Development of Nanostructurated Platforms for Sensing and Destroying of Pollutants

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TSUKUBA (JAPAN), 2013, MARCH 5th
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- Introduction – Our motivation and detection systems
- Lab-on-a-chip systems: Detection of pesticides and phenols
- Lateral flow / nanomotors based biosensing platforms
- Future perspectives & conclusions
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- Introduction – Our motivation and detection systems
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NANOBIOELECTRONICS & BIOSENSORS’s research aims to integrate nanotechnology methods, tools and materials into low cost, user friendly and efficient (bio)sensors with interest for diagnostics, safety/security and other fields.
State of the art nanobiosensing technologies

Recent Trends in Macro-, Micro-, and Nanomaterial-Based Tools and Strategies for Heavy-Metal Detection
Gemma Aragay,¹,‡ Josefina Pons,⁷ and Arben Merkoçi⁶,†,§
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Nanomaterials for Sensing and Destroying Pesticides
Gemma Aragay,† Flavio Pino,† and Arben Merkoçi†,⊥†⊥
Chemical Reviews, 2012, 112, 5317–5338

Cancer detection using nanoparticle-based sensors†
Maëlle Perlezou,⁶ Anthony Turner⁴ and Arben Merkoçi⁶,⊥⊥
Chem Soc Rev
Cite this: Chem. Soc. Rev., 2012, 41, 2606–2622
www.rsc.org/csr
TUTORIAL REVIEW

Paper-based nanobiosensors for diagnostics
Claudio Parolo and Arben Merkoçi⁶,⊥⊥
Received 11th July 2012
Chem Soc Rev
Cite this: DOI: 10.1039/c2cs35255a
www.rsc.org/csr
TUTORIAL REVIEW

ACS Nano, 2012, DOI: 10.1021/nn301368z
Nanochannels Preparation and Application in Biosensing
Alfredo de la Escosura-Muñiz and Arben Merkoçi†,⊥⊥⊥
E.Morales, A.Merkoçi, Graphene oxide as an optical biosensing platform”,
Advanced Materials, 2012, 24, 3298–3308
I. Detection after previous dissolving

II. Direct /onto-electrode detection

III. Electrocatalytic detections (silver enhancement, hydrogen evolution)

IV. Indirect detection through nanochannels blocking

Nanomaterials based electrochemical detection tools
NANOPARTICLES & ELECTROCHEMICAL STRIPPING

Chemical dissolving followed by stripping analysis

\[
\begin{align*}
\text{CdS} & \xrightarrow{\text{HNO}_3} \text{Cd}^{2+} \\
\text{Au} \, \text{Fe} & \xrightarrow{\text{HBr}/\text{Br}_2} \text{Fe}^{3+} \\
\text{Ag} \, \text{Au} & \xrightarrow{\text{HNO}_3} \text{Ag}^+ \\
\text{Au} & \xrightarrow{\text{HBr}/\text{Br}_2} \text{Au}^{3+}
\end{align*}
\]

Multicoding technology
Breast cancer DNA related

\[
\begin{align*}
\text{ZnS} & \xrightarrow{} \text{Zn}^{2+} \\
\text{CdS} & \xrightarrow{} \text{Cd}^{2+} \\
\text{PbS} & \xrightarrow{} \text{Pb}^{2+}
\end{align*}
\]

I (A)
E (V)

TRAC 24 341-349 (2005)

JACS, 125 3214-3215 (2003)
Protein detection- direct detection of AuNP

Streptavidin-MB

Au-α-human-HRP

Human IgG (μg/ml)

Abs (492 nm)

Peak current (μA)

DPV of AuNPs

Optical anti-Human-HRP-Au

Optical anti-Human-HRP

L.O.D: 52 and 260 pg of human IgG/mL for HRP and electrochemical AuNP-based detections

Analytical Chemistry, 2007, 79, 5232-5240

Analytical Chemistry, 2010, 82, 1151–1156
Indirect gold nanoparticles detection

Catalytic effect of AuNPs towards Ag deposition

Detection of α-HepB in human serum
L.O.D.: 3 mUI mL\(^{-1}\)

Detection of human IgG
L.O.D.: 23 fg mL\(^{-1}\)

Biosens. Bioelectron., 2009, 24, 2475 (8pp)

Catalytic effect of AuNPs towards H\(_2\) evolution

Detection of α-HepB in human serum
L.O.D.: 3 mUI mL\(^{-1}\)

Biosens. Bioelectron., 2010, 26, 1710(4pp)

Electrochem. Commun., 2010, 12, 1501(3pp)
Salmonella detection based on differential voltammetry of AuNP

Schematic (not in scale) of Salmonella detection

DPV using AuNPs electrochemical detection

Protein detection - AuNP & nanochannels

Nanochannels immunoblocking using nanoparticles

Effect of AuNP size and Ag enhancement on blocking

Responses to human IgG using 20-nm AuNPs; 80-nm AuNPs; 80-nm AuNP tags and Ag enhancement

RSD of 8% ([CA15-3]: 120 U/mL; n=3)
LOD: 52 IU/mL of CA15-3

Small, 2011
Protein detection - AuNP & nanochannels

200 nm nanochannel casted with 50 µL blood
Spiked with CA15-3

RSD of 8% ([CA15-3]: 120 U/mL; n=3)
LOD: 52 IU/mL of CA15-3

Small, 2011
Cell studies based on CdS QDs

Electrochemical interrogation of cellular uptake of quantum dots decorated with peptide

CdS QD-SAP interaction with HeLa cells:

SWV and CLSM images of cells incubated with QDs including blanks
Cells detection based on AuNP & H₂ catalysis
Collaboration with Dr. A. González (UV)

Cancer cell detection (ICN&UV patent)

HMY: Tumoral human B cell line with expressed HLA-DR molecules

PC3: Tumoral human prostate cell line

4000 cells per 700 µL suspension

AuNP & AuNP-Ab detection

Analytical Chemistry, 2009, 81, 10268–10274
Catalytic Nanoparticles for Detection of circulating Cancer Cells (CTC)
(Collaboration with Prof. C. Nogues, UAB)

HER based biosensing device developed by Nanobioelectronics & Biosensors Group
LEITAT

Simple nanoparticle based technology

AuNP/anti-CEA antibody

L.O.D. $1.6 \times 10^2$ cells

SEM characterization

Small 2012, 8, No. 23, 3605–3612
Nano Lett., 2012, 12 (8), pp 4164–4171
Tailoring graphene production toward biosensors applications

Merkoçi et al. Carbon 2012, 50:2987

- roll to roll
- ink-jet printing
- screen-printing
- graphene composites / inks

Graphene Oxide as an Optical Biosensing Platform
DOI: 10.1002/adma.201200373
Water pollution causes 40% of deaths worldwide. [http://www.news.cornell.edu](http://www.news.cornell.edu)

Water-related diseases are one of the leading causes of death worldwide. Over 3 million people die each year. [http://worldsavvy.org/monitor](http://worldsavvy.org/monitor)

Common pollutants include:
- Pesticides
- Phenols
- Heavy metals
- Bacteria
- Toxins etc.
Monitoring water quality should be done periodically to check for aquatic problems. In-field sensing systems are necessary.
Solutions are needed for smart systems that can detect pollutants and evaluate the efficiency of their removal.
In-situ smart sensors and evaluators of the pollutants removal efficiency

- High sensitivity for various potential pollutants
- Versatility in evaluating pollutants removal efficiency
- Easy to be integrated
- Cost / efficiency

Detect pollutants and gives qualitative & quantitative information for their destruction/removing strategies.
Nanomaterials based biosensing devices

Nanomaterials with high and selective adsorbing / photacatalytic properties

Sensitivity  Stability  Versatility  Cost / efficiency
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Lab-on-a-chip for ultrasensitive detection of carbofuran by enzymatic inhibition with replacement of enzyme using magnetic beads.

Pesticides detection

Lab Chip, 9, 213–218, 2009
Pesticides detection

\[
\% I = \frac{S_{\text{blank}} - S_{\text{inhibition}}}{S_{\text{blank}}} \times 100
\]

L.O.D: 0.34 ppb
(90” inhibit. time; 5% inhibit)

Phenolic compounds detection

REACTION OF CATECHOL & TYROSINASE USING A BIO-CONJUGATE ON SCREEN PRINTING ELECTRODE (SPE)

Advanced Functional Materials, 2010
Phenolic compounds detection

REACTION OF CATECHOL & TYROSINASE USING A BIO-CONJUGATE ON SCREEN PRINTING ELECTRODE (SPE)

MWCNT
Magnetic nanoparticle (size: 100 nm)
Tyrosinase
SPE
Magnet

LOD = 5.4 nM
LOQ = 17.9 nM

Advanced Functional Materials, 2010
Tyrosinase-magnetic nanoparticles & CNTs based biosensor

ON-OFF EFFECT INDUCED BY THE MAGNET

REACTION OF CATECHOL & TYROSINASE USING A BIO-CONJUGATE ON SCREEN PRINTING ELECTRODE (SPE)

Phenolic compounds detection

Advanced Functional Materials, 2010
CaCO$_3$/Tyr Biosensor for phenol detection

Fluidic System for Phenol Detection

Optical and SEM Characterization of CaCO$_3$ microparticles

Electrochemical enzyme-based biosensors constitute promising technology for the *in situ* monitoring of phenolic compounds

Electrophoresis 2013
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PAPER BASED NANOBIOSENSORS
Lateral flow / nanoparticles biosensing platforms

μPAD
microfluidic paper-based analytical device

What can nanoparticles bring?
- More stability
- Multidetection capability
- Higher sensitivity
- Novel / versatile detection platforms

http://www.chimicabioanalitica.unito.it/immunoassay.htm

Anal. Chem. 2010, 82, 3(8pp)

A 3-Cent HIV Test by Harvard
**LFIA (Cadmium determination in drinking water)**

Collaboration with Prof. D. Blake, Univ. Of Tulane, USA

AuNPs
BSA
EDTA
Cd
Cd-EDTA-BSA-AuNPs
A281G5 mAb
Anti-BSA mAb

Typical image of the cadmium detection by the lateral flow device.

**Graph:**
- Colour intensity difference vs. Cd concentration (ppb)
- Sample with Cd-EDTA

**Formula:**
\[ y = 0.7949x + 3.938 \]
\[ R^2 = 0.9887 \]
Enhancing of biosensing

Template-based catalytic microengines (no need for clean room)

Coupling nanomotors effect with biosensing

Bacterial Isolation by Lectin-Modified Microengines

Nano Letters, 12, 396–401. 2012

Superhydrophobic Alkanethiol-Coated Microsubmarines for Effective Removal of Oil

SAM-modified microsubmarine

Oil droplets

ACS Nano, 2012, 6, 4445-4451

Magnetic Control

Trilayer PANI/Ni/Pt Microengine

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CONCLUSION / Research outcomes

- Nanotechnology allows us to develop smaller, easy to use and cost-effective devices such as biosensors or lab-on-a-chip.

- Nanoparticle based biosensing systems are shown to be high sensitive and cost effective devices with interest for environmental applications between other industries.

- Simple cost/efficient paper based devices as well as nano/micromotors as novel material for enhancing of biosensing technology are promising alternatives in environmental monitoring.

- Further improvement and more efficient designs of pollutants detection systems using nanostructurated detectors including integration of pollutants sensing and removal/destruction at the same platform are still necessary.
Thank you! Any question?

14 nationalities

Nanobioelectronics and Biosensors Group
Catalan Institute of Nanotechnology (ICN)

Read more at: www.nanobiosensors.org