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Nano-Based Optical Chemical Sensors

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Nano-based Optical Chemical Sensors

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SLOVENIA

Area	20,273 sq km
Capital	LJUBLJANA
Neighbouring countries	Austria, Italy, Hungary, Croatia
Population	2 million
Language	The official language is Slovene, as well as Hungarian and Italian in areas of mixed population. English is widely spoken.
Religion	Roman Catholic (82%)
Highest peak	Triglav (2,864 m)
Climate	Alpine, Continental, Mediterranean
Time zone	Central European Time (GMT +1)
Currency	EURO

MARIBOR

Central Square

Slovenska Street

Pohorje

The old vine

The old city - Lent

Content

1. Introduction to optical chemical sensors
2. Introduction to fiber optical sensors
3. Indicator chemistry (indicators, polymers, immobilization techniques)
4. Nano based OP and their applications
5. Conclusions

1. INTRODUCTION TO OPTICAL CHEMICAL SENSORS

DEFINITION OF SENSORS

Chemical Sensors are miniaturized analytical devices that can deliver real-time and on-line information on the presence of specific compounds or ions in complex samples.

*The Cambridge Definition of Chemical Sensors,
by K. Cammann, G. G. Guilbault, E. A. H. Hall, R. Kellner and
O.S. Wolfbeis, 1996*

Analytical aspects of sensors

- sensitivity in the range of interest
- selectivity for the analyte
- broad dynamic range
- reversibility
- lack of frequent calibration
- fast response
- inertness to sample matrix
- small size

Optical chemical sensor

Sensor chip

Fields of Application of Sensors

- * long term monitoring
- * at inaccessible sites (in vivo, on the south pole...)
- * in harsh environment (e.g. chip manufacturing)
- * in areas of high radioactivity
- * In contaminated environment
-
- *

2. INTRODUCTION TO FIBRE OPTICAL CHEMICAL SENSORS

3. Indicator chemistry

Indicators

Polymers

Immobilization techniques

2. OPTICAL SENSORS

“Optrode” - (from optical electrode) and “optode”
(from Greek - the optical way)

- **intrinsic optical property** of the analyte is utilized for its detection
- **indicator (or label) based** sensing is used when the analyte has no intrinsic optical property **INDICATOR CHEMISTRY**

3. Indicators

Absorbance based:

- Undergo colour change
- Detection by “naked eye”
- Detection by colorimetry

Luminiscence based:

Fluorescence
Phosphorescence
Chemiluminiscence
Electroluminiscence

Detection by:

UV lamp

Intensity change

Lifetime measurements

3. Detection of aqueous PA with absorption based indicator dye

Analyte

Indicator-analyte

- Increasing of reflection intensity of doped ETH 4001 upon addition of PA in NaOH

Conc. range: 0.1-608 mM PA in 0.1 M NaOH

Time scan measurements

Conc. range: 0.1-608 mM PA in 0.1 M NaOH

3. Luminiscent based indicator dyes

Luminiscence Spectroscopy

“LUMEN” + “essentia”

Made of light

3. Determination of Aluminium

Indicator Morin

non-fluorescent

Al-Morin complex

yellow-green
fluorescent
(at pH 3.5)

3. Determination of Cobalt and Nickel

Indicator
Calcein

green fluorescent

Calcein- $\text{Co}^{2+}/\text{Ni}^{2+}$
complex

non-fluorescent

3. Lanthanide chelates

- narrow, line-like emission peaks
 - large Stokes' shifts (≥ 200 nm)
 - long lifetimes (from micro- to several milli-seconds range)
 - lifetime-based assays
- advantageous over intensity-based:
highly immune to photobleaching,
changes in fluorophore
concentration, turbidity in the sample,
optical misalignment, etc.
- long lifetimes enable gated detection mode
 - time-resolved luminescence

3. Time-resolved luminescence

3. Determination of phosphate (P) using europium-tetracycline complex (EuTc)

Calibration plots and effect of time-resolved luminescence

5-750 $\mu\text{mol/L}$ PO_4^{3-}
LOD = 5 $\mu\text{mol/L}$

3-10 $\mu\text{mol/L}$ PO_4^{3-}
LOD = 3 $\mu\text{mol/L}$

$$y = A + B \times \log(c_p \times 10^6)$$

	0 μs lag.t. 40 μs int.t.	60 μs lag.t. 100 μs int.t.
A	1,033 $\pm 0,018$	0,955 $\pm 0,081$
B	-0,224 $\pm 0,007$	-0,586 $\pm 0,091$
r^2	0,993	0,954

Ex filter = 405 ± 30 nm, Em filter = 612 ± 10 nm

3. Immobilization methods (indicator chemistry)

The most frequently applied methods include:

- impregnation techniques
- chemical doping
- covalent bonding
- copolymerization of modified reagents

3. Polymeric supports and coatings (Indicator chemistry)

Requirements for Sensor Polymers/Materials

- Solubility of indicator chemistry in polymer matrix
- Selectivity and sensitivity (solubility of the analyte, free analyte diffusion)
- Good operational lifetime and shelf-life
- No crystallization/migration/reorientation of components
- No aging effects
- Stability at elevated temperatures (sterilisability)
- Stability against ambient light
- Stability against chemicals (acids, bases, oxidants)
- Mechanical stability
- Transparency for light
- No intrinsic color/luminescence of the polymer matrix
- Biocompatibility (no toxicity of components)

3. Sol-gel

1. *hydrolysis*

2. *condensation:*

<u>Monomers</u>	<u>Other metals</u>
Si(OR')_4	Zr(OR')_4
$\text{R}_1\text{-Si(OR')}_3$	$\text{R}_1\text{-Zr(OR')}_3$
$\text{R}_1\text{ R}_2\text{-Si(OR')}_2$	$\text{R}_1\text{ R}_2\text{-Zr(OR')}_2$
R: aliphatic, aromatic	Ti, Sn

3. Silica nanoparticles

Nanoparticles are discrete particles that have a diameter of 100 nm or less.

Two most common methods are used:

- Microemulsion
- Precipitation method
- Stöber method

3. Advantages of using nanomaterials for sensors

- Improved sensor characteristic (response time, sensitivity etc.)
- In-vivo measurements and
- small sample volumes
- Multi-analyte sensing

3. Design of Optical nanosensor

Borisov SM, Klimant
I (2008) Analyst
133:1302-1307

a, macromolecular nanosensors; b, NSs based on polymer materials and sol-gels; c, multi-functional core-shell systems; d, multi-functional magnetic beads; e, NSs based on quantum dots; f, NSs based on metal beads

Magnetic nanoparticles

1. Our research activities

preparation and characterization of monodispersed superparamagnetic iron oxide nanomaterials

- magnetite, Fe_3O_4
- maghemite, $\gamma\text{-Fe}_2\text{O}_3$
- Co-ferrite, CoFe_2O_4
- MnZn-ferrite, $\text{MnZnFe}_2\text{O}_4$
- ...etc.

2. Narrow particle size distribution - (10 ± 1) nm

3. Many novel “wet-chemical” preparation techniques:

sol-gel, microemulsion, hydrothermal method, thermal decomposition

Magnetic nanoparticles (surface chemistry)

Magnetic nanoparticles
coated with **organic** layer

Magnetic nanoparticles
coated with **silica** (SiO_2) layer

nanoparticle
Core

Inorganic
Shell

Magnetic nanoparticles (magnetoluminescence properties)

1. Magnetic nanoparticles coated with CdS quantum dots

- microemulsion method

Microemulsion system:

- **CTAB** as surfactant
- **n-butanol** as cosurfactant
- **n-hexanol** as an oil phase
- **aq. sol. of reactants** as water phase

Magnetic nanoparticles - applications

Sensor Applications - magnetic luminescent materials (ML)

- iron-oxide magnetic core, coated with amorphous silica shell and functionalized with fluorescent dyes
- fluorescent dyes integrated into silica shell
- iron oxide magnetic core coated with quantum dots

Quantum dots

1. Quantum dots

- small particles of a semiconductor material

2. Typical dimensions: from 1 nm to 10 nm

3. The energy levels are quantized due to the confinement of electrons

Quantum dots - properties

Unique spectral properties:

- Broader absorption
- Narrow emission
- Wavelength depends on size

Quantum dots - surface modification

Quantum dots - sensor applications

1. Temperature sensor

- core-shell CdSe/ZnS nanocrystals entrapped in – PLMA source 488nm laser
- photoluminescence intensity increases in the order of -1.3% per °C

2. Chemical sensors

- the luminescence of core QDs can be very sensitive to the surrounding chemical environment.
- surface modified QD nanoparticles - detection of heavy metals:
 - polyphosphate-capped QD
 - thioglycerol-capped QD

pH nanosensor

- Ind: FITC (covalently): Shell
- Ref: TRITC (covalently): Core

Confocal fluorescence microscopy images

Burns A, Sengupta P, Zedayko T, Baird B, Wiesner U: Small 2 (2006), 723-726

Nanosensor for Pb^{2+}

MPS-mercaptopropyltriethoxysilane
Dansyl dye

Arduini M, Mancin F, Tecilla P, Tonellato U: Langmuir 23 (2007), 8632-8636

Nanosensor for Cu^{2+}

- Cascade FRET: 1. energy transfer from a donor D (fluorophore) to a proximal acceptor A
2. quenching of acceptor A due to copper–cyclam complexation

Nanosensor for Cu^{2+}

Dynamic range: 10^{-8} - 10^{-5} M; LOD: 2×10^{-8} M

Frigoli M, Ouadahi K, Larpent C: Chem Eur J, 15 (2009), 8319-8330

Nanosensor for OP

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$$\begin{array}{c} \text{O} \\ || \\ \text{R}_2\text{O}-\text{P}-\text{X} \\ | \\ \text{R}_1 \end{array}$$

Development of optical chemical sensor for determination of toxic substances OP.

Sarin

Soman

Personal optical chemical sensors for personal protection against toxic substances. The sensors are integrated into textiles by using optical fibers.

SEM of silica nanoparticles

Development of optical sensor chip (OSC)

Tests of sensor chips

Combining optical sensor chip and optical fibers

Luminiscence measurements of OP

**NANOTECHNOLOGIES
AND
NANOMATERIALS ARE
IMPORTANT PART IN
FUTURE SENSOR
DEVELOPMENT**

**AND LIMITED ONLY BY
OUR IMAGINATION**

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