NanoSpain Conf 2017

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Fluorescent sensing probes based on quantum nanodots immersed into nanocellulose hydrogels

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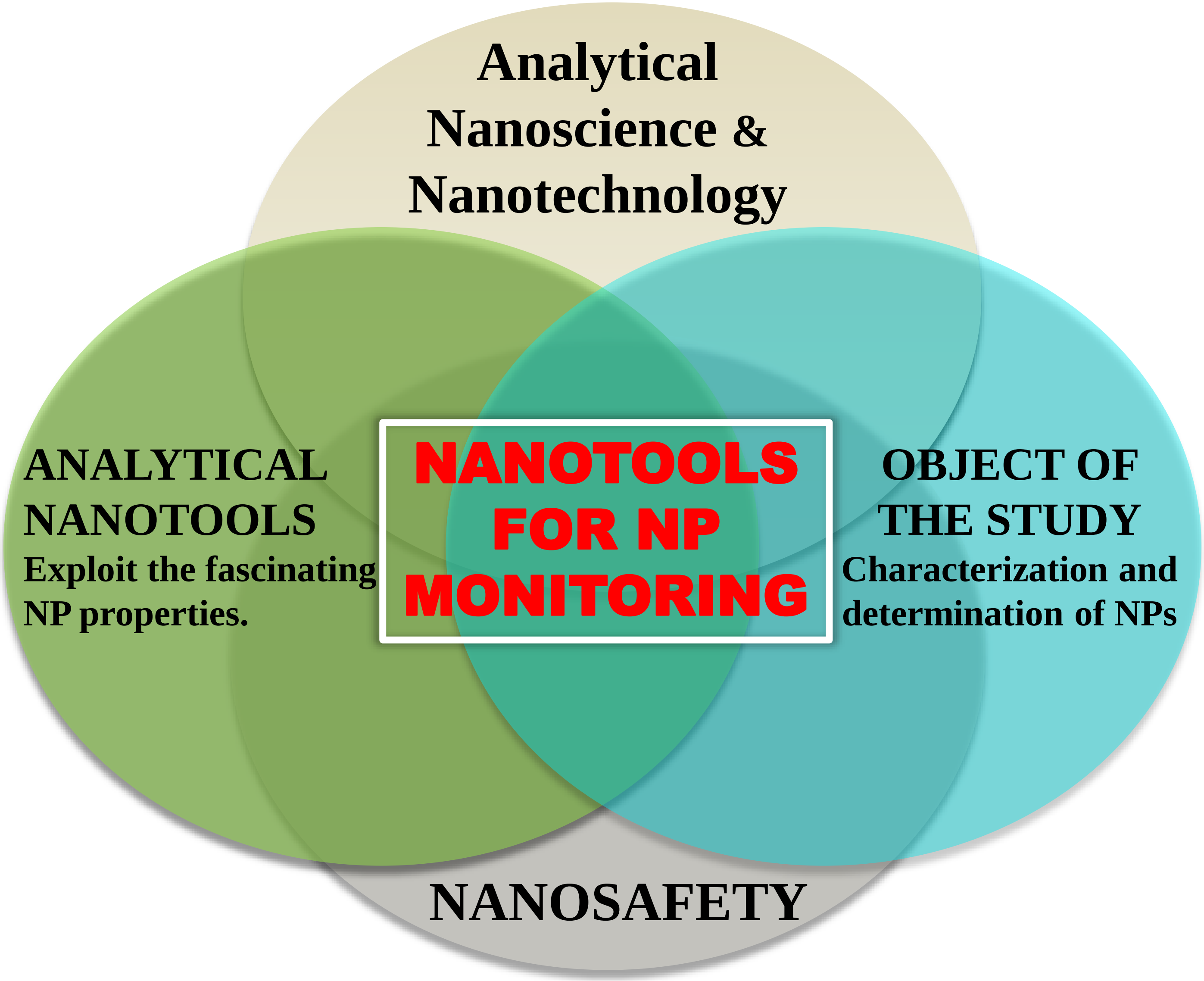
RESEARCH LINES



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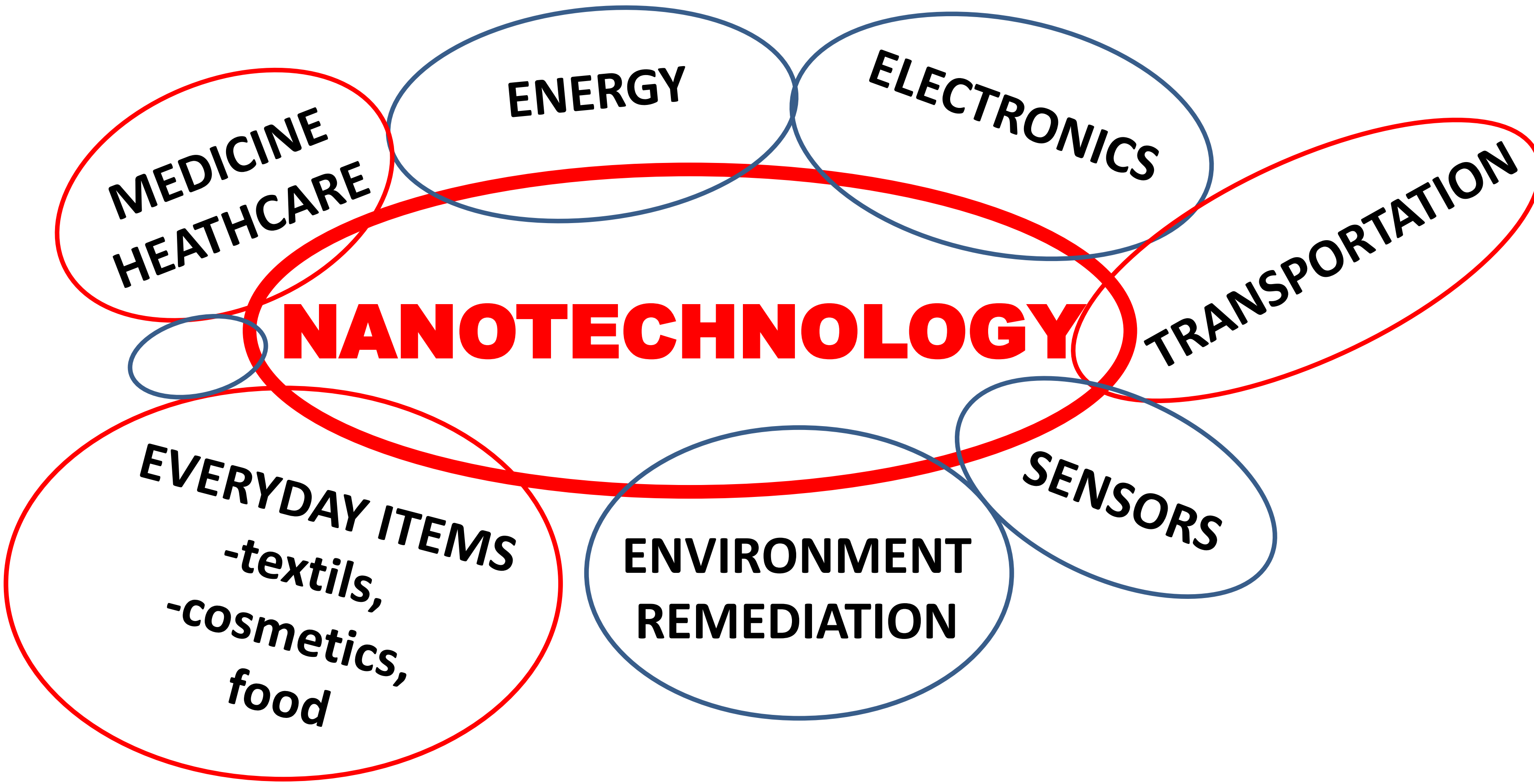
1a. IMPORTANCE OF NANOTECHNOLOGY

MULTIDISCIPLINAR CHARACTER

•**Engineering Nanoparticles** are creating new opportunities in a variety of applications to increase the performance of tradicional products and develop unique ones in….

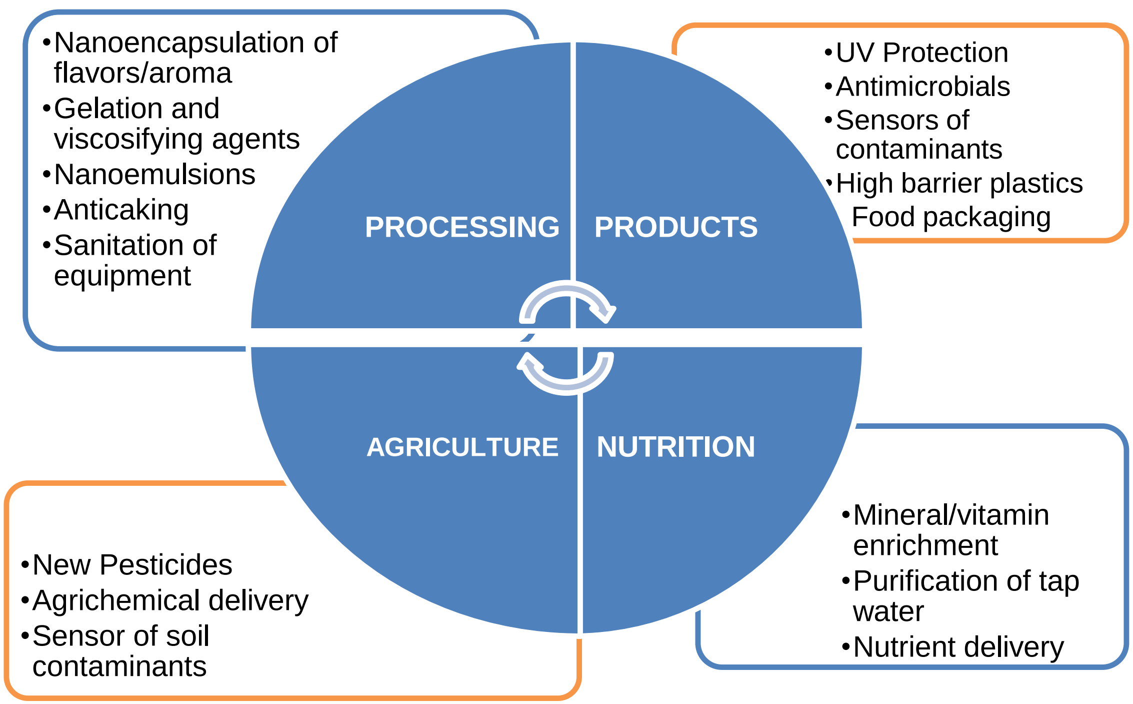


INTRODUCTION

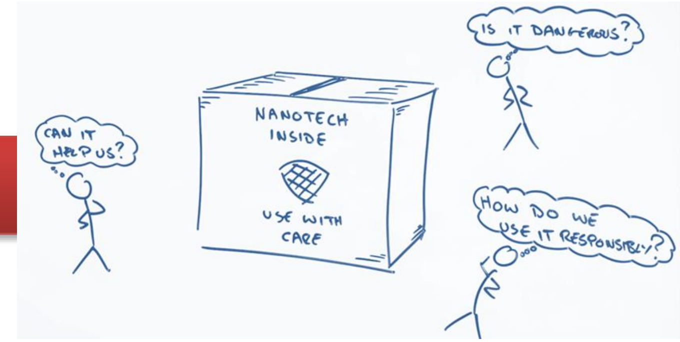
1a. IMPORTANCE OF NANOTECHNOLOGY

EXAMPLES OF THE NANOTECHNOLOGY USES

Nanotechnology has applications in all areas of food science, and can transform the entire *agri-food* sector with an increase in agricultural productivity and economic growth for industries.



1b. IMPACTS OF NANOTECHNOLOGY



Exponencial increase of NP uses

However, nanotoxicological effects are unknown.
Non parallelism in both novel developments and toxicological impact.

Nanoimpact is one major issue facing the application of nanotechnology in many everyday-items; there are many concerns on the effect of NPs in the human health, and in the environment after their release from those items containing NPs.

Ongoing discussion about how to handle on the **risk-benefit** balance.

INTRODUCTION

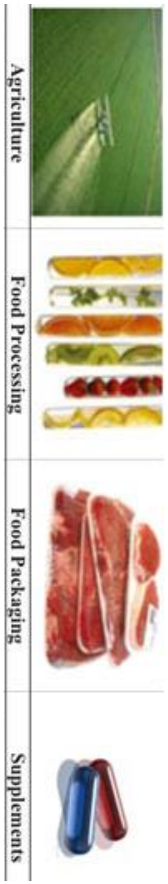
1b. IMPACTS OF NANOTECHNOLOGY

AN **URGENT NEED** TO MONITOR THE EXPOSURE OF CONSUMERS TO NANOPARTICLES

Hazardous Nanoparticles

- TiO_2, SiO_2, CeO_2, ZnO,..
- Carbon nanotubes
- Fullerenes
- Magnetic NPs
- Graphene, Graphene oxide
- AgNPs, AuNPs
- Semiconductor quantum dots

Nanoparticle as target analyte



1b. IMPACTS OF NANOTECHNOLOGY

The interdisciplinary projects for monitoring ENPs in food and cosmetics

INSTANT

INSTANT

Innovative Sensor for the fast Analysis of Nanoparticles in Selected Target Products

SEVENTH FRAMEWORK PROGRAMME

NANOLYSE

SMARTNANO

A new method for the detection of nanoparticles in consumer products

NANOdetector

Ultrasensitive plasmonic detection of single nanoparticles

2. Analytical Nanoscience and Nanotechnology (AN&N)

STRATEGY

Analytical Nanoscience and Nanotechnology

AN&N

CLASIFICATIONS

Exploitation of the nanosize and properties of NPs

Role of the NPs in the analytical process

2. Analytical Nanoscience and Nanotechnology (AN&N)

- Classification according to the exploitation of size and the excellent properties of the nanoparticles (NPs)

EXPLOTAITION PROPERTIES

NANOSIZE

EXCEPTIONAL PROPERTIES OF THE NANOMATTER

INCREMENT OF THE NANOTECHNOLOGICAL CHARACTER

Analytical Nanometric Systems

Analytical Nanotechnological Systems

ANALYTICAL NANOSYSTEMS

2. Analytical Nanoscience and Nanotechnology (AN&N)

- Classification according to the role played by the NPs

The two main facets of AN&N

- Nano-tool
- Nano-analyte

Nanoparticles as nano-tools

- Oxide NPs
- Metallic NPs
- Graphene
- Carbon nanotubes
- Nanocellulose
- Carbon-based dots
- Semiconductor quantum dots

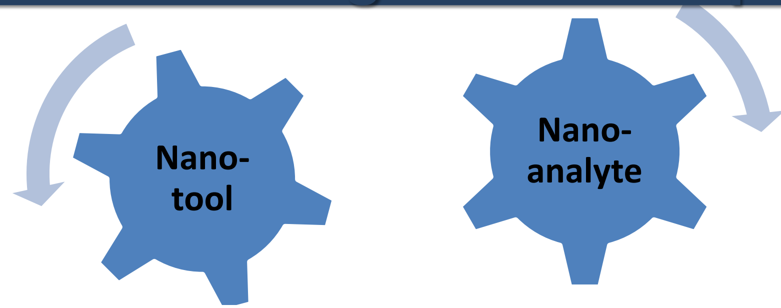
SAMPLE PREPARATION → SEPARATION → DETECTION

Analytical process

2. Analytical Nanoscience and Nanotechnology (AN&N)

- Classification according to the role played by the NPs

The two main facets of AN&N



Nanoparticles as nano-analyte

Identification

Size, shell, shape

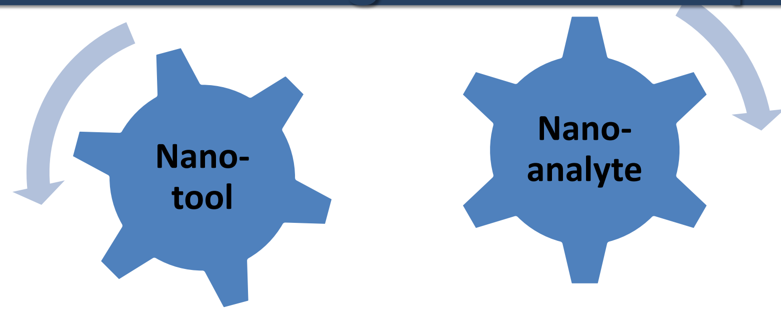
Quantitation

INTRODUCTION

2. Analytical Nanoscience and Nanotechnology (AN&N)

- Classification according to the role played by the NPs

The two main facets of AN&N



The Third Way of AN&N

Miguel Valcárcel

In Trends Anal. Chem. 75 (2016) 1–9.

I N D E X

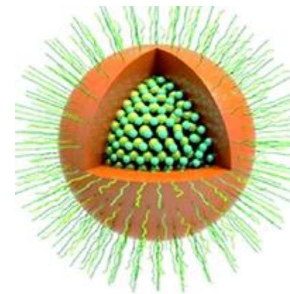
- INTRODUCTION
  - NANOTECHNOLOGY: BENEFITS AND IMPACTS
  - ANALYTICAL NANOSCIENCE & NANOTECHNOLOGY
- FLUORESCENT QUANTUM NANODOTS
  - TYPES AND APPLICATIONS
  - TOXICITY
- ANALYTICAL METHODS FOR NANOPARTICLE MONITORING
  - SENSORS OF NANOPARTICLES
- FINAL REMARKS

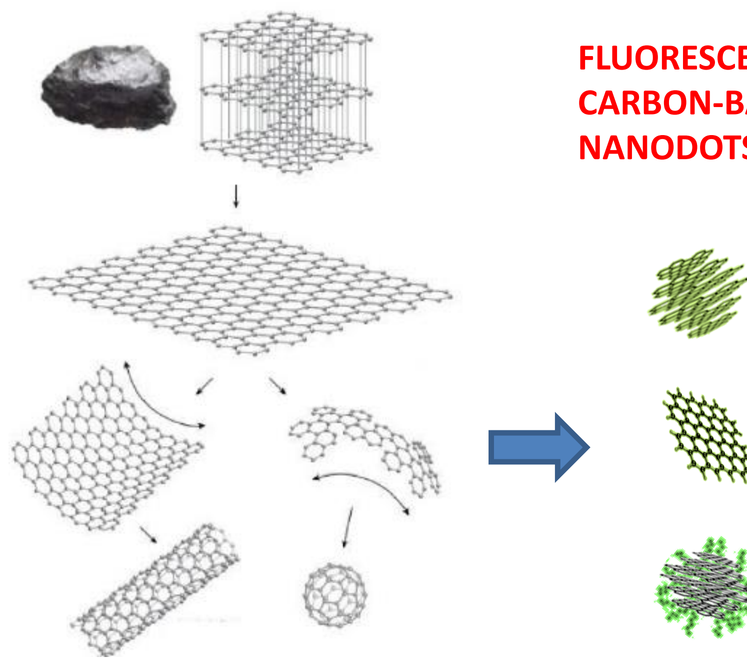
1a. Types of quantum nanodots

FLUORESCENT QUANTUM NANODOTS are an exciting new class of fluorescent nanomaterial that can be considered as nanometric spheres with fascinating PL properties, such as emission wavelength sized-dependent and PL tunable depending on their size distribution and changes in their surface caused by different functional groups.

Isn't it incredible all the different things that you find inside a pencil?

FLUORESCENT SEMICONDUCTOR QUANTUM DOTS



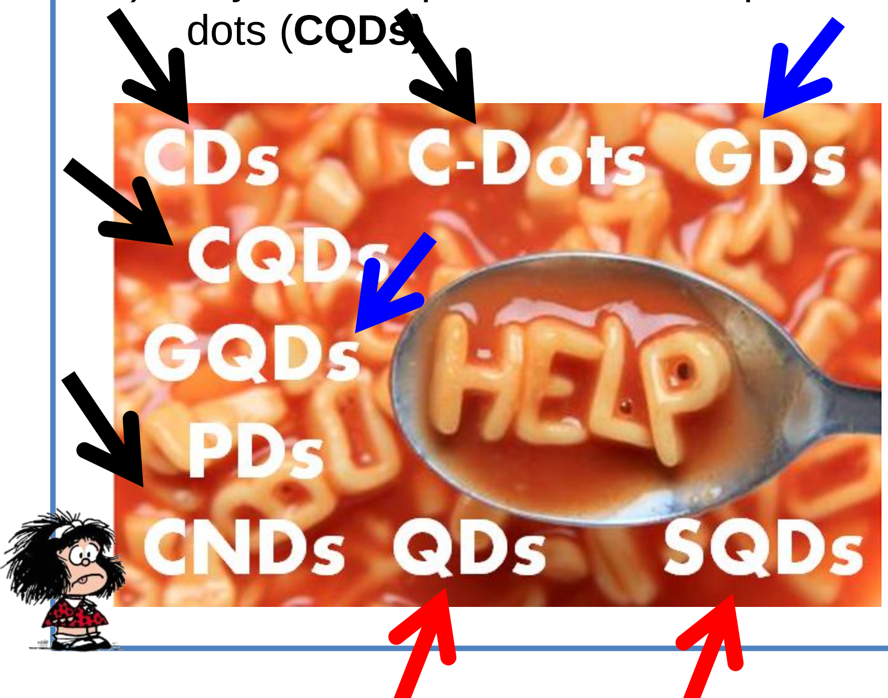


FLUORESCENT CARBON-BASED NANODOTS

1a. Types of quantum nanodots

FLUORESCENT QUANTUM NANODOTS are divided into three main groups:

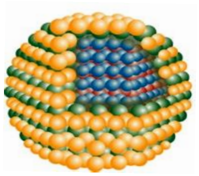
i) Semiconductor quantum dots (**SQDs**) with quasi-spherical shape,
ii) π-conjugated single sheet referred as graphene quantum dots (**GQDs**)
iii) Crystalline spherical carbon quantum dots (**CQDs**)



NEED FOR CONSISTENCY IN THE NOMENCLATURE OF FLUORESCENT NANODOTS

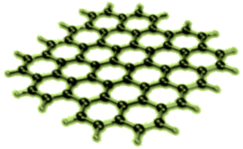
Semiconductor quantum dots

SQDs



Carbonaceous quantum dots

GQDs **CQDs**



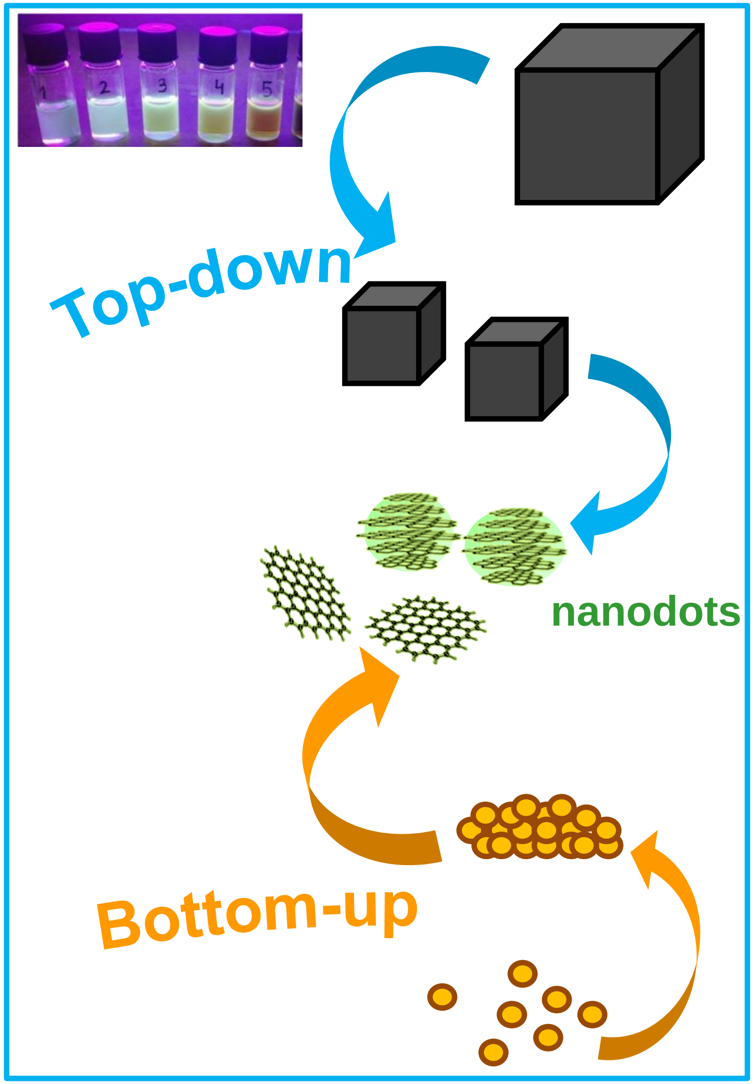
A. Cayuela, M.L. Soriano, et. al., Chemical Communications, 2016, 56, 1311-1326.

1a. Types of quantum nanoparticles

CARBON BASED FLUORESCENT DOTS can be prepared following two methodologies:

-TOP-DOWN

-BOTTOM-UP



MAIN CHARACTERISTICS

-LOW TOXICITY

-BIOCOMPATIBILITY

-EXCELLENT WATER-SOLUBILITY

-ROBUST CHEMICAL INERTNESS

-FACILE SURFACE MODIFICATION

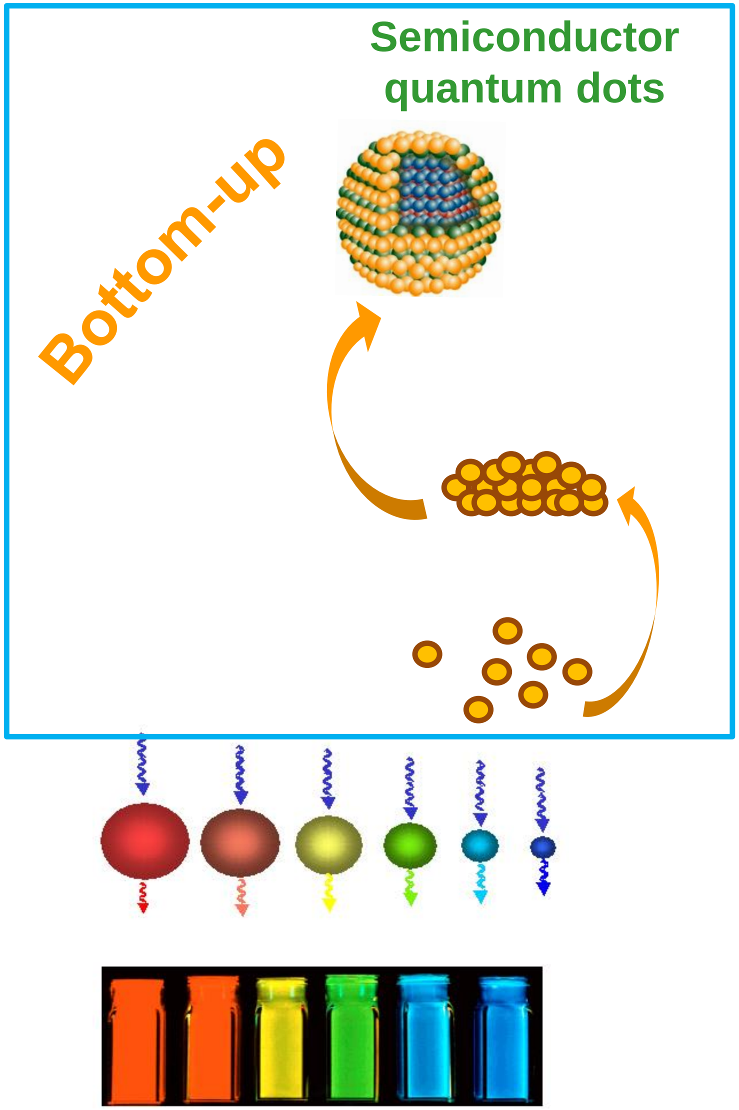
-TUNABLE FLUORESCENCE

- HIGH RESISTANCE TO PHOTOBLEACHING

1a. Types of quantum nanodots

SEMICONDUCTOR QUANTUM DOTS can be prepared following two methodologies:

-BOTTOM-UP



MAIN CHARACTERISTICS

-HIGH BRIGHTNESS, SIZE-TUNABLE

-HIGH TOXICITY*

-LOW BIOCOMPATIBILITY DEPENDING ON CORE/SHELL AND SURFACE FUNCTIONALIZATION*

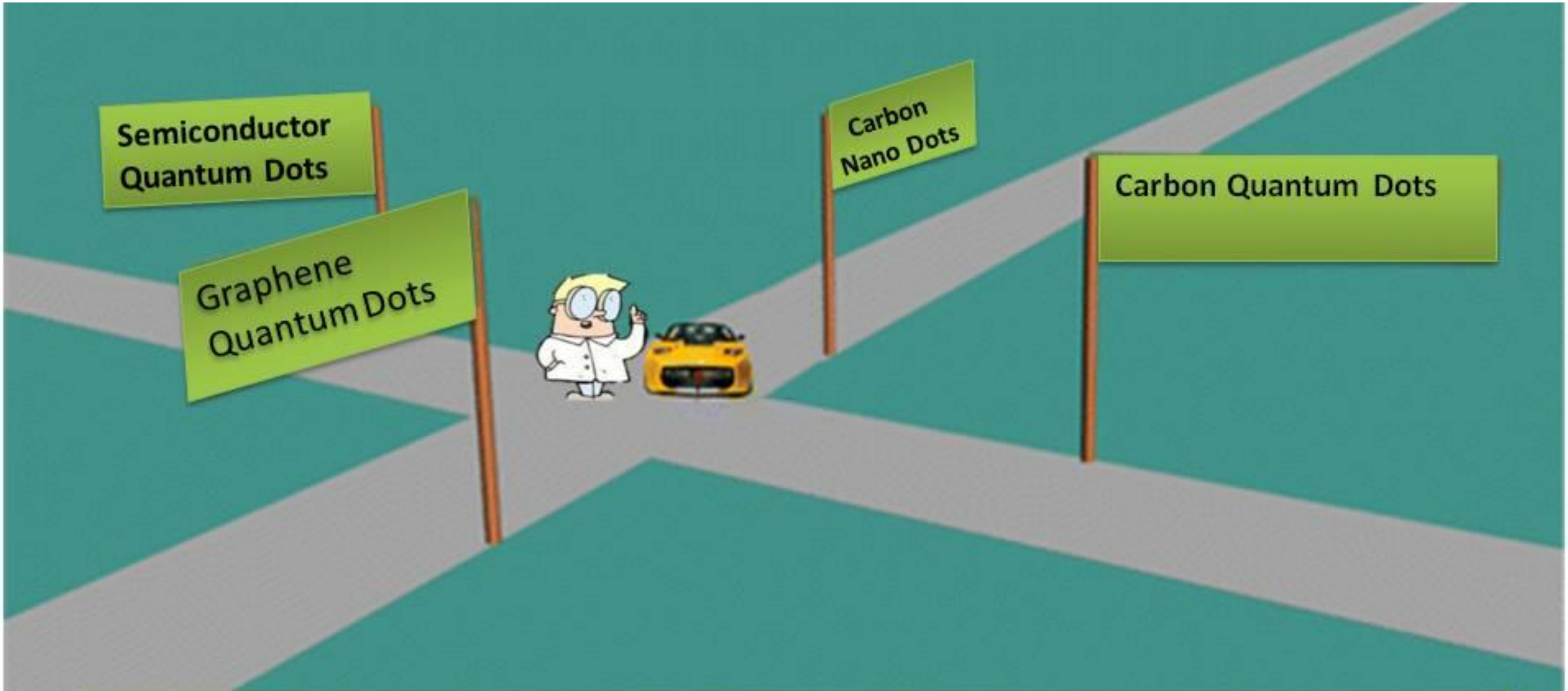
- LOW SOLUBILITY IN WATER*.

*** NEED TO EXCHANGE SURFACE LIGANDS WITH MORE POLAR ONES TO MAKE BIOCOMPATIBLE SQDs.**

1b. Applications of quantum nanodots

- PHOTOSENSITIZERS OF SINGLET OXYGEN
- SENSING PLATFORMS
- OPTRONICS
- PHOTOCATALYSIS
- BIOMEDICINE
- (BIO)IMAGING
- DRUG DELIVERY

2. Toxicity of quantum nanodots

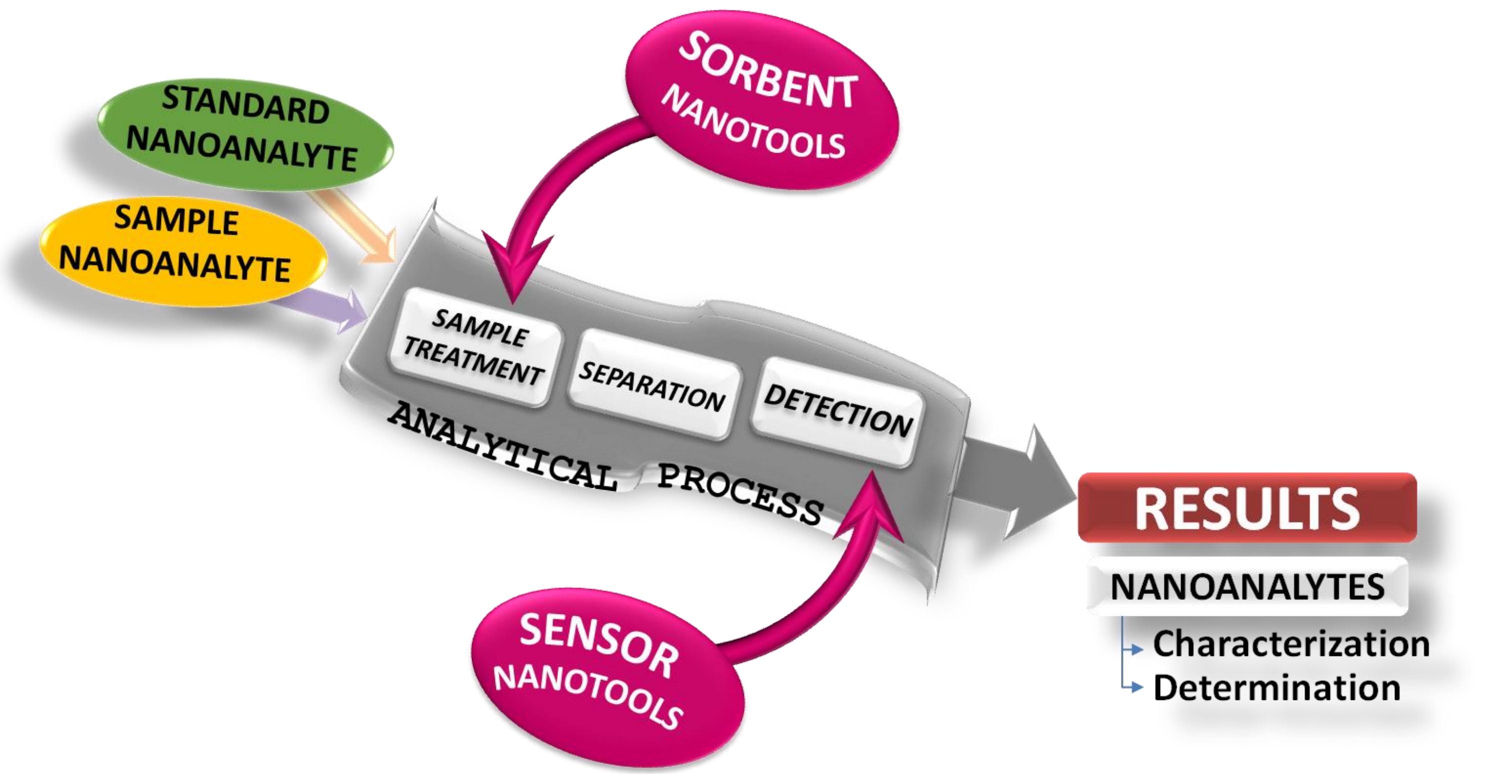


Need of settle down the bases and definitions of PL semiconductor and carbonaceous nanodots for highlighting the state-of-the-art of analytical and biomedical research fields related to these types of fluorescent nanodots.

I N D E X

1. Determination of Nanoparticles

Roles of NPs in the Third Way of the AN&N



TrAC Trends in Analytical Chemistry, 2016, 84, 172–180

I N D EX

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  - NANOTECHNOLOGY: BENEFITS AND IMPACTS

1. Sensors based on carbonaceous nanodots in aqueous solution
2. Fluorescent hydrogel sensors based on organic gelators.
3. Fluorescent hydrogel sensors based on nanocellulosic fibers as gelators

  - SENSORS OF NANOPARTICLES

- FINAL REMARKS

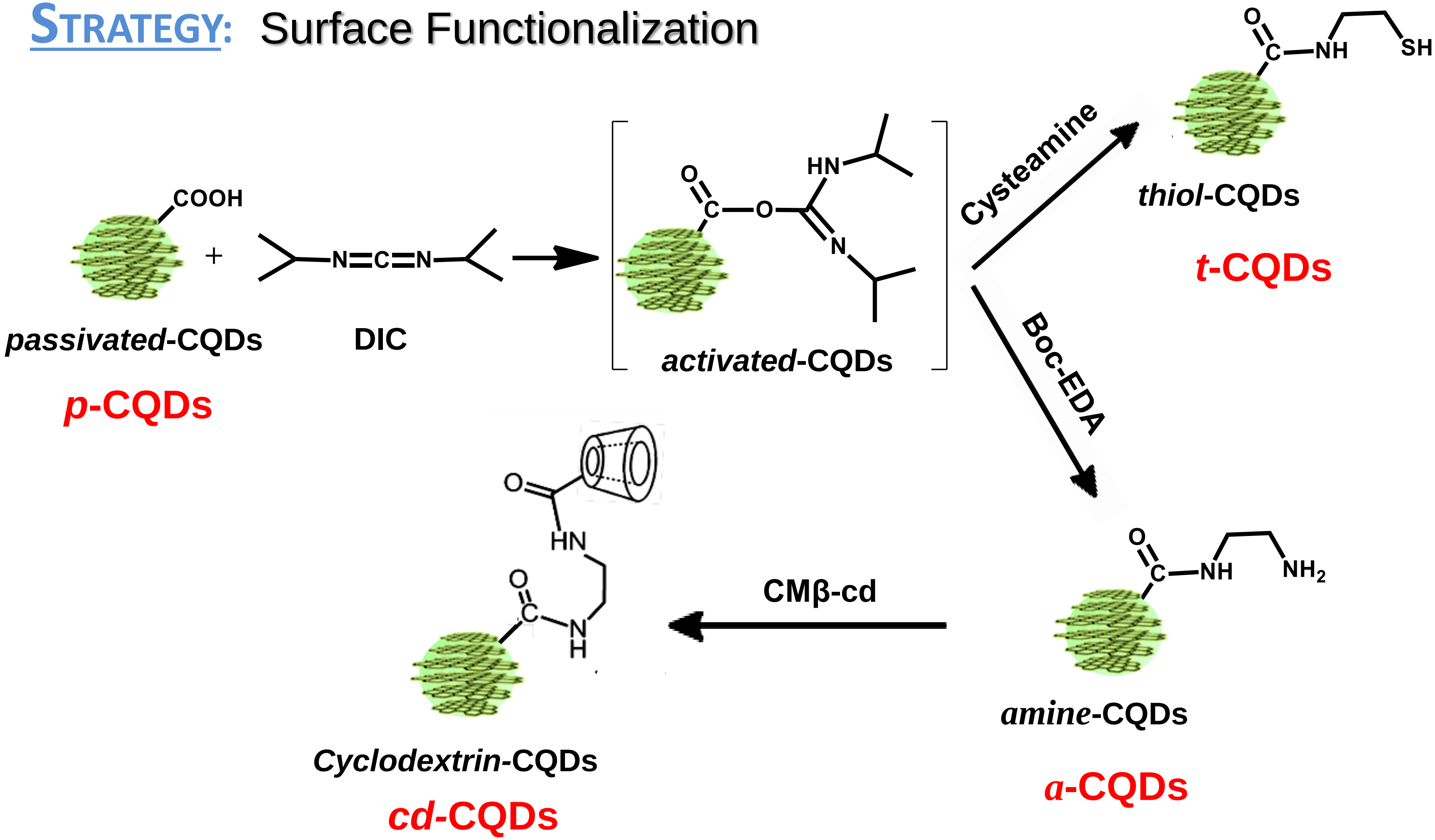
1. Determination of Nanoparticles

-Nanoparticles (within the Third Way of AN&N)

NANOSENSOR Type	NANOSENSOR Role	ANALYTE	SAMPLES Type	SAMPLES Matrix
GQDs	Sensor	GO, TiO_2	Environmental	Water
CQDs	Sensor	MWCNTs, C_{60}	Environmental	Water
CQDs	Sensor	AuNPs	Consumer products	Mussels
CQDs	Sensor	AgNPs	Consumer products	Creams

1. Determination of Nanoparticles: Design of the nanosensor

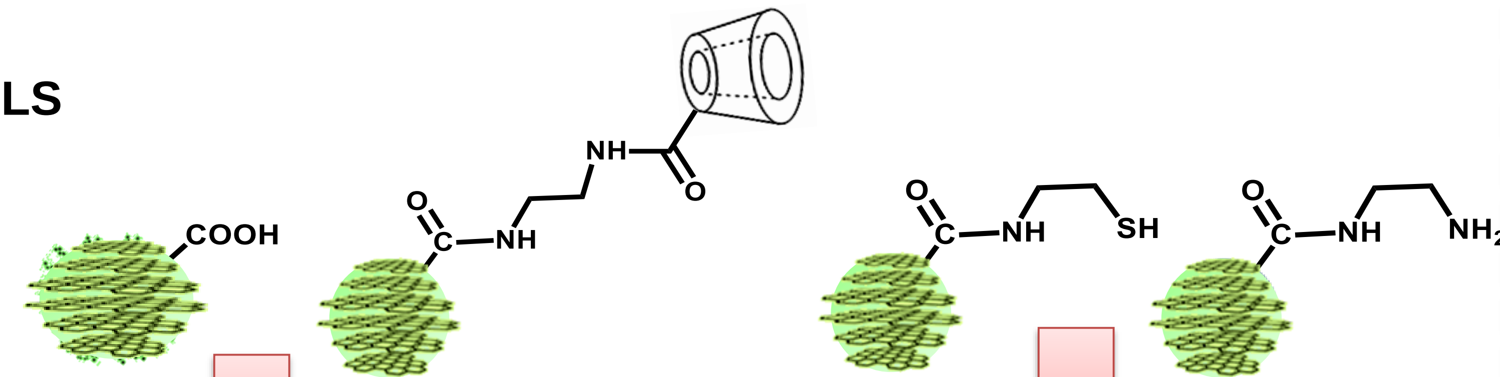
STRATEGY: Surface Functionalization



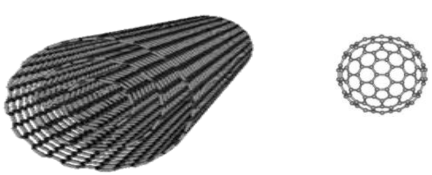
1. Determination of Nanoparticles

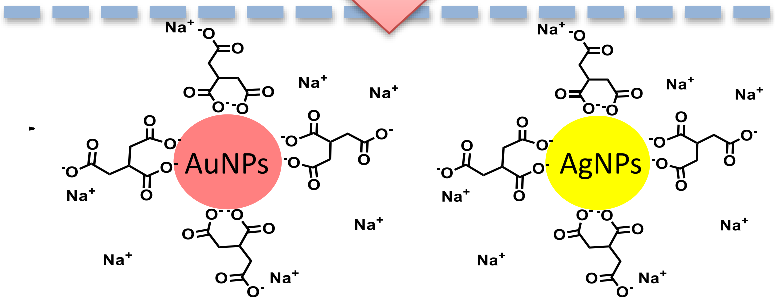
SENSORS IN AQUEOUS MEDIA

SENSING NANOTOOLS



NANO-ANALYTES





CARBONACEOUS NANOPARTICLES

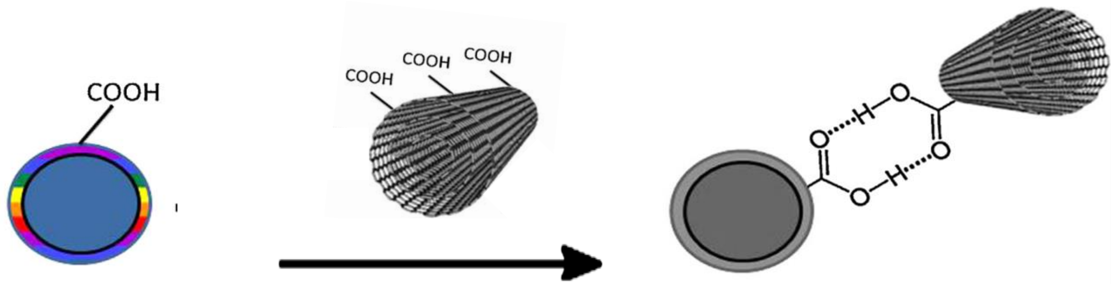
METALLIC NANOPARTICLES (AuNPs & AgNPs)

1. Determination of NPs

SENSORS IN AQUEOUS MEDIA

Carbonaceous NPs

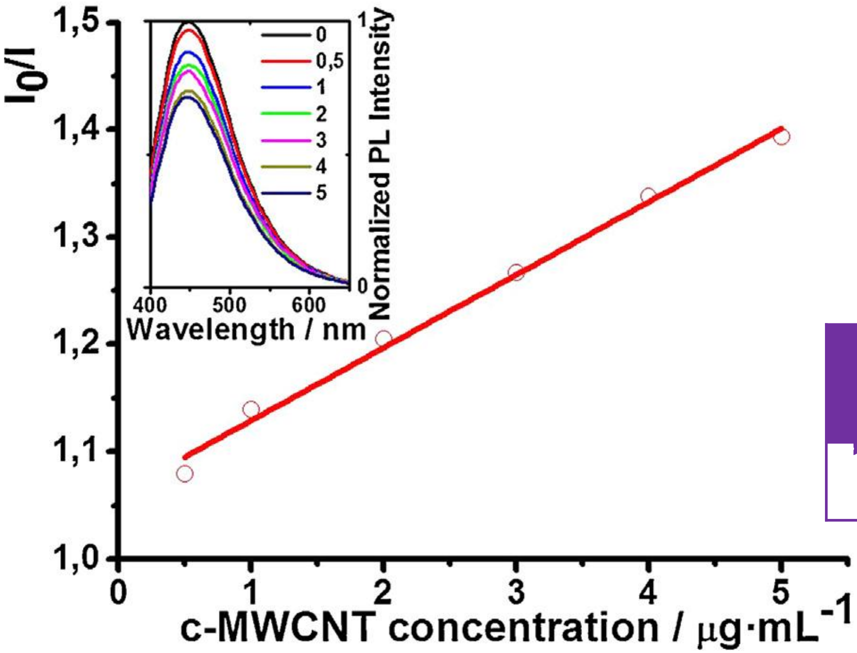
Detection of MWCNTs



c-CQDs

Hydrogen bonds

c-MWCNT/*c*-CQDs



River water

Analyte	LOD (µg·mL^{-1})	LOQ (µg·mL^{-1})	RSD (%)
c-MWCNTs	0.37	1.25	0.83

Sensors and Actuators B: Chemical, 2015, 207, 596-601.

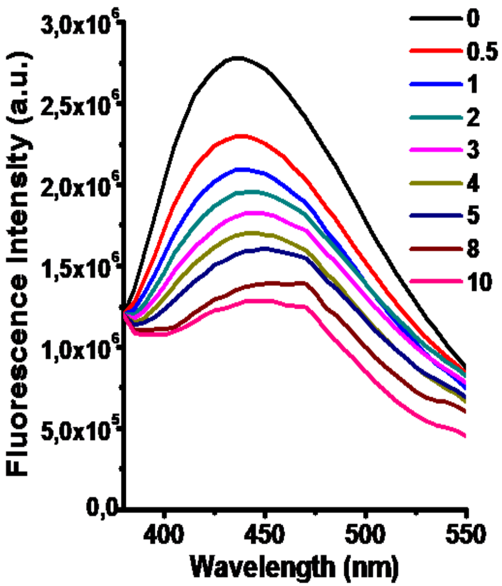
ANALYTICAL METHODS FOR NANOPARTICLES MONITORING

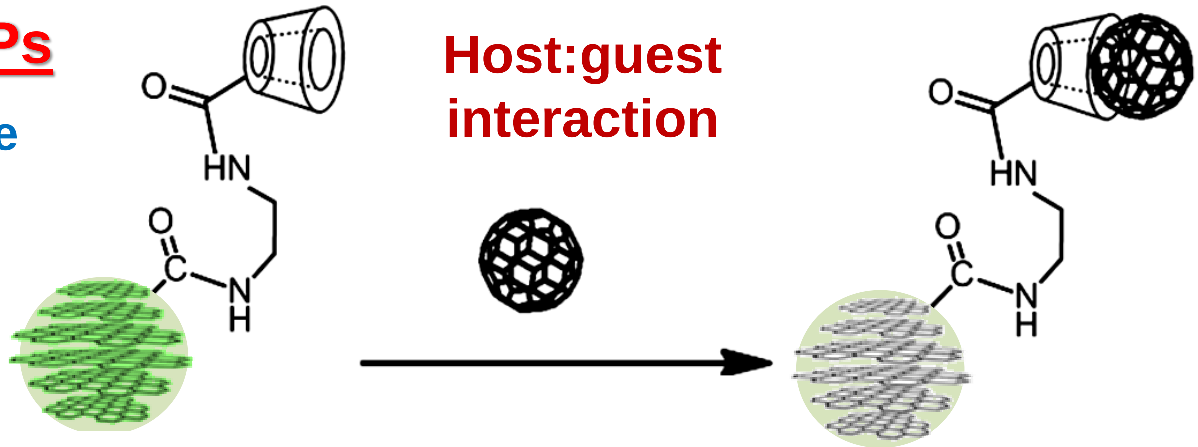
1. Determination of NPs

SENSORS IN AQUEOUS MEDIA

Carbonaceous NPs

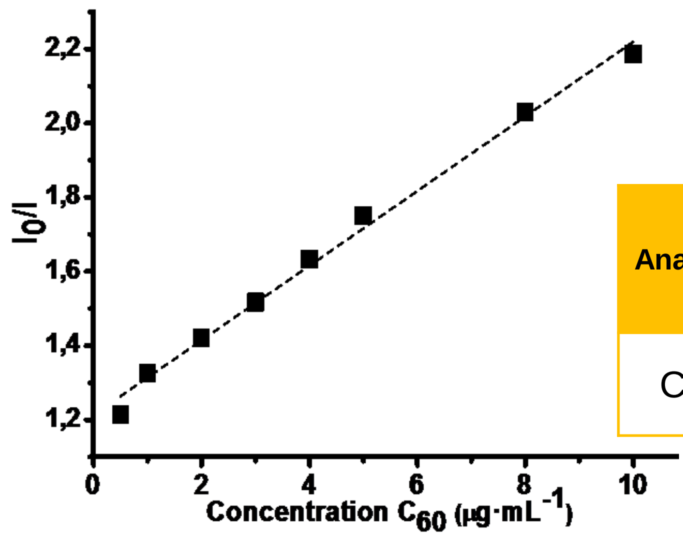
Detection of fullerene





cd-CQDs

C_{60}/*cd*-CQDs



River water

Analyte	LOD (µg·mL⁻¹)	LOQ (µg·mL⁻¹)	RSD (%)
C_{60}	0.525	1.751	6.6

Analyst, **2016,** *141*, 2682 - 2687

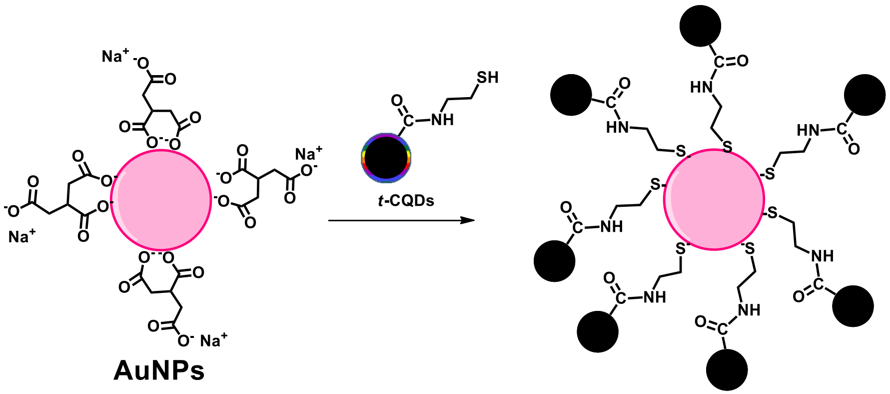
1. Determination of NPs

SENSORS IN AQUEOUS MEDIA

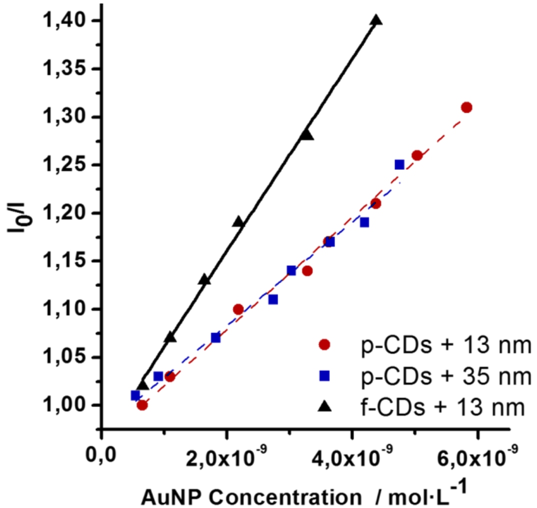
Metallic NPs

Detection of AuNPs

Citrate-capped AuNPs of 13-35 nm.



STATIC QUENCHING MECHANISM elucidated from high-temperature fluorescence measurements and lifetime tests



River water and mussels

Analyte	LOD (nmol·L^{-1})	LOQ (nmol·L^{-1})	RSD (%)
AuNPs	0.46	1.52	3.0

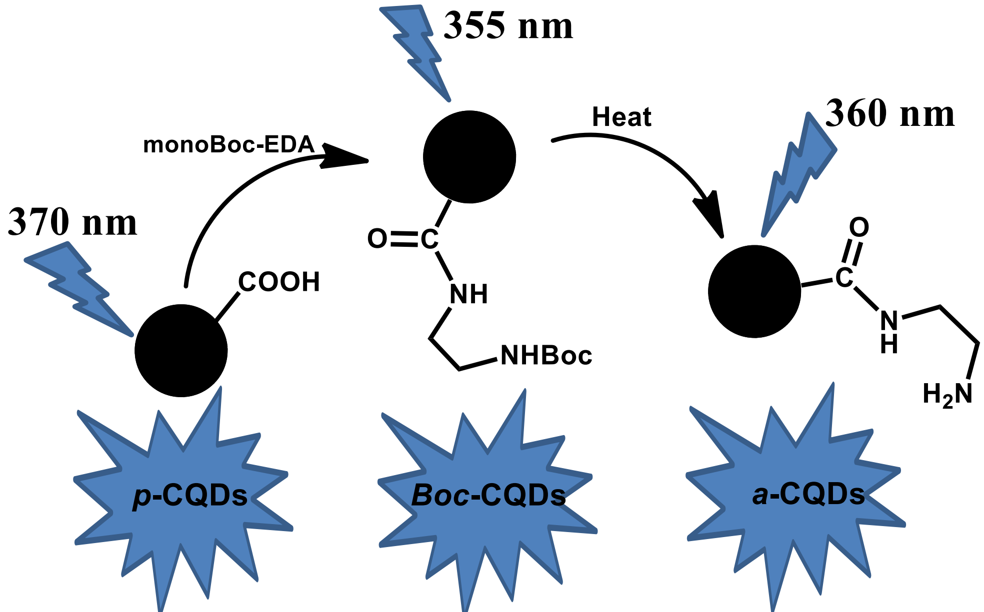
Analytica Chimica Acta, 2014, 820, 133-138.

1. Determination of NPs

SENSORS IN AQUEOUS MEDIA

Metallic NPs

Detection of AgNPs



EXCELLENT FLUORESCENT SENSOR, BUT…

SELECTIVITY FOR SILVER NANOPARTICLES ?

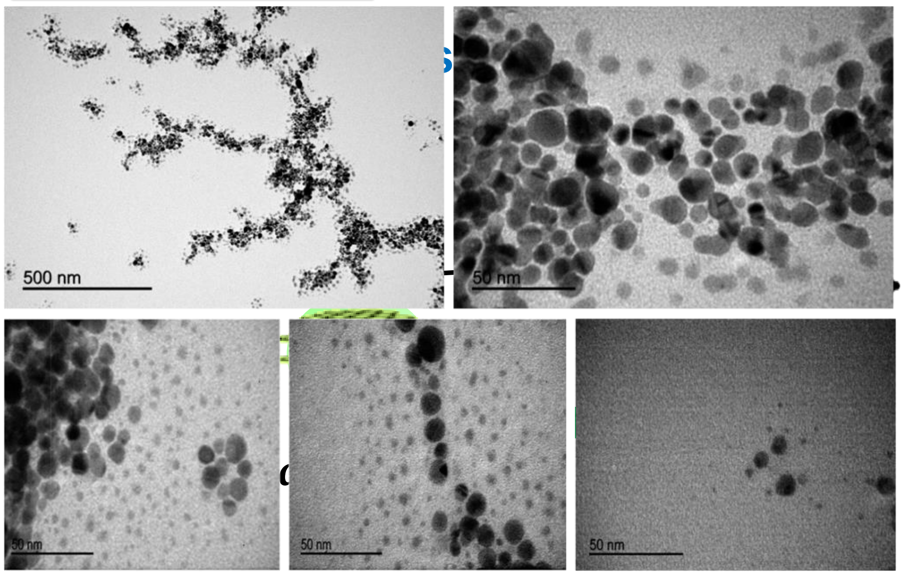
p-CQDs COSMETIC CREAM a-CQDs

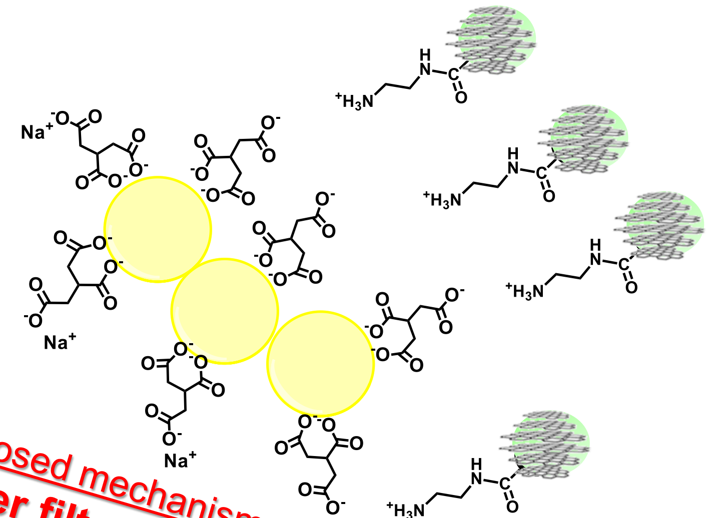
Analytica Chimica Acta, 2015, 872, 70-76.

1. Determination of NPs

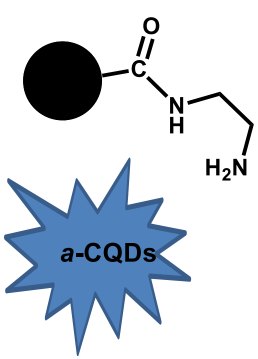
SENSORS IN AQUEOUS MEDIA

Metallic NPs



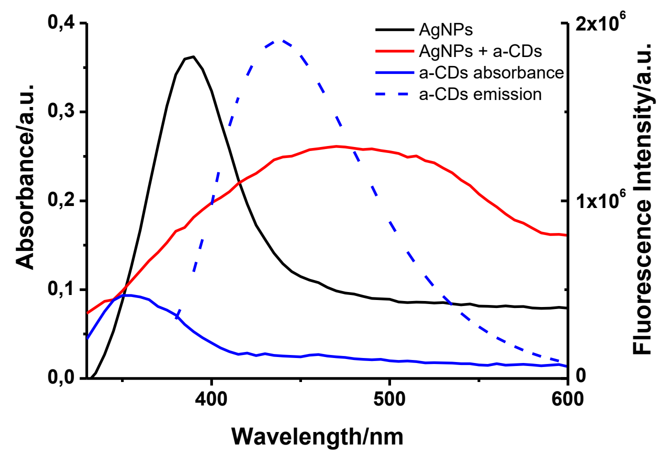


Proposed mechanism:
Inner filter effect (IFE)



Are *a*-CQDs selective towards AgNPs??

a-CQDs exhibit selectivity towards citrate-coated AgNPs. No effect was observed in case of PVP-coated AgNPs.
Due to this PVP protecting layer, stable AgNPs-containing aqueous dispersion remained unchanged and thus aggregation does not occur.



Analytica Chimica Acta, 2015, 872, 70-76.

1. Determination of NPs

SENSORS IN AQUEOUS MEDIA

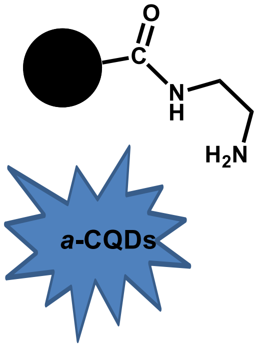
Metallic NPs

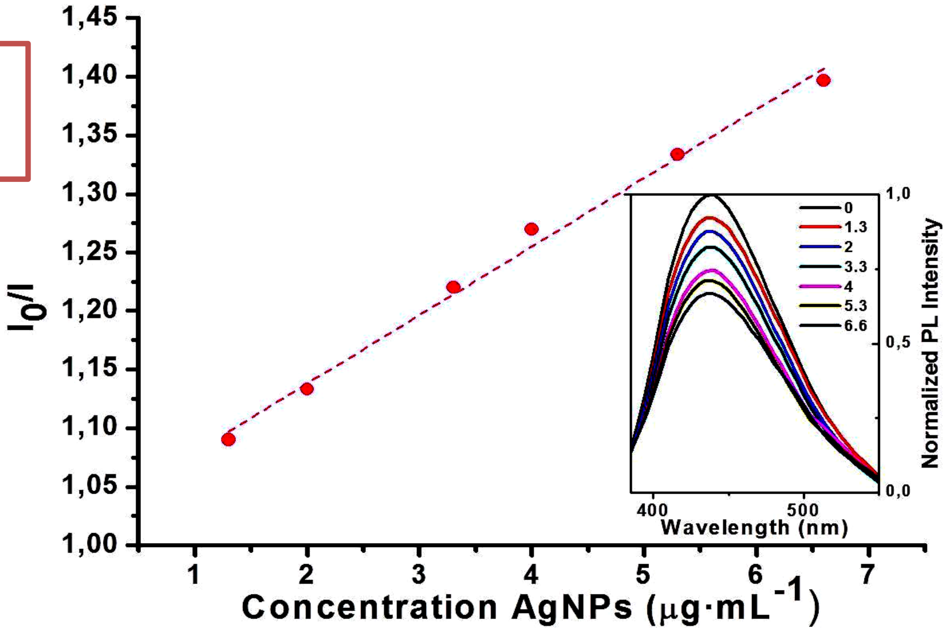
Detection of AgNPs

Cosmetic creams

Citrate-capped AgNPs.

LOD and LOQ of 0.50 and 1.68 $\mu g \cdot mL^{-1}$, respectively.





Analytica Chimica Acta, 2015, 872, 70-76.

I N D EX

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3. Fluorescent hydrogel sensors based on nanocellulosic fibers as gelators

- …NG
  - SENSORS OF NANOPARTICLES

- FINAL REMARKS

2. Gel formation

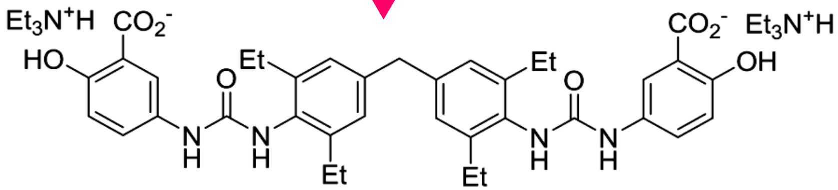
HYDROGEL SENSORS

STRATEGY: USE AN ORGANIC MOLECULE AS THE GELATOR

WHY A BISTHIOUREA DERIVATIVE?

Bisthiourea ligand + Water → NO GELS

Bisthiourea ligand (LMWG) + Carbonaceous nanodots → GELS



Hydrophilic Carbon (Quantum) Dots

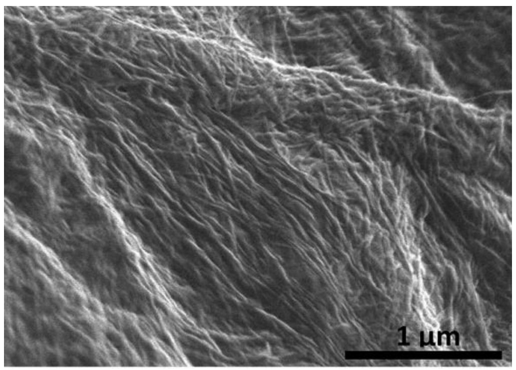
Bottom-up → *Cellulose*-CQDs, *c*-CQDs

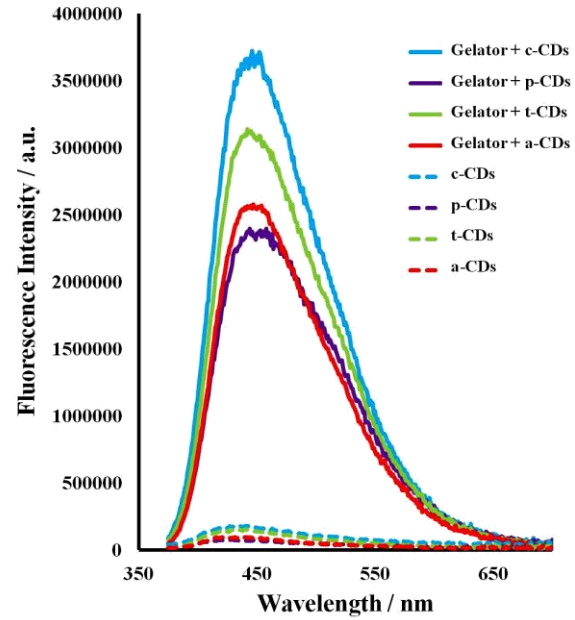
Top-down → *p*-CQDs, *t*-CQDs, *a*-CQDs

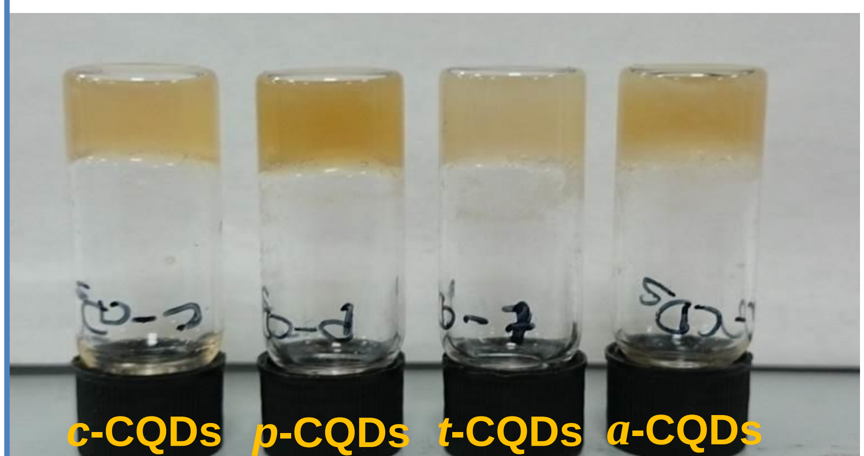
2. Gel formation

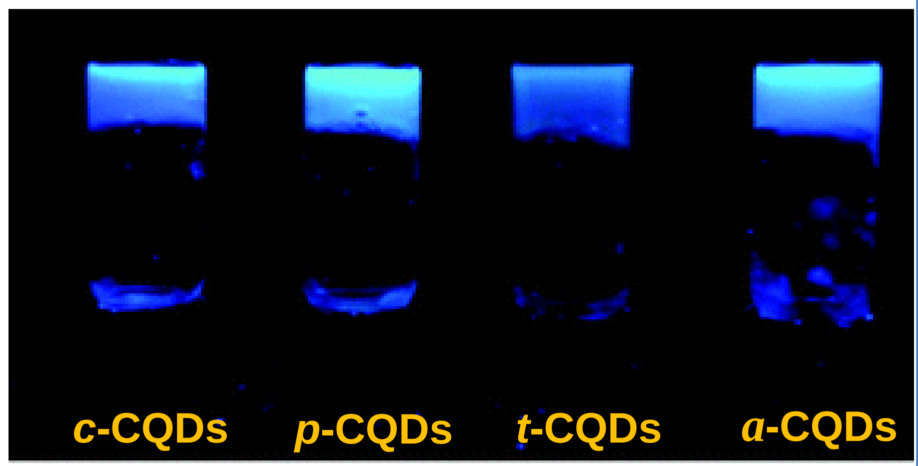
HYDROGEL SENSORS

LMWG	+	CQDs	+	Ionic liquid ($BMIM-BF_4$)
1%wt		500µL		2%v/v







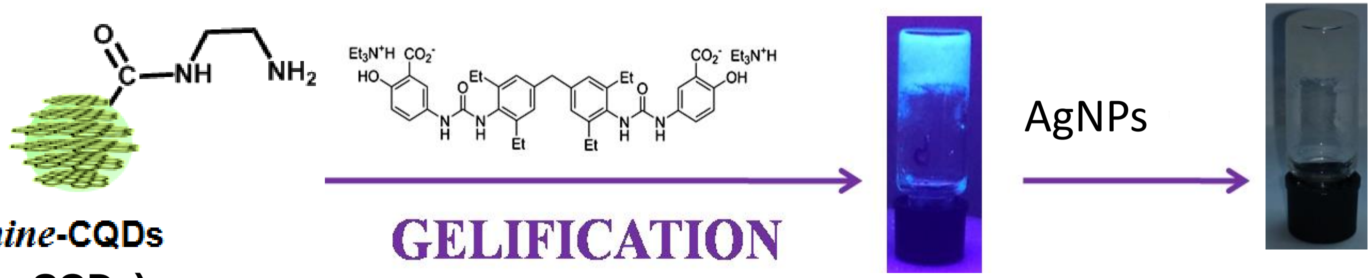


A. Cayuela et al. Chemical Science, 2015, 6, 6139-6146.

2. Gel formation

HYDROGEL SENSORS

a-CQDGs for AgNPs determination



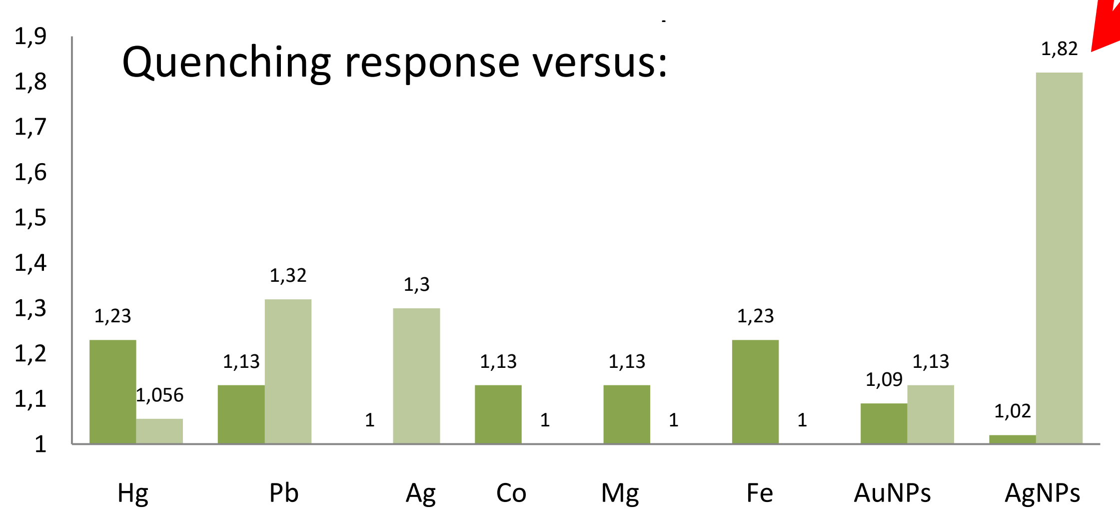
amine-CQDs
(*a*-CQDs)

Emission of
a-CQDGs

Fluorescence
quenching of
a-CQDGs

■ *a*-CQD solution

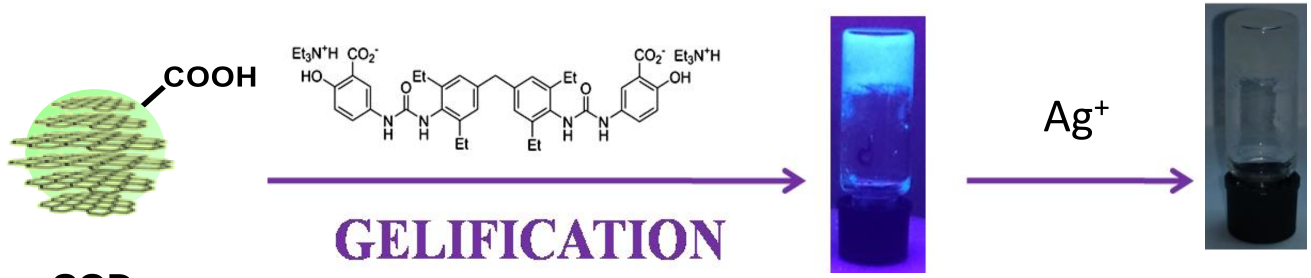
■ *a*-CQD Gels



2. Gel formation

HYDROGEL SENSORS

p-CQDGs for Ag^+ determination (quantification of Ag+ ion release of AgNPs)

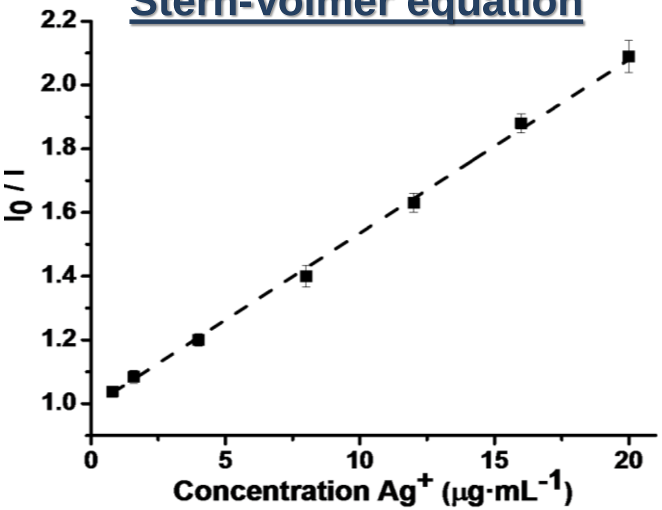


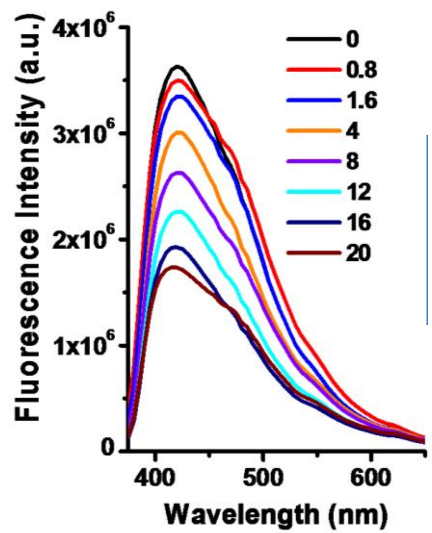
p-CQDs

Emission of *p*-CQDGs

Fluorescence quenching of *p*-CQDGs

Stern-Volmer equation





River water

Analyte	LOD ($\mu g \cdot mL^{-1}$)	LOQ ($\mu g \cdot mL^{-1}$)	RSD (%)
Ag^+	0.55	1.83	4.91

A. Cayuela et al. Talanta, 2016, 151, 100-105.

I N D EX

- INTRODUCTION
  - NANOTECHNOLOGY: BENEFITS AND IMPACTS

1. Sensors based on carbonaceous nanodots in aqueous solution
2. Fluorescent hydrogel sensors based on organic gelators.
3. Fluorescent hydrogel sensors based on nanocellulosic fibers as gelators

- ...NG
  - SENSORS OF NANOPARTICLES

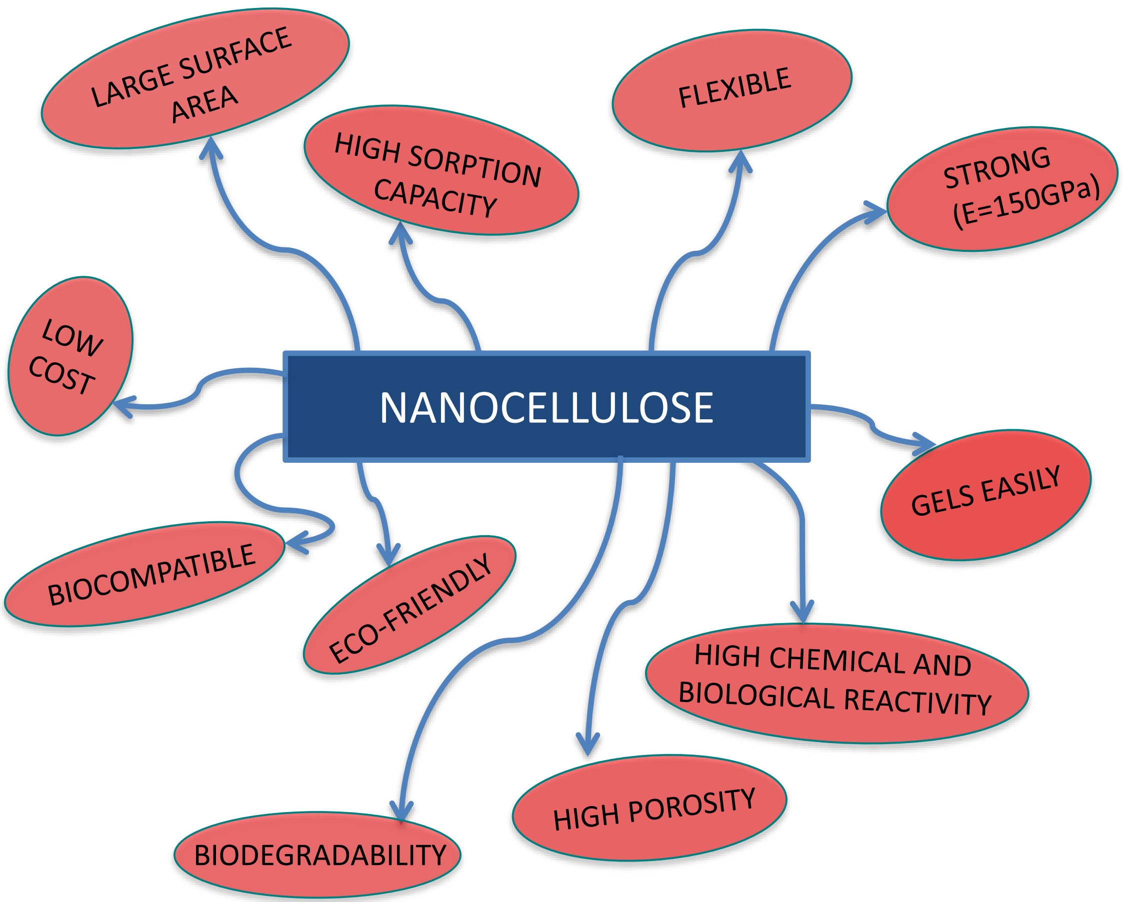
- FINAL REMARKS

2. Gel formation

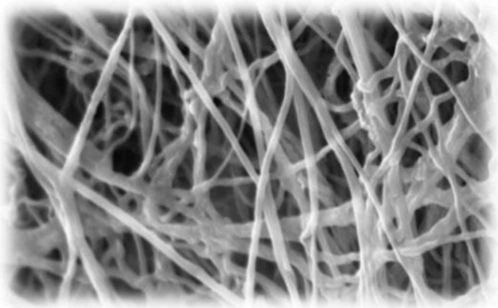
HYDROGEL SENSORS

STRATEGY: USE NANOCELLULOSE AS THE GELATOR

Why NC?

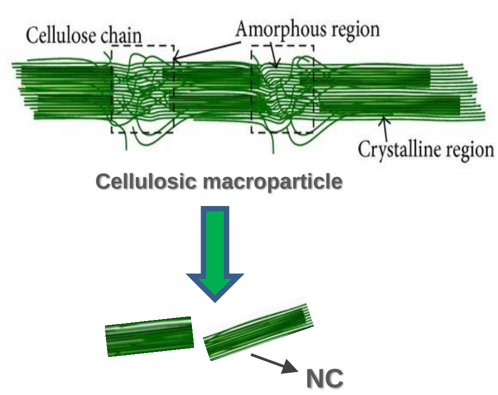


Cellulose Nanofibrils



Length: 100-3000 nm
Diameter: 10-100 nm

SYNTHESIS: TOP-DOWN

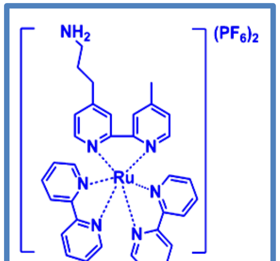


2. Gel formation

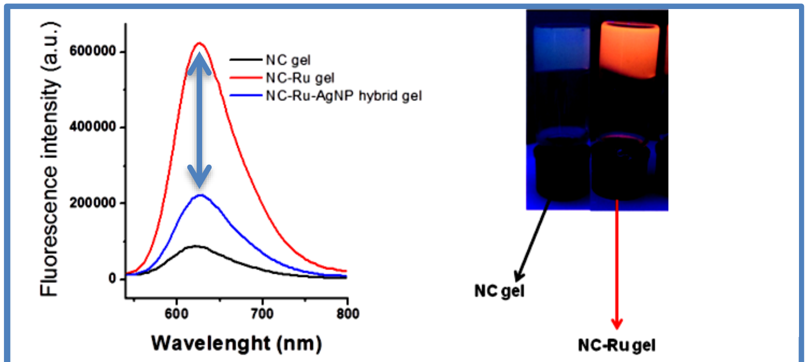
HYDROGEL SENSORS

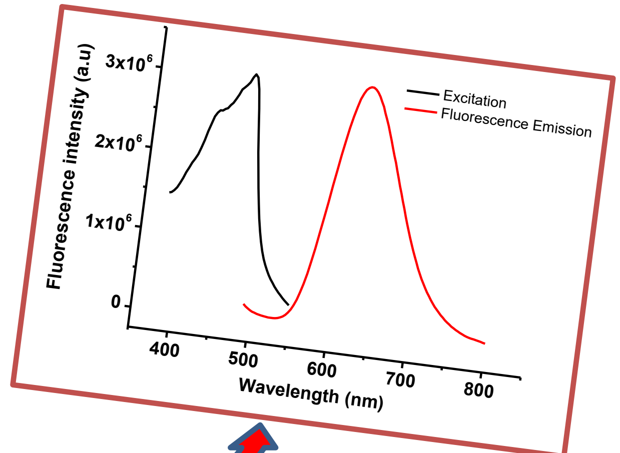
NC hydrogels based on Ruthenium(II)-bpy complex for AgNPs determination

Fluorophore & photosensitizer



$[Ru(bpy)_2(a\text{-}bpy)](PF_6)_2$





- PREPARATION OF A SENSOR BASED ON NC AS GELATOR & Ru(II) COMPLEX AS PHOTOSENSITIZER
  - ENHANCEMENT OF THE PHOTOLUMINISCENT PROPERTIES LIQUID-GEL TRANSITION
- METHOD VALIDATED BY THE GOOD RECOVERIES IN DEODORANT AND SOCKS WITH NANOSILVER

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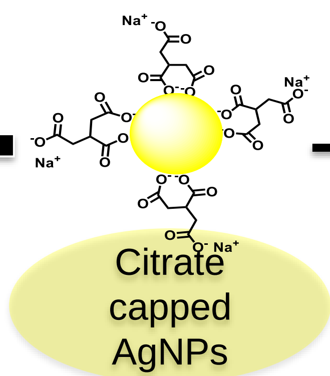
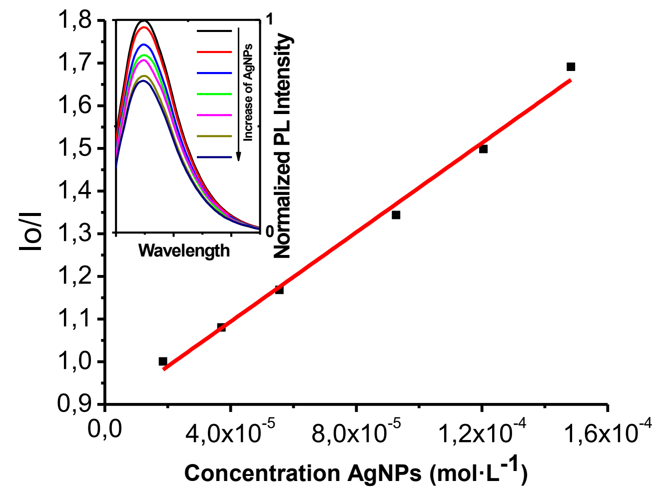
Analysis of the photoluminescence quenching of hydrogels by the Stern-Volmer eq.
(taking into account the dilution effects)

NC-Ru gel



NC-Ru-AgNP hybrid gel



Figures of merit

Linear range (mol L^{-1})	R^2	LOD (mol L^{-1})	LOQ (mol L^{-1})	Recovery (%)	Reproducibility (RSD %)
$1.85 \cdot 10^{-5}$-$1.48 \cdot 10^{-4}$	0.995	$1.11 \cdot 10^{-5}$	$3.66 \cdot 10^{-5}$	83.7-94.2	2.46

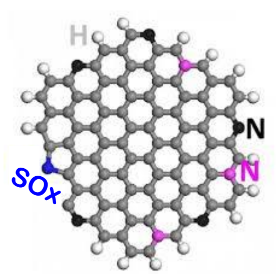
C. Ruiz-Palomero, M.L. Soriano, M. Valcárcel, Sensors and Actuators B, 2016, 229, 31-37.

2. Gel formation

HYDROGEL SENSORS

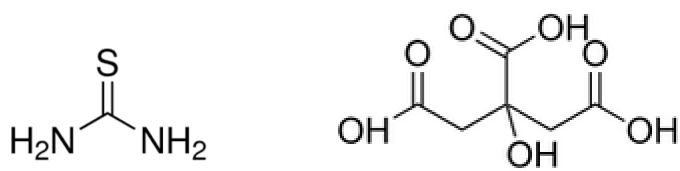
NC hydrogels based on GRAPHENE QUANTUM DOTS for analytical applications

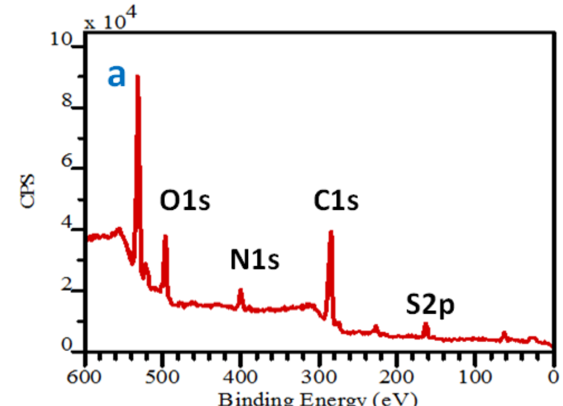
Fluorophore & photosensitizer

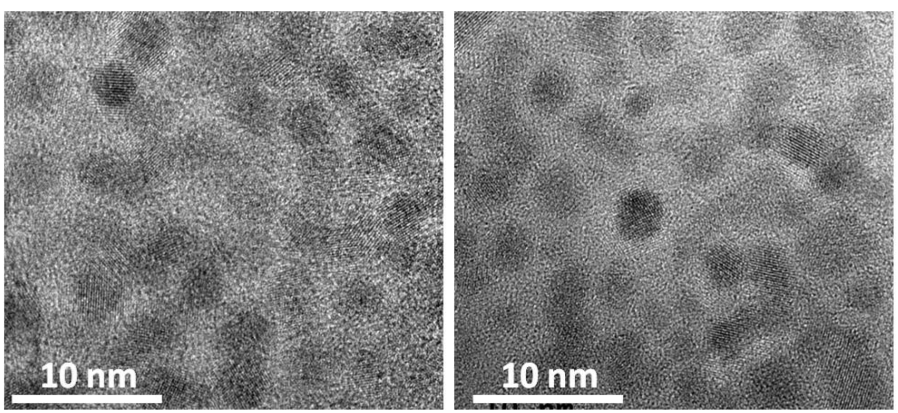


S,N-codoped GQDs

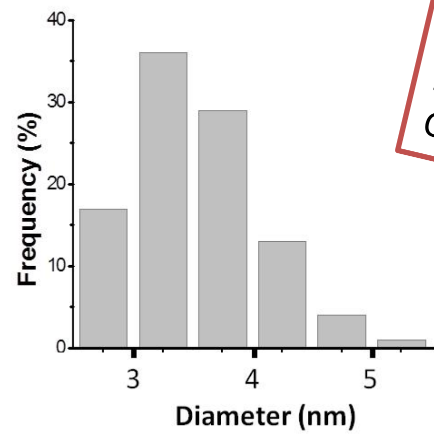
Synthesis: *Bottom-up* strategy using as precursors







3.52 ± 0.5 nm



The **blue fluorescence** attributed to the ordered sp^2 clusters within the sp^3 C-O matrix.

Fluorescence emission: 439 nm when excited at 376 nm.

PL quantum yield was of 30%

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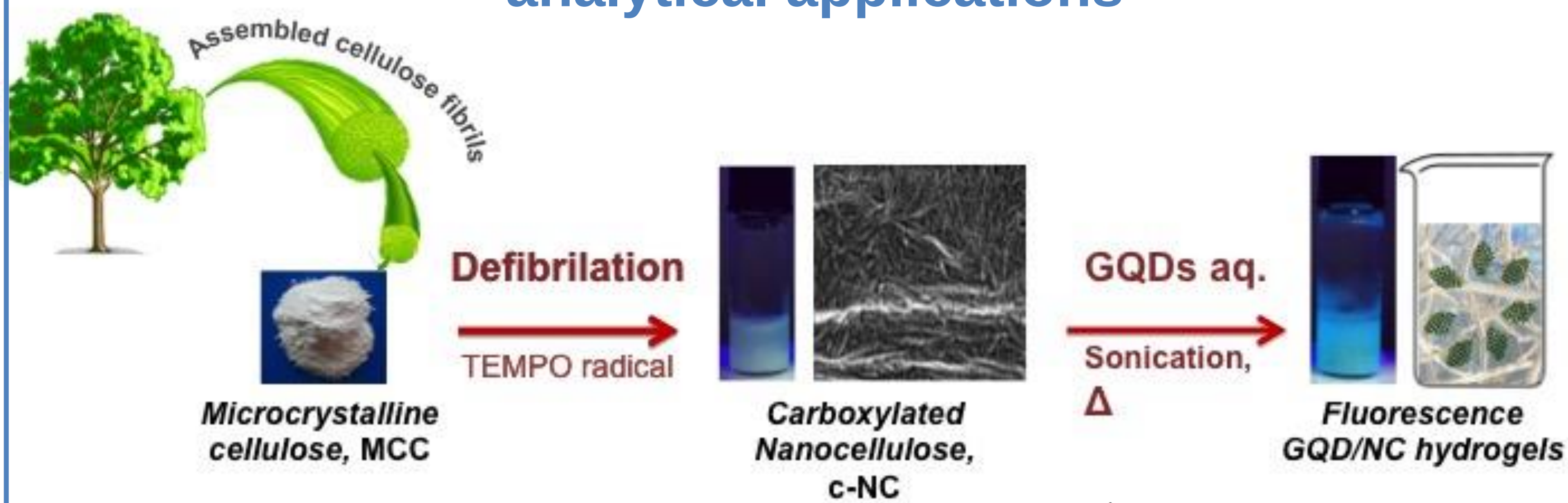
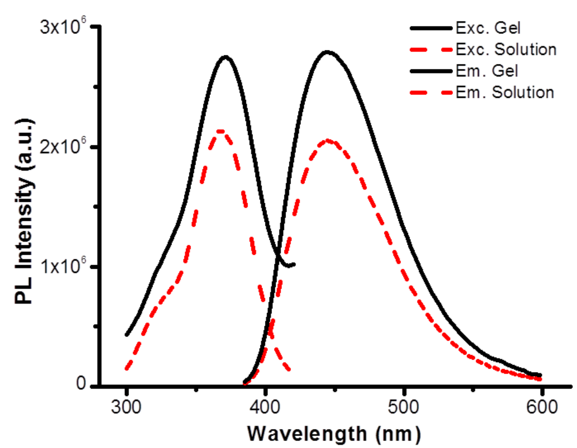
NC hydrogels based on GRAPHENE QUANTUM DOTS for analytical applications





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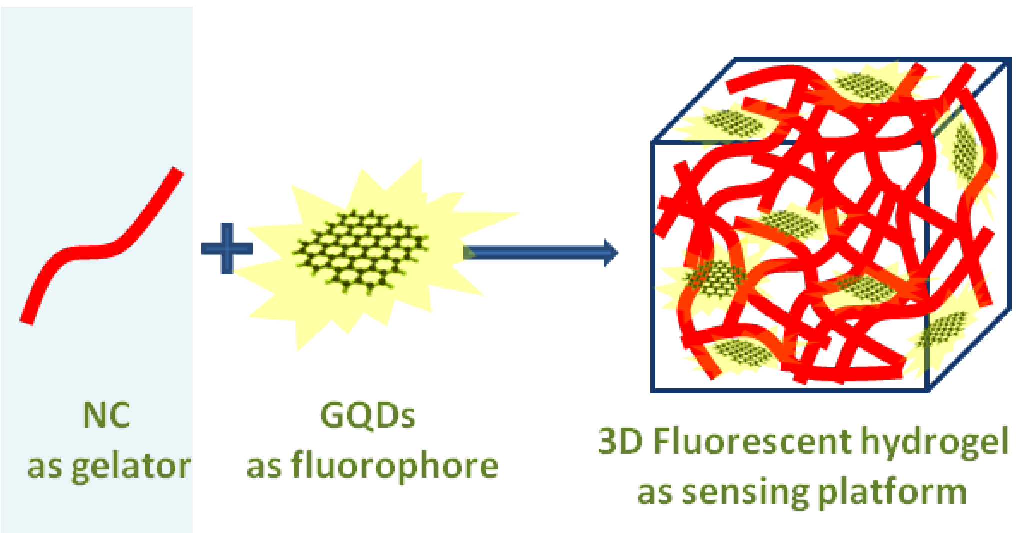

Is this sensing platform suitable for detection of pesticides ?

Evaluation of fungicide (chlorophenols), herbicides (linuron, atrazine) and antimicrobial nanoparticles (AuNPs); only response to chlorophenols was found.

I N D EX

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  - NANOTECHNOLOGY: BENEFITS AND IMPACTS
  - ANALYTICAL NANOSCIENCE & NANOTECHNOLOGY
- FLUORESCENT QUANTUM NANODOTS
  - TYPES AND APPLICATIONS
  - TOXICITY
- ANALYTICAL METHODS FOR NANOPARTICLE MONITORING
  - SENSORS OF NANOPARTICLES
- FINAL REMARKS

1. Conclusions

1 Comparison of toxicity of a variety of quantum nanodots in cells

2 Design of carbonaceous quantum dots: functionalization strategies.

3 Preparation of a variety of well-defined self-assembling hydrogels, varying the gelator and the fluorophore.

4 Analytical applications: sensors in aqueous solution and gel media.

5 Analytical methods for NP determination in environmental samples and cosmetics.

1. Future trends

- **New applications for the fluorescent hydrogels.**

Stabilization of fragile systems into such hydrogels

Novel tools in bioimaging and drug delivery

Hydrogels as sensors of drugs & biomarkers

Self-healing and sensing in one concept

THANKS FOR YOUR ATTENTION

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