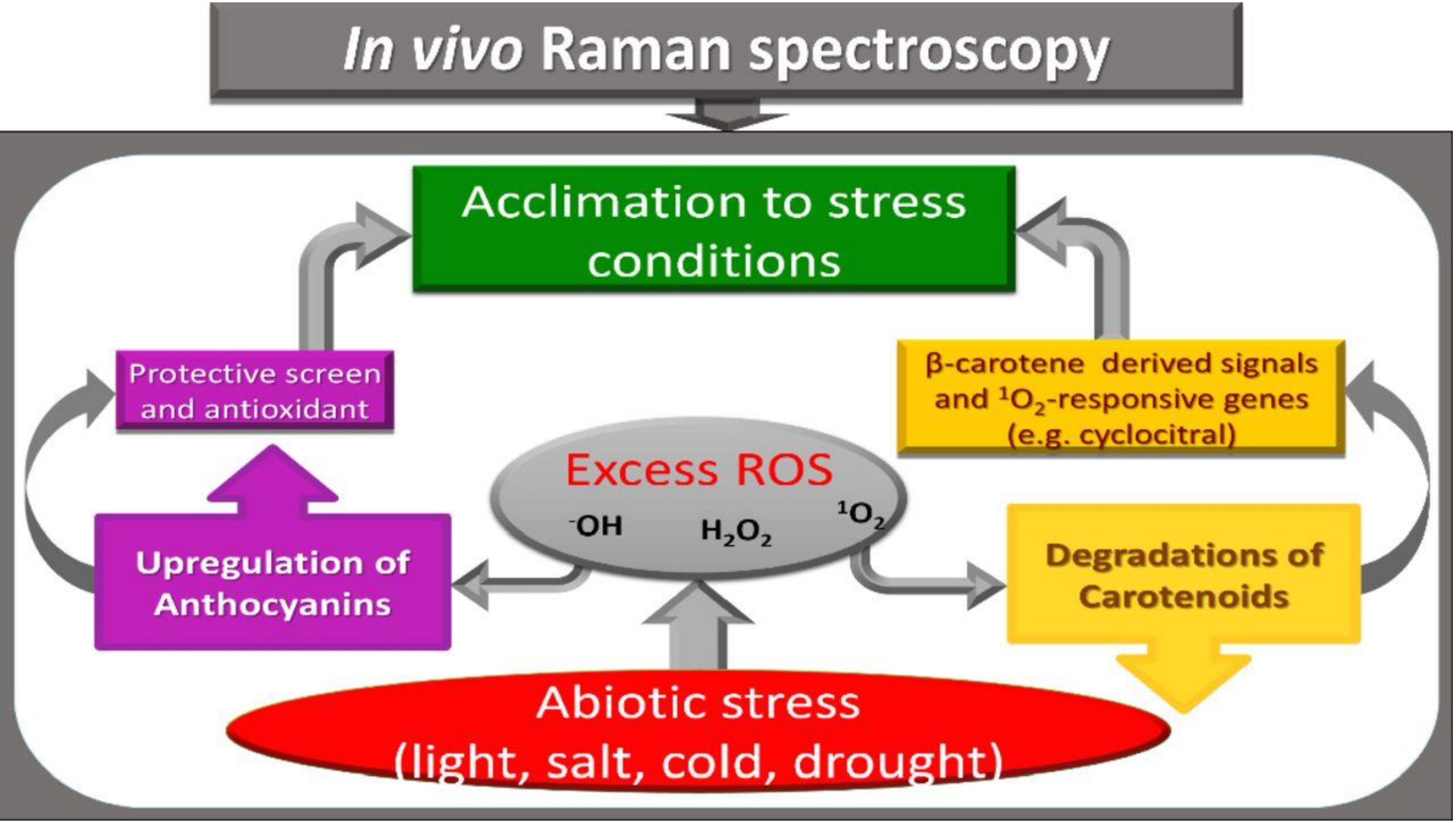
b.

# Emerging Nanodiagnostic Tools

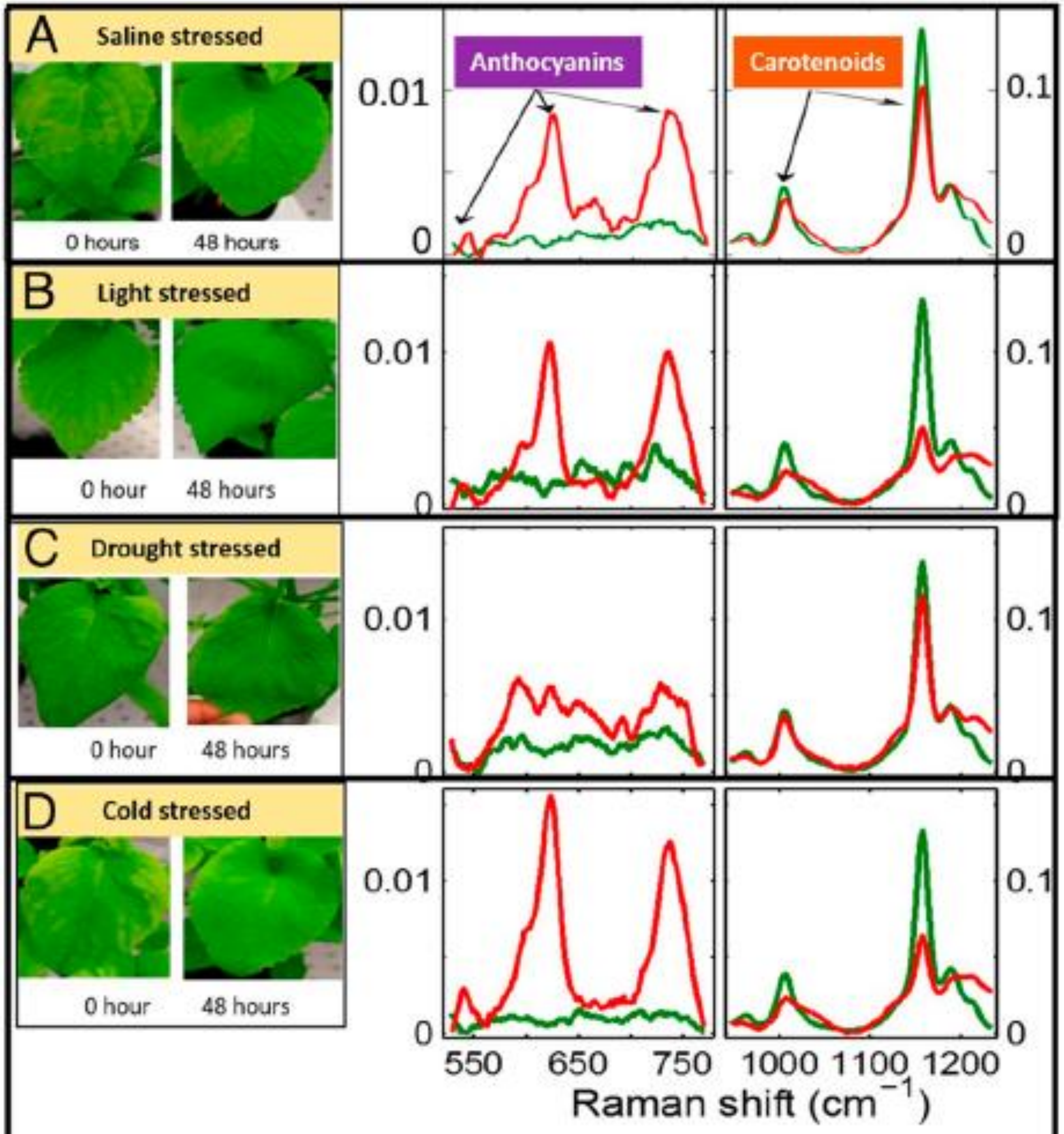
- Wearable Nanosensors
- Array-based Nanosensors
- Point-of-Care Technology
- Mobile/Wireless  Network Technology
- Nanosensor Communication
- Actuation System with Machines



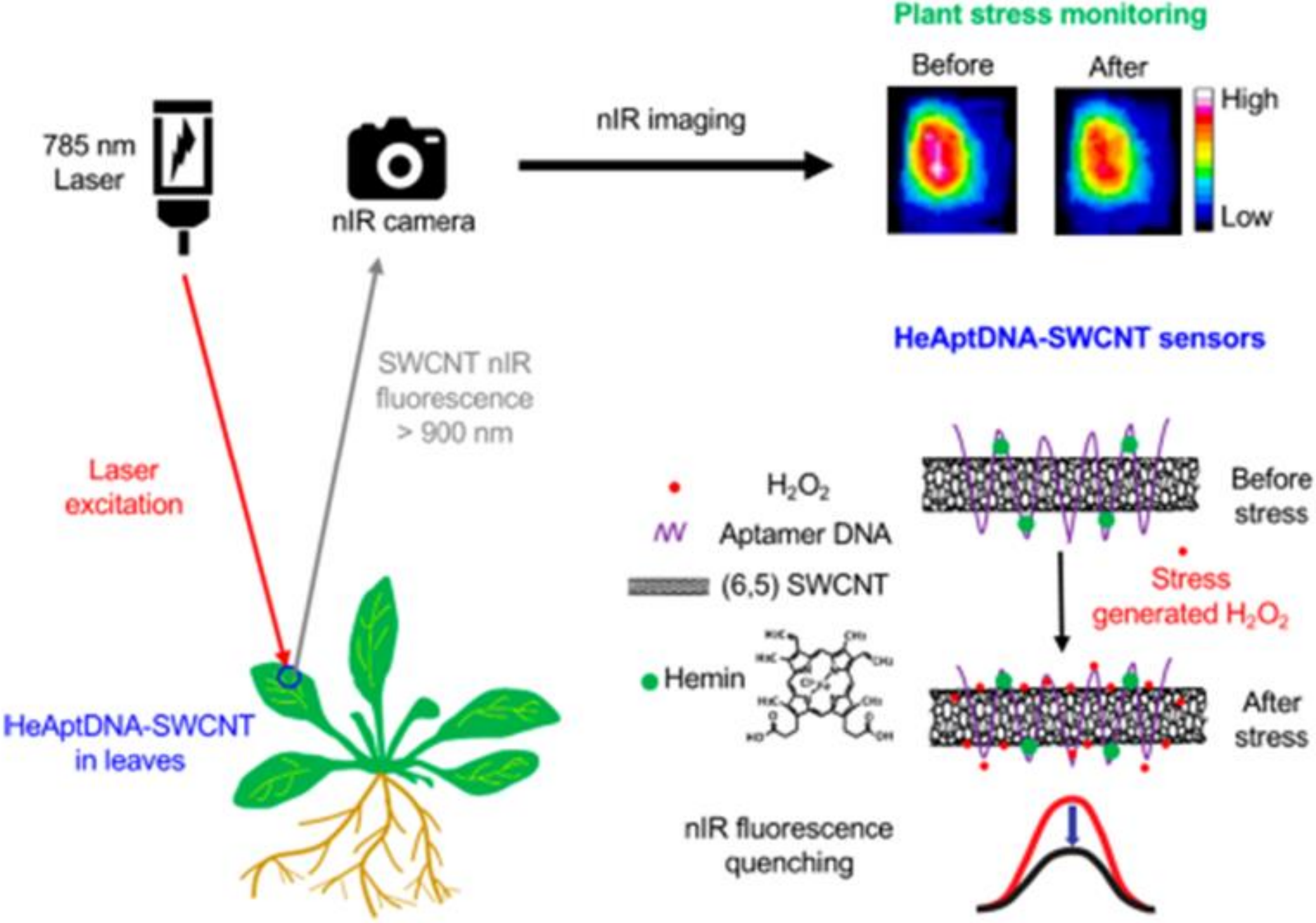
Smart
plant sensors
Stresses
Abiotic
For example, drought, temperature, salinity
Biotic
Fungi, viruses, bacteria, pests
Resource deficiencies
Nutrients and water
Plant
chemical signals
For example, $H_2O_2$, $Ca^{2+}$, NO, ABA
DNA
Biosensors delivered by nanomaterials
Wearable sensors
Optical nanosensors
Digital information
Optical and radio waves, and electric signals
Electronic devices
Smartphones
Hyperspectral imaging camera
Plant screening systems
Autonomous or manned terrestrial and aerial vehicles
Applications
Laboratory research
Plant phenotyping
Urban farming
Precision agriculture
Sensing
Actuation



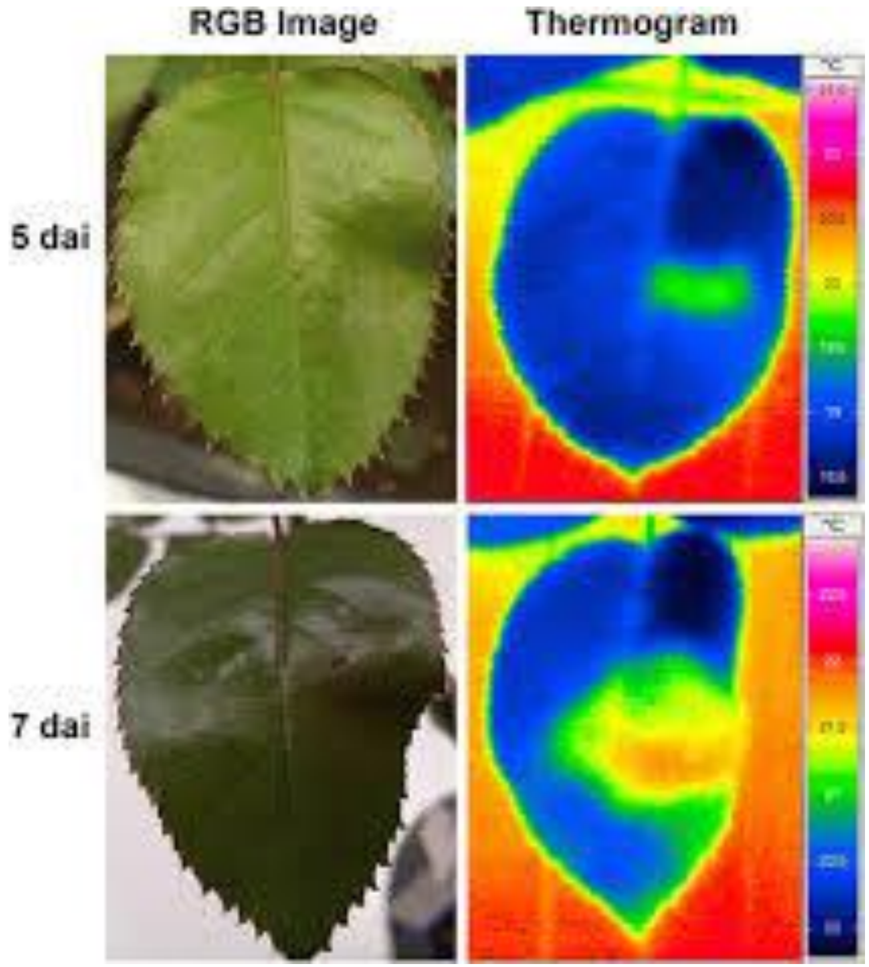
*In vivo* Raman spectroscopy
Acclimation to stress conditions
Protective screen and antioxidant
β-carotene derived signals and $^1O_2$-responsive genes (e.g. cyclocitral)
Excess ROS
$^-OH$
$H_2O_2$
$^1O_2$
Upregulation of Anthocyanins
Degradations of Carotenoids
Abiotic stress (light, salt, cold, drought)

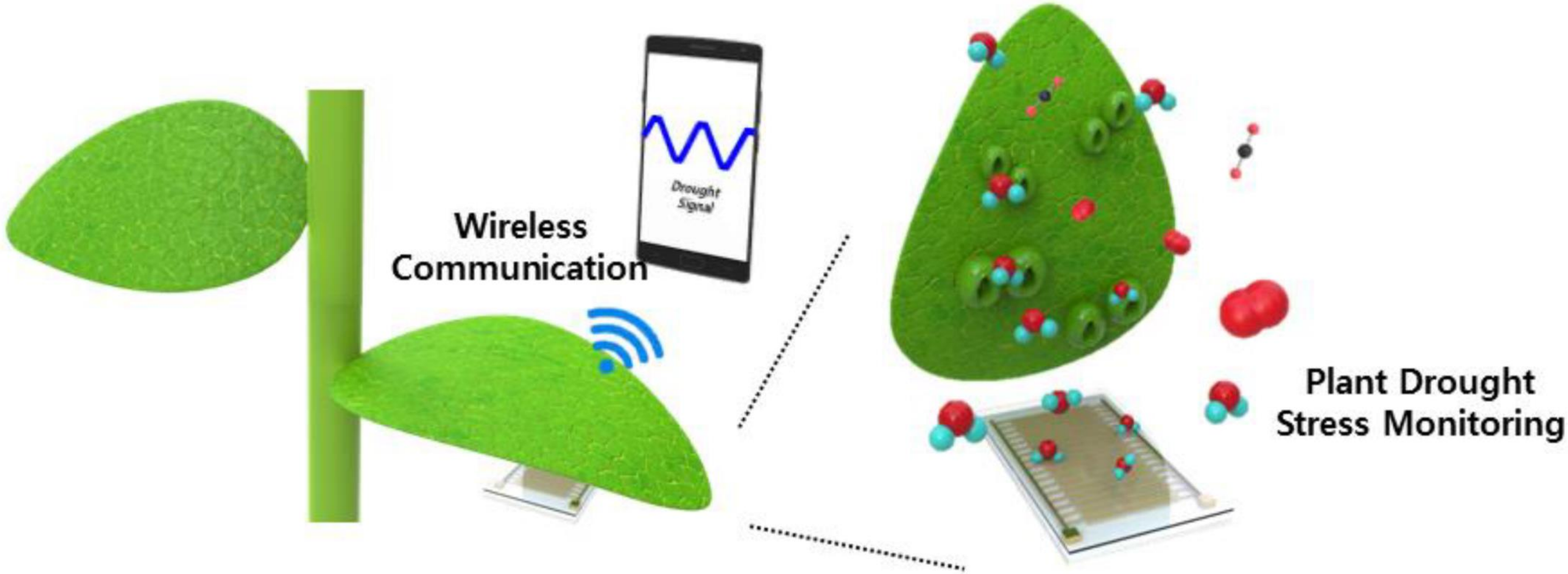


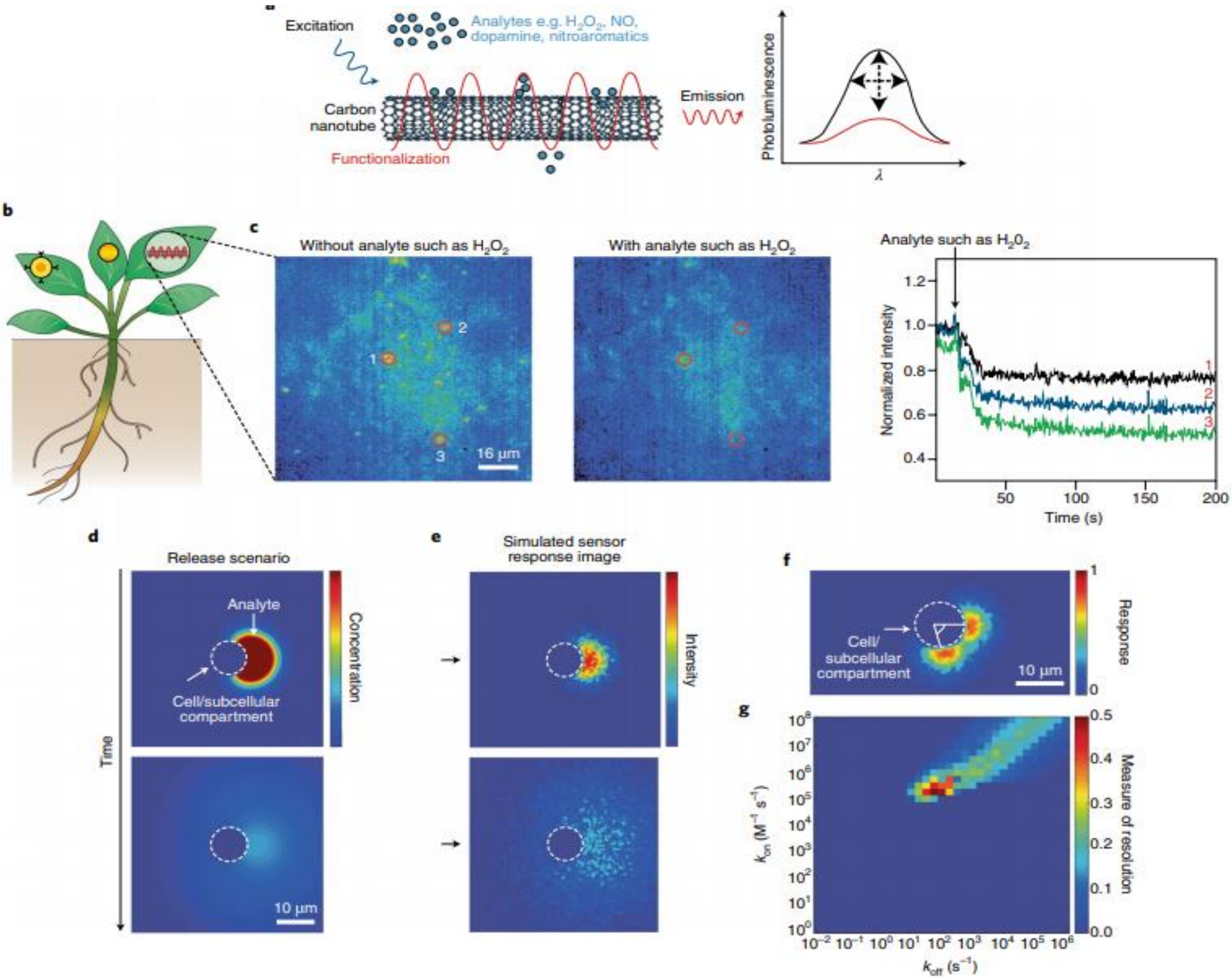
A
Saline stressed
0 hours
48 hours
B
Light stressed
0 hour
48 hours
C
Drought stressed
0 hour
48 hours
D
Cold stressed
0 hour
48 hours
Anthocyanins
Carotenoids
0.01
0
0.1
550
650
750
1000
1100
1200
Raman shift (cm$^{-1}$)



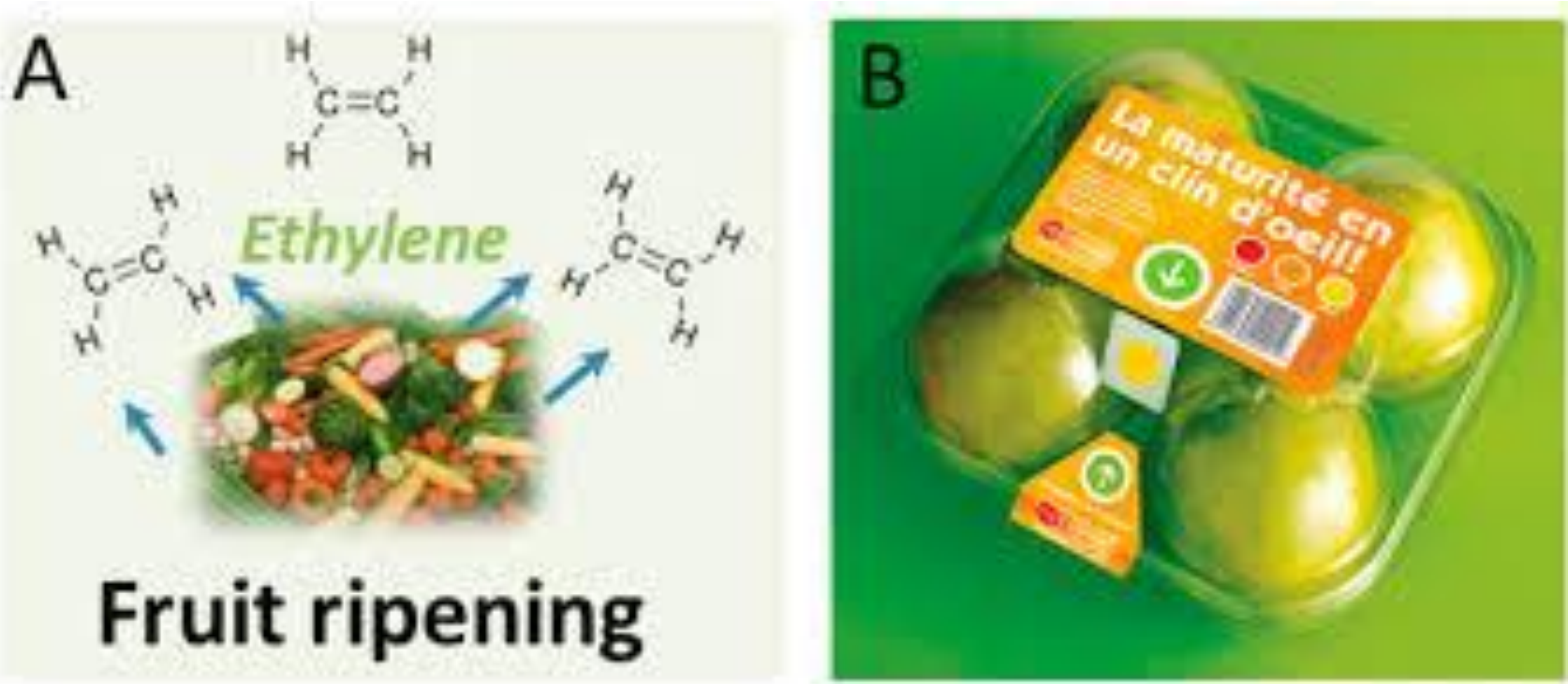
Plant stress monitoring
Before
After
High
Low
785 nm Laser
nIR camera
nIR imaging
SWCNT nIR fluorescence > 900 nm
Laser excitation
HeAptDNA-SWCNT in leaves
HeAptDNA-SWCNT sensors
$H_2O_2$
Aptamer DNA
(6,5) SWCNT
Hemin
Before stress
Stress generated $H_2O_2$
After stress
nIR fluorescence quenching

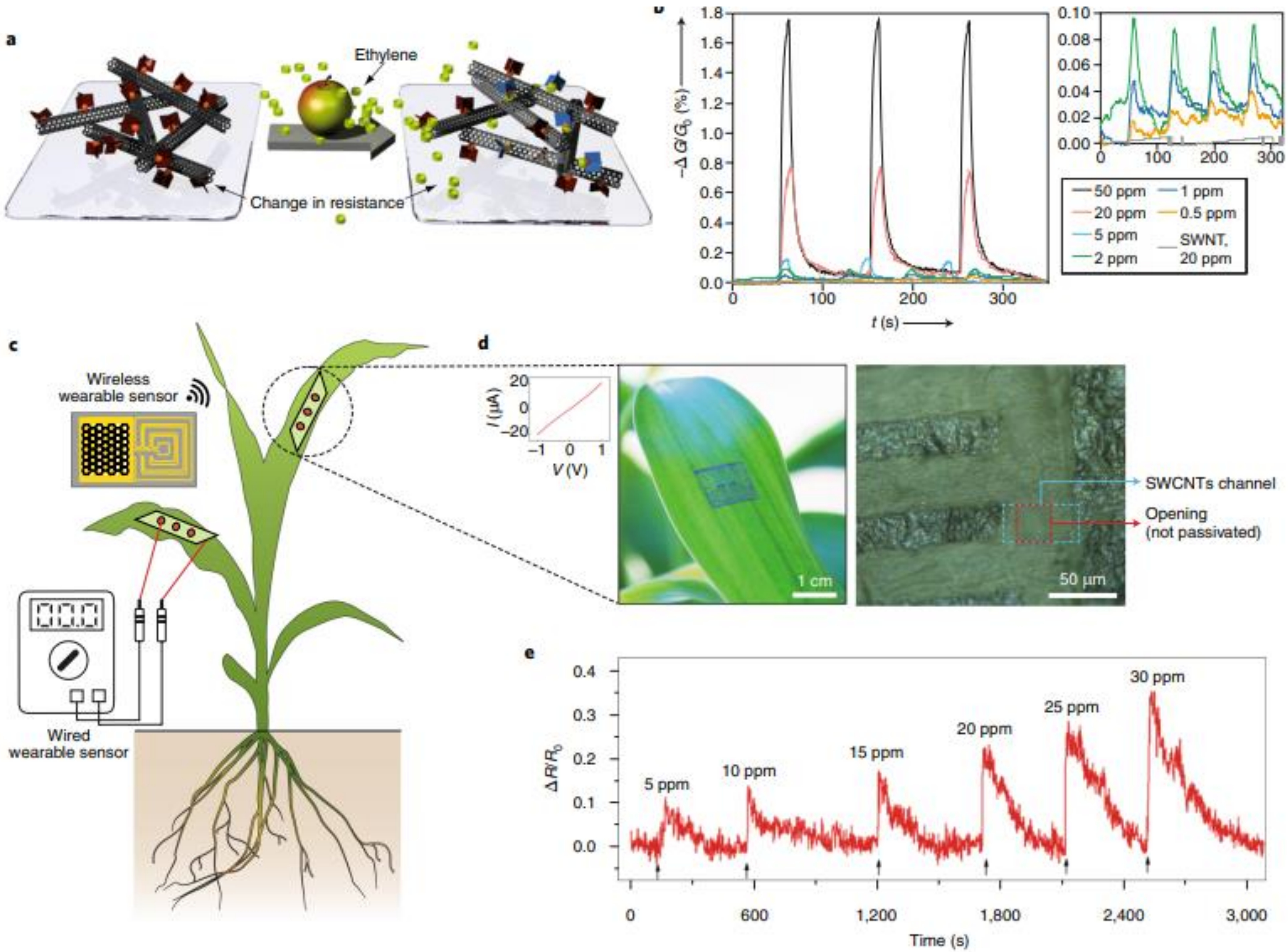

RGB Image
Thermogram
5 dai
7 dai
°C
°C


Drought Signal
Wireless Communication
Plant Drought Stress Monitoring

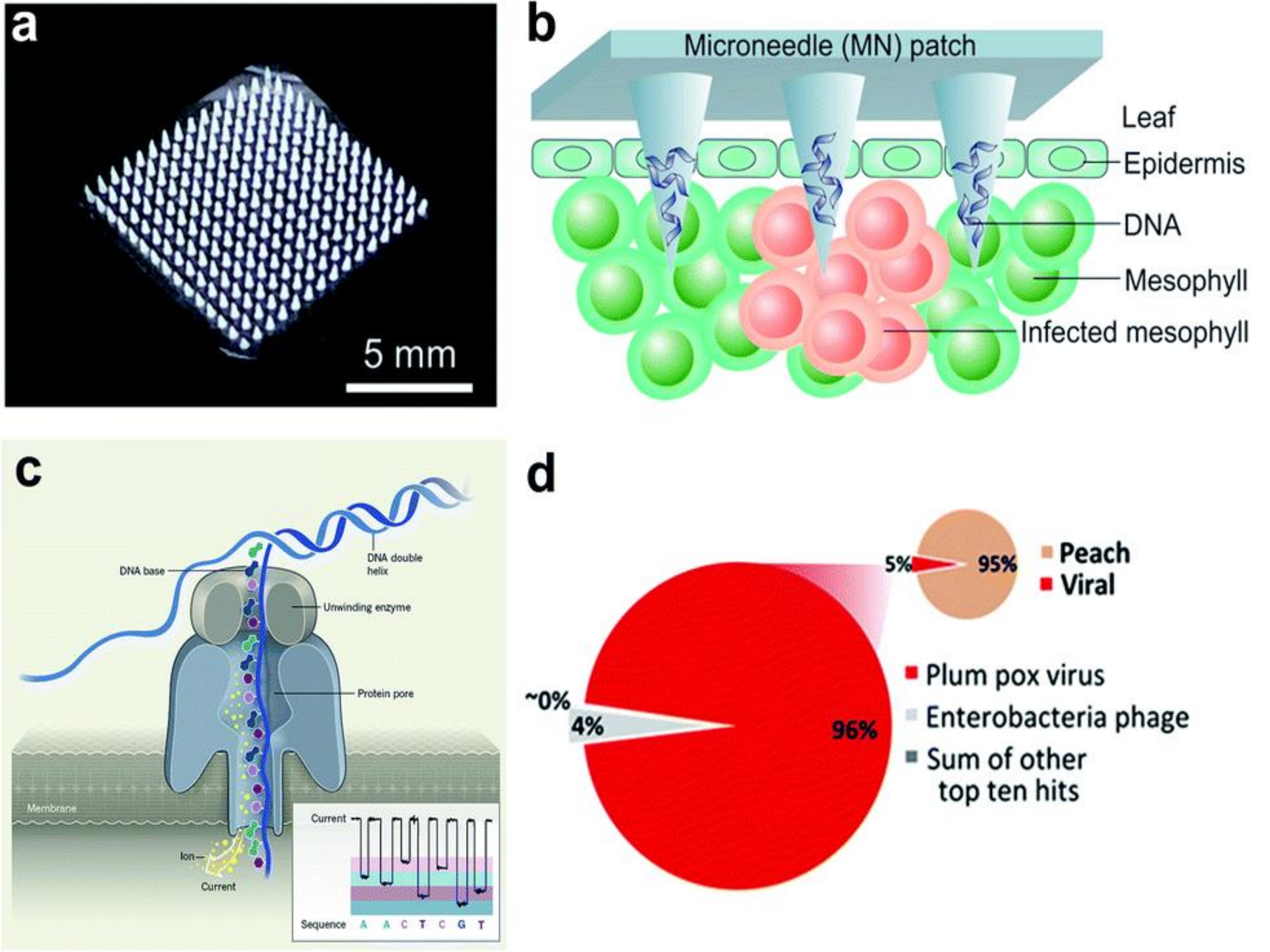


a
Excitation
Analytes e.g. $H_2O_2$, NO, dopamine, nitroaromatics
Carbon nanotube
Functionalization
Emission
Photoluminescence
λ
b
c
Without analyte such as $H_2O_2$
With analyte such as $H_2O_2$
16 μm
Analyte such as $H_2O_2$
Normalized intensity
Time (s)
d
Release scenario
Analyte
Cell/subcellular compartment
Concentration
Time
10 μm
e
Simulated sensor response image
Intensity
f
Cell/ subcellular compartment
10 μm
Response
g
$k_{on}$ ($M^{-1}$ $s^{-1}$)
$k_{off}$ ($s^{-1}$)
Measure of resolution


A
Ethylene
Fruit ripening
B
La maturité en
un clin d'oeil!



a
Ethylene
Change in resistance
b
−Δ G/G0 (%)
t (s)
50 ppm
20 ppm
5 ppm
2 ppm
1 ppm
0.5 ppm
SWNT, 20 ppm
c
Wireless wearable sensor
Wired wearable sensor
d
I (μA)
V (V)
1 cm
50 μm
SWCNTs channel
Opening (not passivated)
e
ΔR/R0
Time (s)
5 ppm
10 ppm
15 ppm
20 ppm
25 ppm
30 ppm

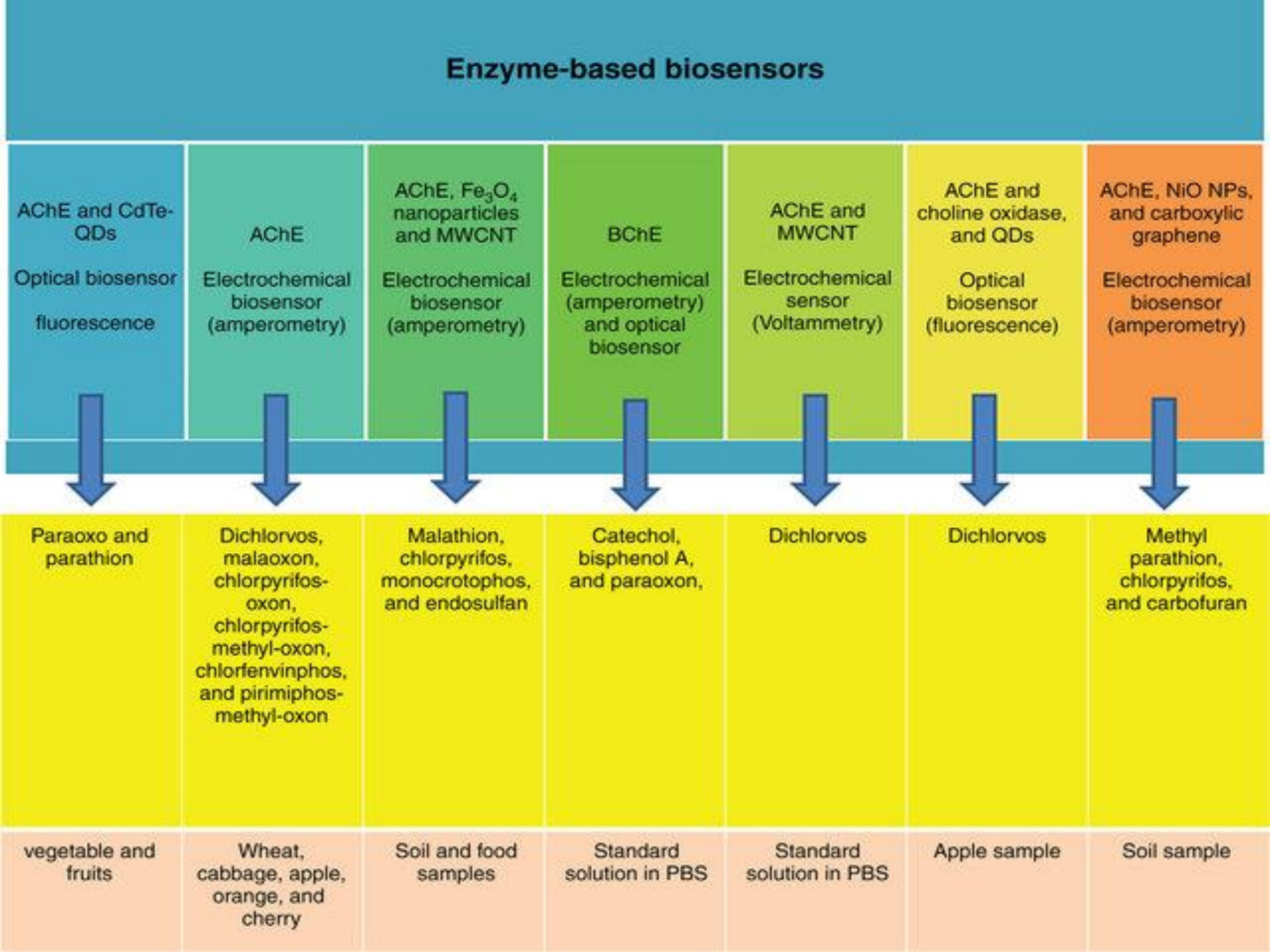


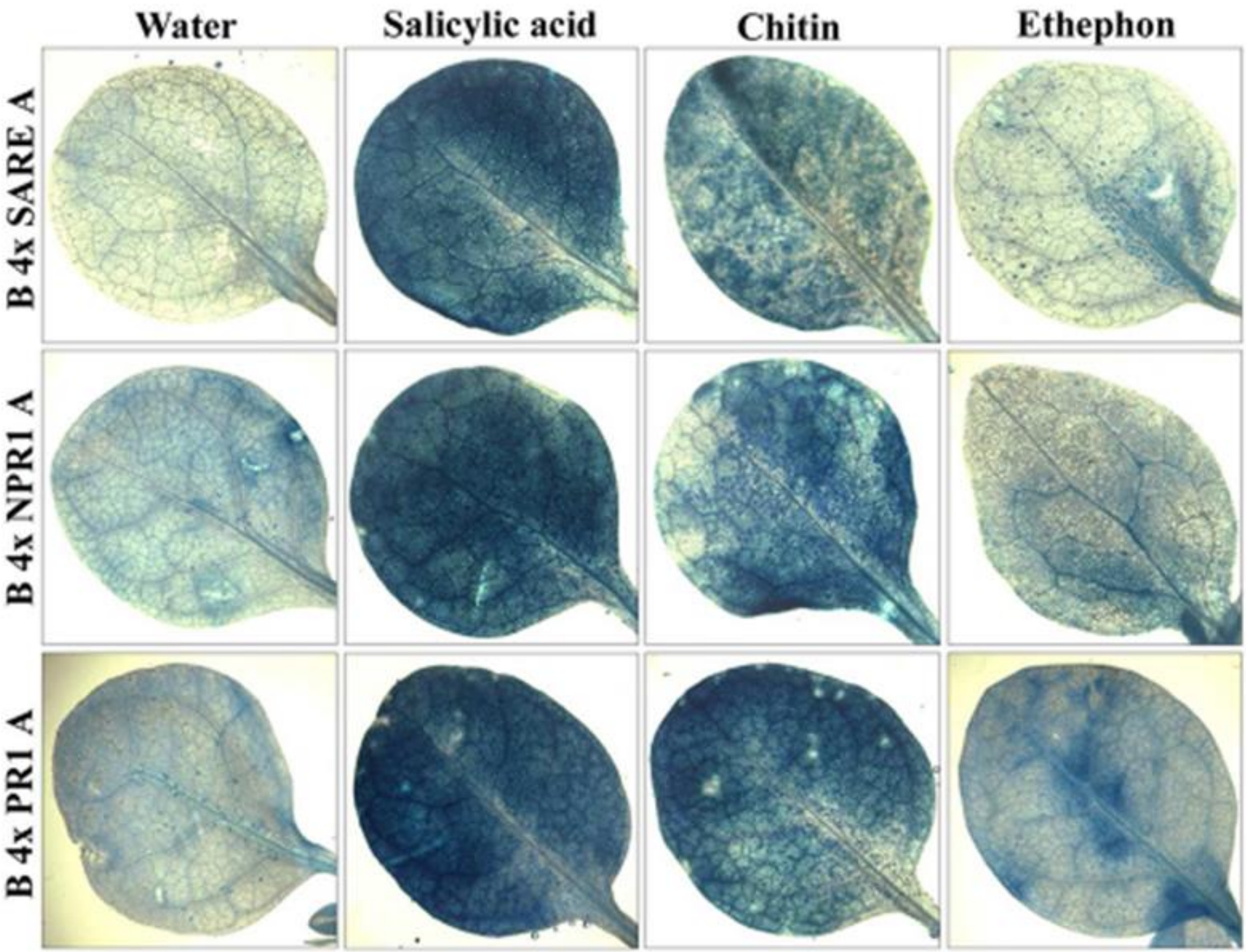
a
5 mm
b
Microneedle (MN) patch
Leaf
Epidermis
DNA
Mesophyll
Infected mesophyll
c
DNA double helix
DNA base
Unwinding enzyme
Protein pore
Membrane
Ion
Current
Current
Sequence A A C T C G T
d
5%
95%
Peach
Viral
~0%
4%
96%
Plum pox virus
Enterobacteria phage
Sum of other top ten hits

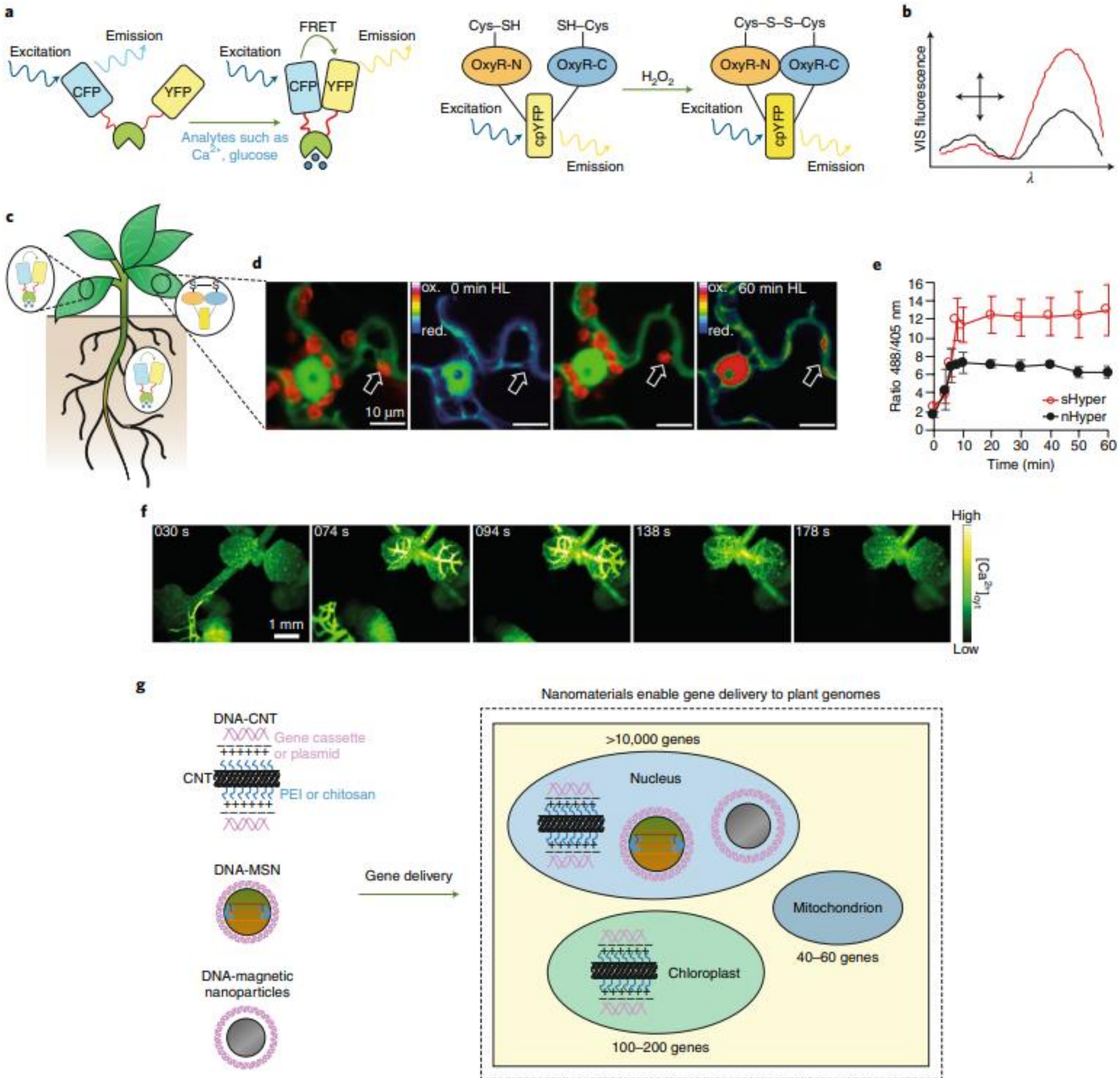
# Quantum dot and surface resonance-based virus biosensor

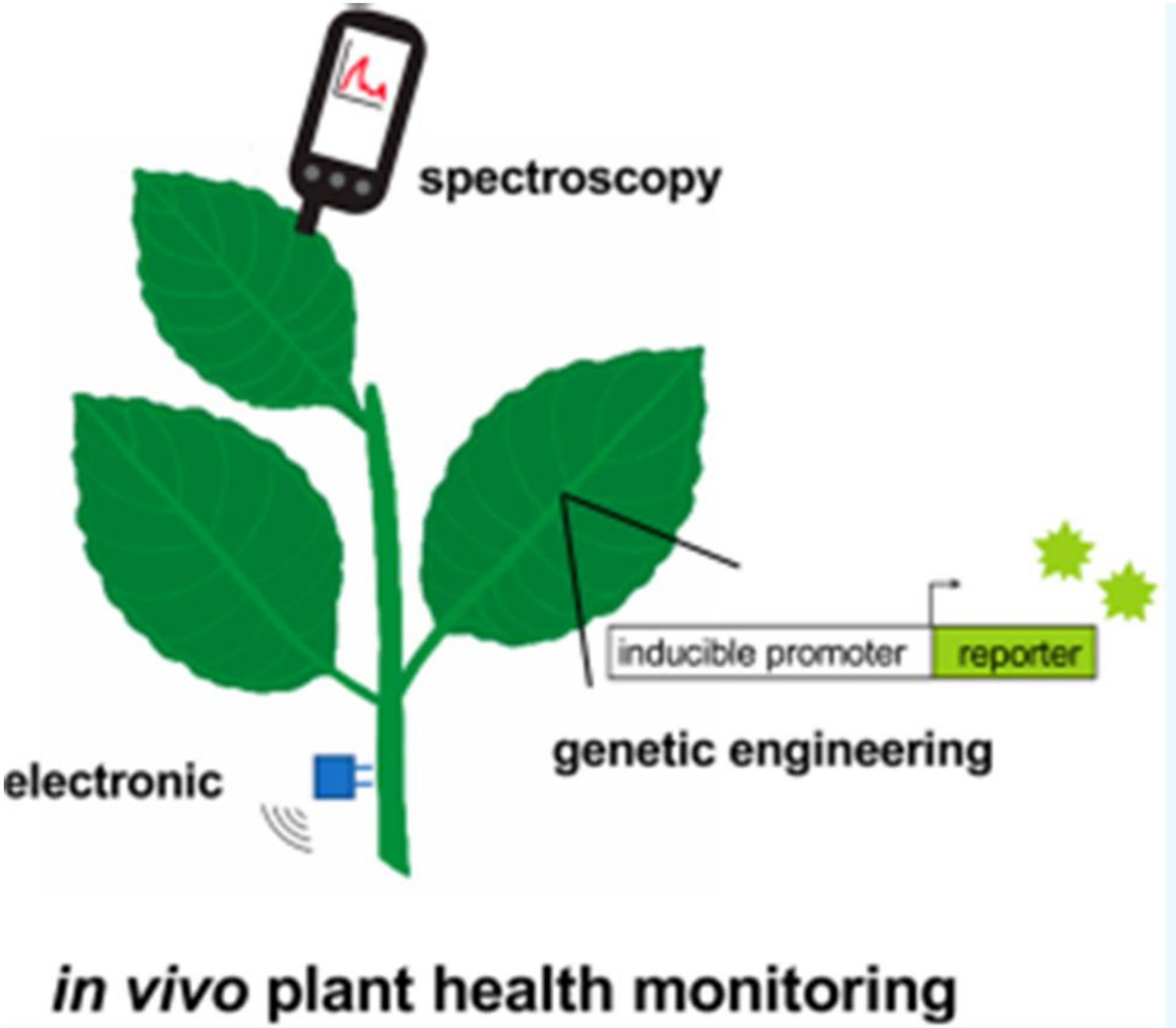
| Mode of detection | Virus | Biomolecular and nano conjugate |
|---|---|---|
| **SPR** | PVY | Monoclonal antibody |
| **SPR** | MCMV | Anti-MCMV antibody |
| **SPR** | BSMV | Specific oligonucleotide from RNA |
| **SPR** | ASPB | DNA aptamer from coat protein |
| **SPR** | CPMV | Monoclonal antibody |
| **FRET** | CPMV | Surface immobilized CPMV CdSc-ZnS core |
| **FRET** | CaMV | 23 mer derived from CaMV 35S PbS nanoparticle |
| **FRET** | CTV | CTV-CP antibody-CdTe |
| **FRET** | CTV | AuNPs-CTV-CP/Ads-CTV-CV antibody, AuNP/QD |
| **FRET** | GVA | Grapevine virus A type proteins ZnO films |
| **FRET** | BPMV, ArMV and ToRSV | Antibody, $Fe_2O_3/SiO_2$ MNPs and $SiO_2$/UNCPs |
| **Electrochemical** | CTV | Antibody to CTV coat protein-InP |
| **Electrochemical** | CTV | CTV-CP antibody-CdTe |

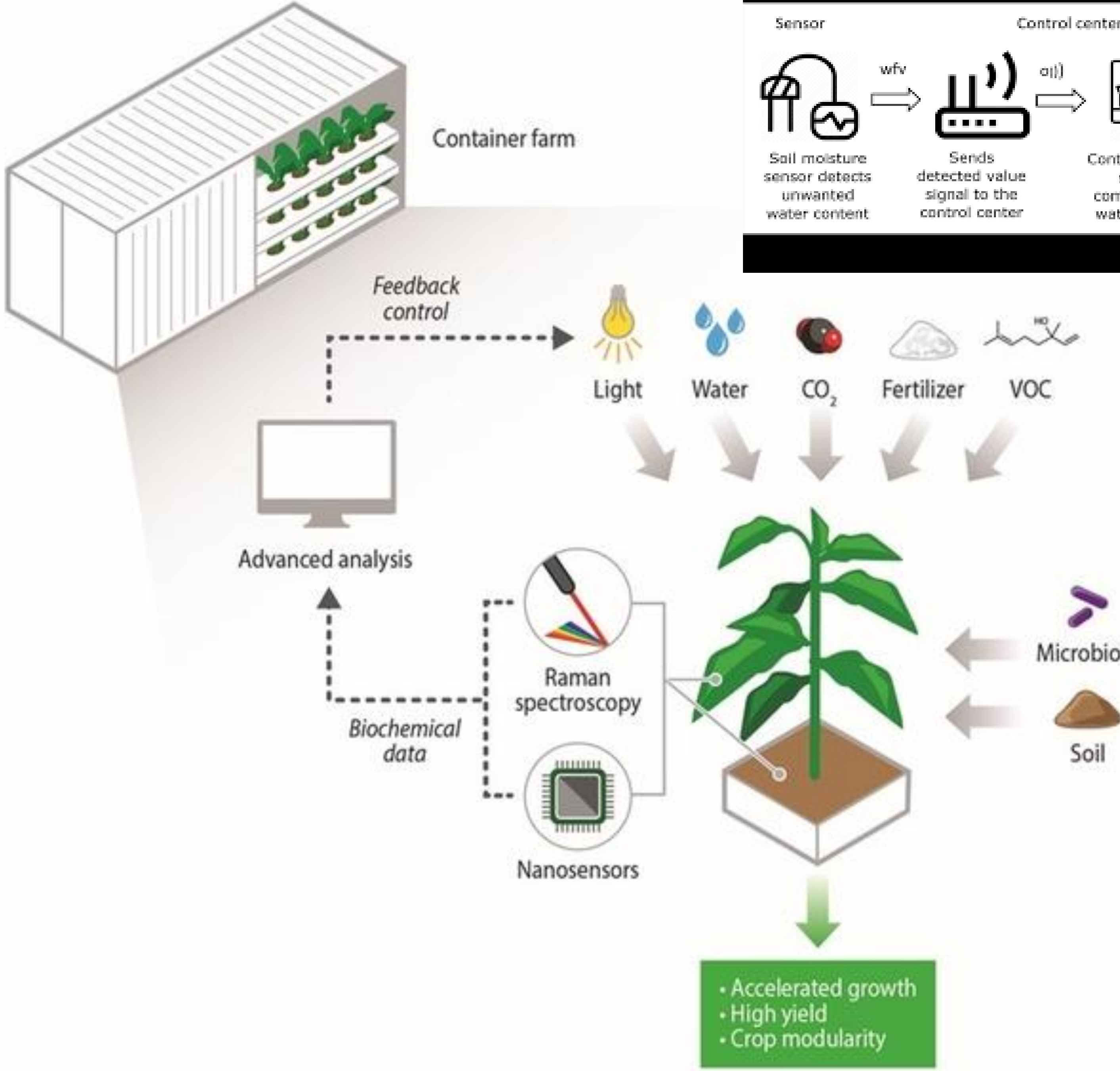
(Source: Adapted from Hong and Lee 2018)

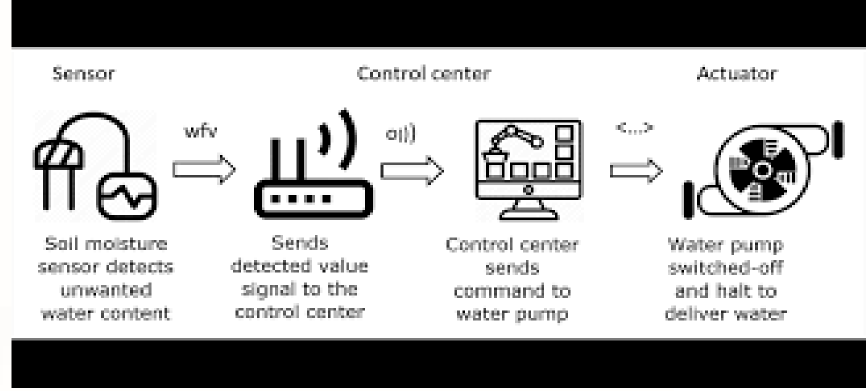

Enzyme-based biosensors
AChE and CdTe-QDs
Optical biosensor
fluorescence
AChE
Electrochemical biosensor (amperometry)
AChE, Fe3O4 nanoparticles and MWCNT
Electrochemical biosensor (amperometry)
BChE
Electrochemical (amperometry) and optical biosensor
AChE and MWCNT
Electrochemical sensor (Voltammetry)
AChE and choline oxidase, and QDs
Optical biosensor (fluorescence)
AChE, NiO NPs, and carboxylic graphene
Electrochemical biosensor (amperometry)
Paraoxo and parathion
Dichlorvos, malaoxon, chlorpyrifos-oxon, chlorpyrifos-methyl-oxon, chlorfenvinphos, and pirimiphos-methyl-oxon
Malathion, chlorpyrifos, monocrotophos, and endosulfan
Catechol, bisphenol A, and paraoxon,
Dichlorvos
Dichlorvos
Methyl parathion, chlorpyrifos, and carbofuran
vegetable and fruits
Wheat, cabbage, apple, orange, and cherry
Soil and food samples
Standard solution in PBS
Standard solution in PBS
Apple sample
Soil sample

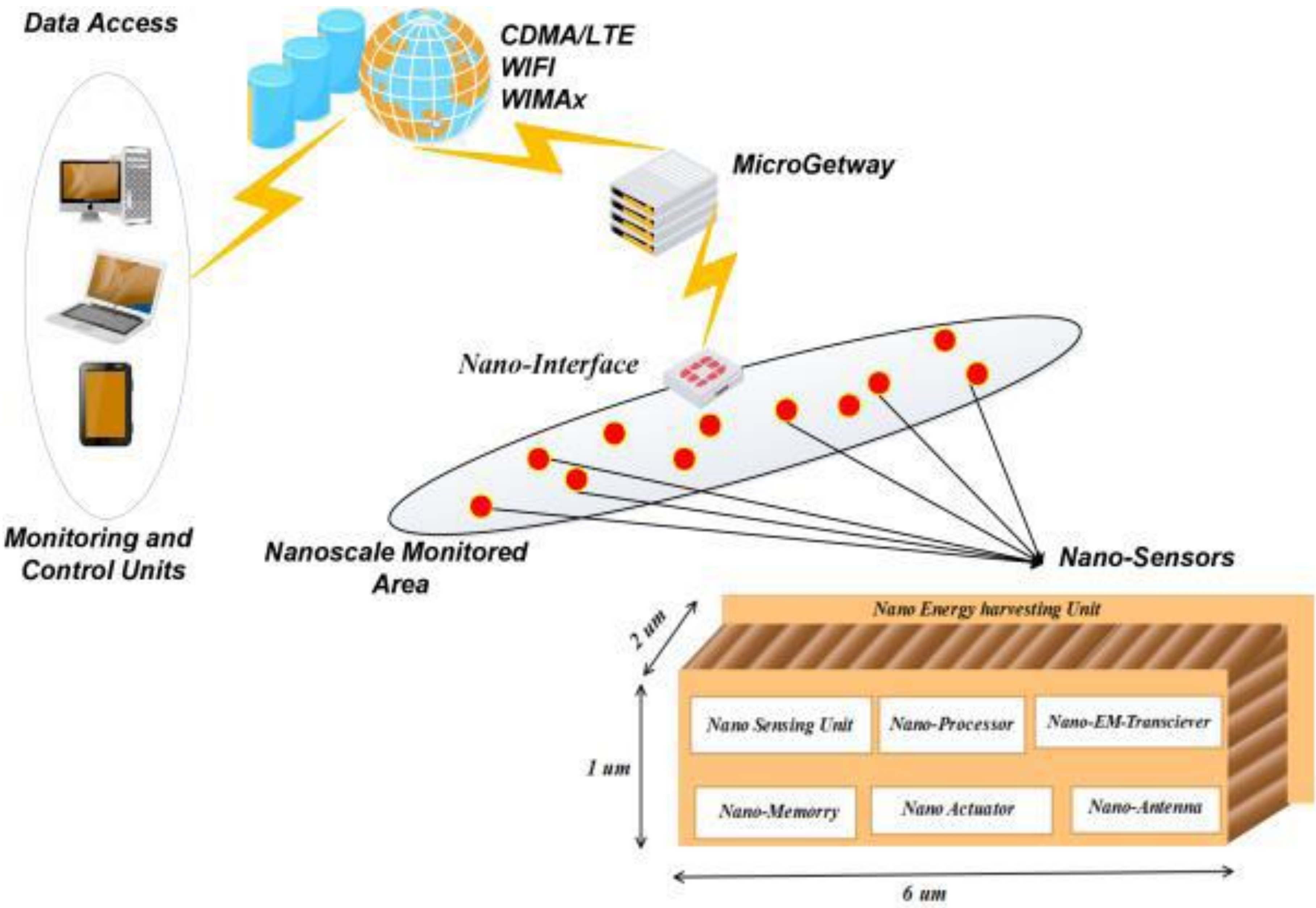

Water
Salicylic acid
Chitin
Ethephon
B 4x SARE A
B 4x NPR1 A
B 4x PR1 A


a
Excitation
Emission
CFP
YFP
Analytes such as
Ca2+, glucose
FRET
Excitation
Emission
Cys–SH
SH–Cys
OxyR-N
OxyR-C
Excitation
cpYFP
Emission
H2O2
Cys–S–S–Cys
OxyR-N
OxyR-C
Excitation
cpYFP
Emission
b
VIS fluorescence
λ
c
d
ox.
0 min HL
red.
10 µm
ox.
60 min HL
red.
e
Ratio 488/405 nm
Time (min)
sHyper
nHyper
f
030 s
074 s
094 s
138 s
178 s
1 mm
High
Low
[Ca2+]cyt
g
DNA-CNT
Gene cassette
or plasmid
CNT
PEI or chitosan
DNA-MSN
DNA-magnetic
nanoparticles
Gene delivery
Nanomaterials enable gene delivery to plant genomes
>10,000 genes
Nucleus
Mitochondrion
40–60 genes
Chloroplast
100–200 genes


spectroscopy
inducible promoter
reporter
genetic engineering
electronic
*in vivo* plant health monitoring


Container farm
Feedback control
Light
Water
$CO_2$
Fertilizer
VOC
Advanced analysis
Raman spectroscopy
Nanosensors
Biochemical data
Microbiota
Soil
• Accelerated growth
• High yield
• Crop modularity

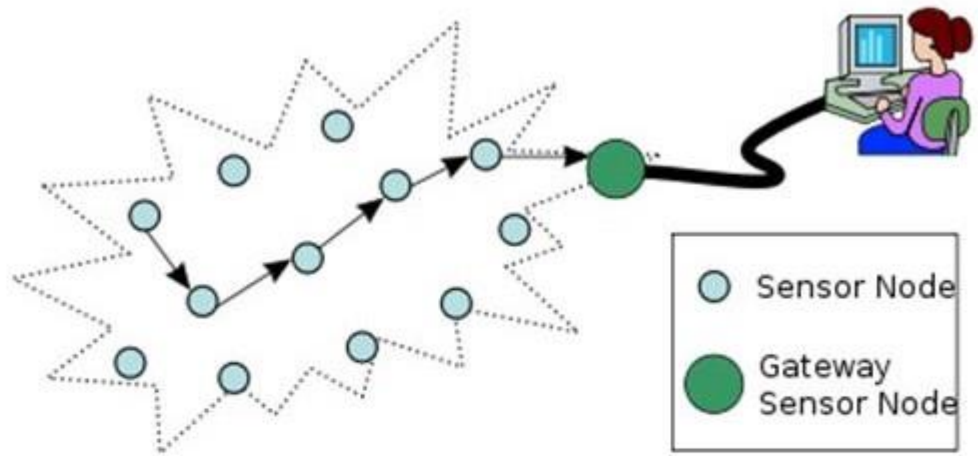

Sensor
Control center
Actuator
Soil moisture sensor detects unwanted water content
Sends detected value signal to the control center
Control center sends command to water pump
Water pump switched-off and halt to deliver water

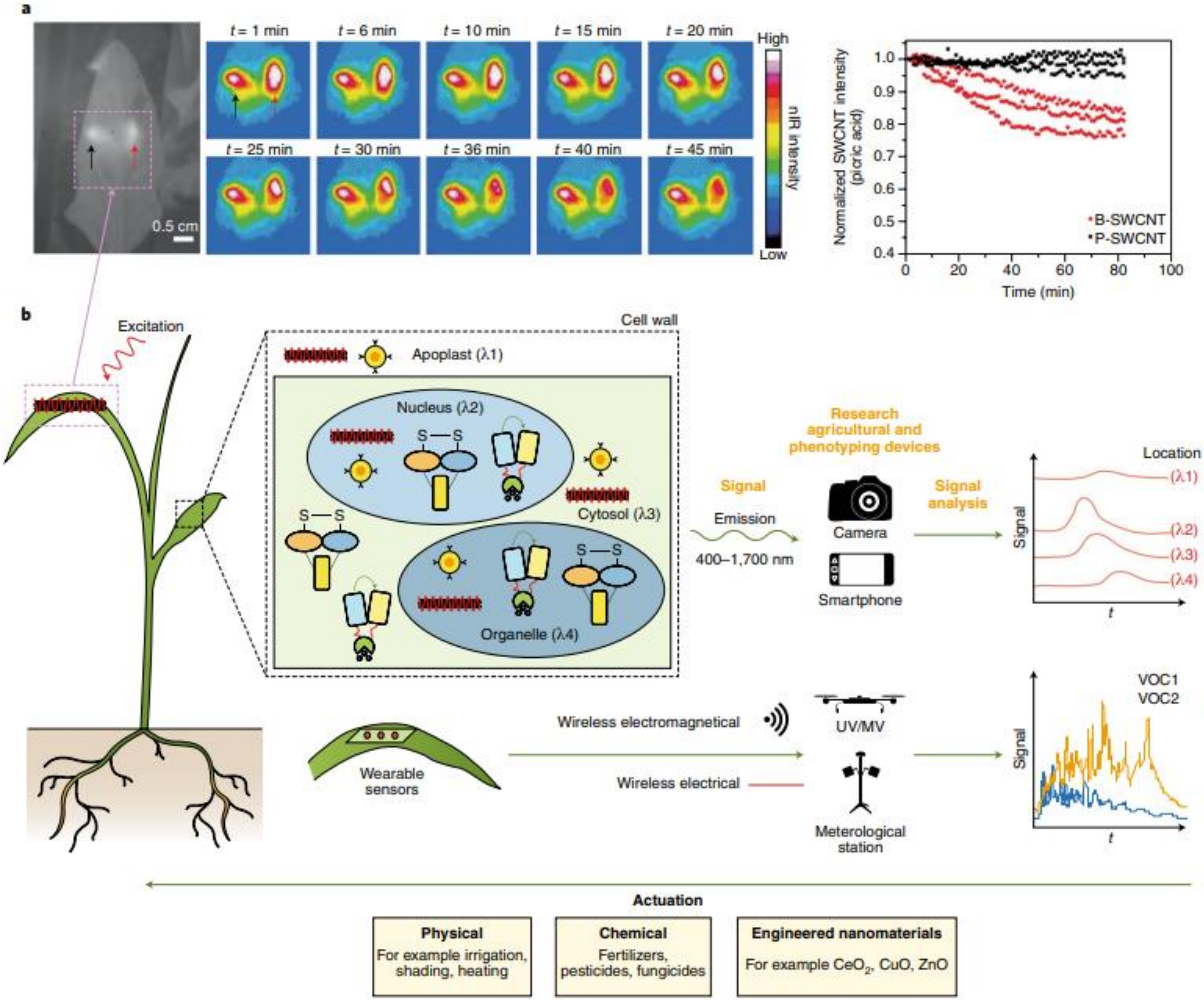


Data Access
CDMA/LTE
WIFI
WIMAx
MicroGetway
Nano-Interface
Monitoring and Control Units
Nanoscale Monitored Area
Nano-Sensors
Nano Energy harvesting Unit
2 um
1 um
6 um
Nano Sensing Unit
Nano-Processor
Nano-EM-Transciever
Nano-Memorry
Nano Actuator
Nano-Antenna

# Wireless nanosensor network architectures

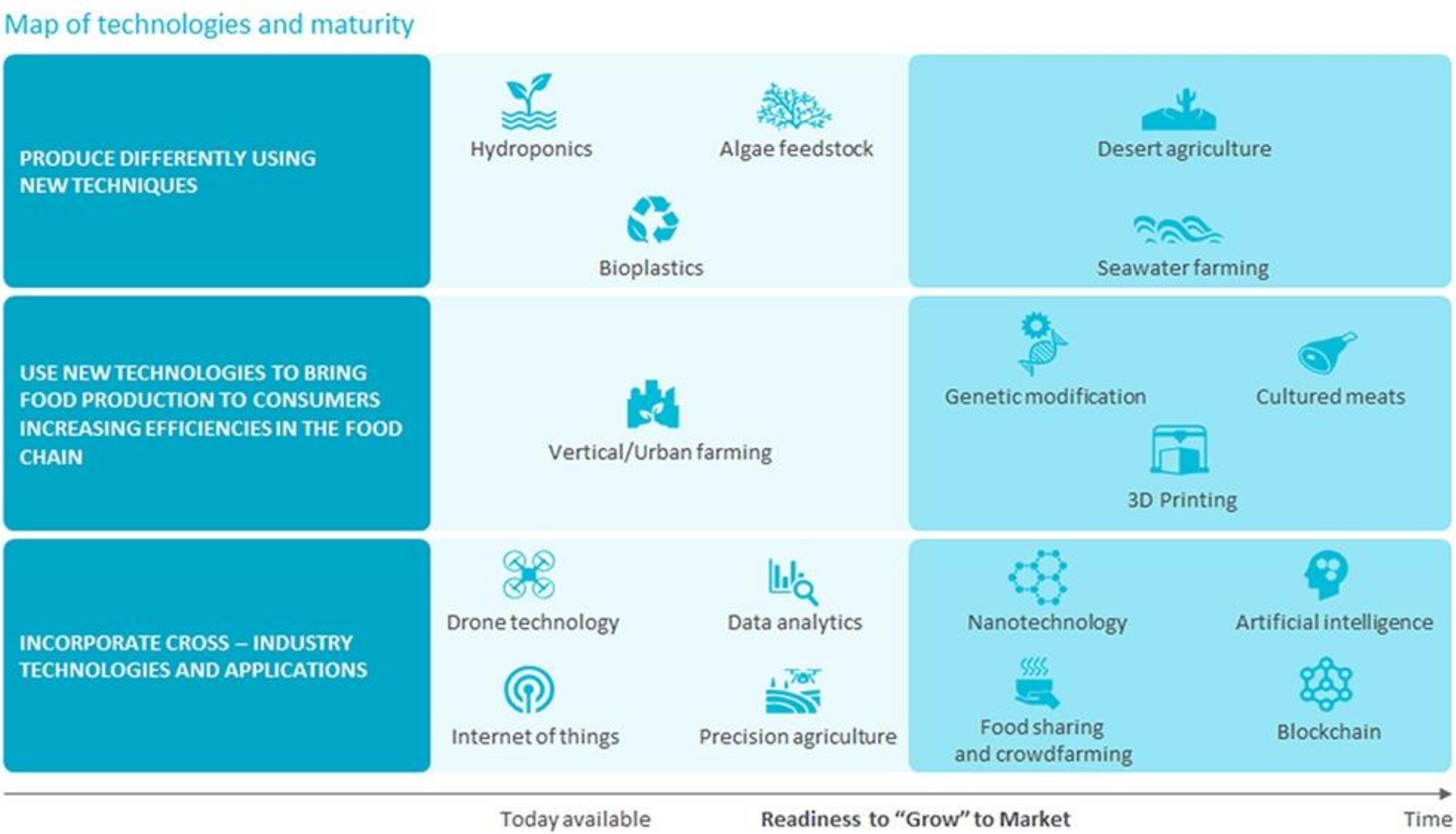
- Components in the network architecture of WNSNs
  - Nano-nodes
  - Nano-routers
  - Nano-micro interface devices
  - Gateway





a
t = 1 min
t = 6 min
t = 10 min
t = 15 min
t = 20 min
t = 25 min
t = 30 min
t = 36 min
t = 40 min
t = 45 min
0.5 cm
High
nIR intensity
Low
Normalized SWCNT intensity (picric acid)
Time (min)
B-SWCNT
P-SWCNT
b
Excitation
Cell wall
Apoplast (λ1)
Nucleus (λ2)
Cytosol (λ3)
Organelle (λ4)
S—S
Research agricultural and phenotyping devices
Signal
Emission
400–1,700 nm
Camera
Smartphone
Signal analysis
Location
Signal
t
Wireless electromagnetical
Wireless electrical
UV/MV
Meterological station
Wearable sensors
VOC1
VOC2
Actuation
Physical
For example irrigation, shading, heating
Chemical
Fertilizers, pesticides, fungicides
Engineered nanomaterials
For example CeO2, CuO, ZnO

# Futuristic Smart Intelligent Agriculture



# Conclusions

- **Various types of nanosensors have been reported for detection and monitoring plant signal molecules and metabolic contents related with biotic and abiotic stresses.**
- **Nanobiosensors have unprecedented levels of performance for sensing ultra-trace amount of various analytes for *in vivo* measurement.**
- **These nanosensors communicate with and actuate electronic devices for agricultural automation.**
- **Both biotic and abiotic plant stresses and nutritional deficiency could be monitored in real-time to report crop health status for precise and efficient use of resources.**
- **Recent applications of smart intelligent nanosensors and electronic devices can play an important role for improving crop productivity by monitoring crop health status in real-time**

# References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- Giraldo JP, Wu H, Newkirk GM, Kruss S (2019) Nanobiotechnology approaches for engineering smart plant sensors. Nature Nanotechnology 14 (6):541-553
- Hong S, Lee C (2018) The Current Status and Future Outlook of Quantum Dot-Based Biosensors for Plant Virus Detection. The plant pathology journal 34 (2):85-92
- Kumar V, Arora K (2020) Trends in nano-inspired biosensors for plants. Materials Science for Energy Technologies 3:255-273

Thank You