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Synthesis of graphene-based nanomaterials: their applications in electrochemical detection of organic molecules

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NANOGENTOOLS Autumn School
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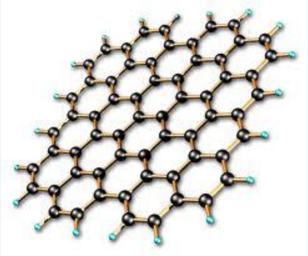
TOPICS

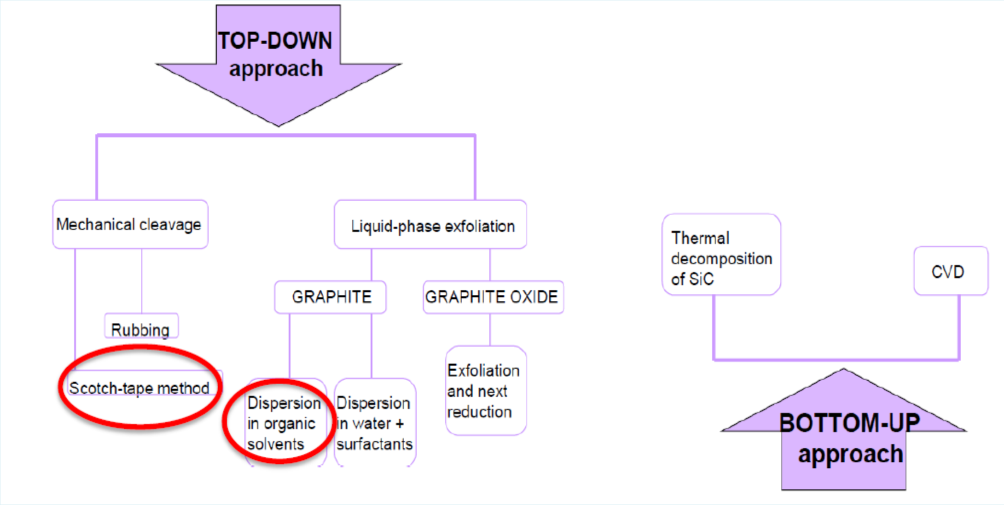
1. Graphene synthesis
   - TEM/HRTEM characterization
   - XRD and UV-Vis characterization

2. Electrochemical detection of catechol
3. Photo-degradation of pollutants with graphene-TiO_2 based materials
4. Conclusions

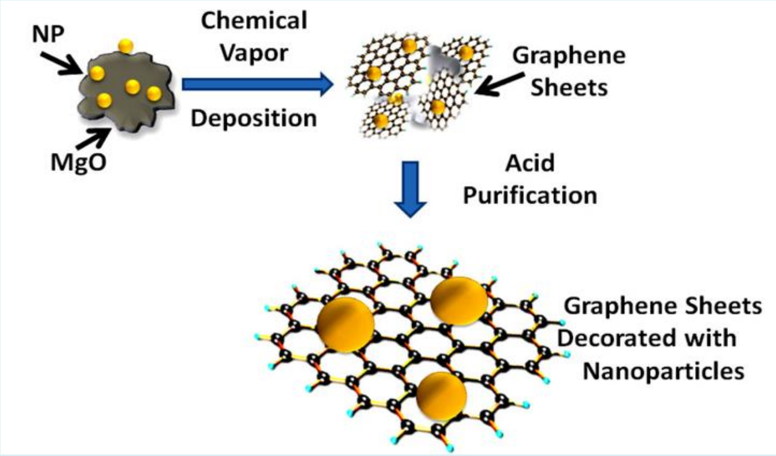
1. Graphene synthesis



- ❑ Single layer of sp^2 hybridized carbon atoms
- ❑ High mobility of charge carriers: 200.000 $cm^2V^{-1}s^{-1}$
- ❑ Surface area of a single graphene sheet is 2630 m^2/g
- ❑Graphene is resistant to attack by powerful acids and alkalis (hydrofluoric acid, ammonia)



A) Chemical Vapor Deposition (CVD)-bottom up



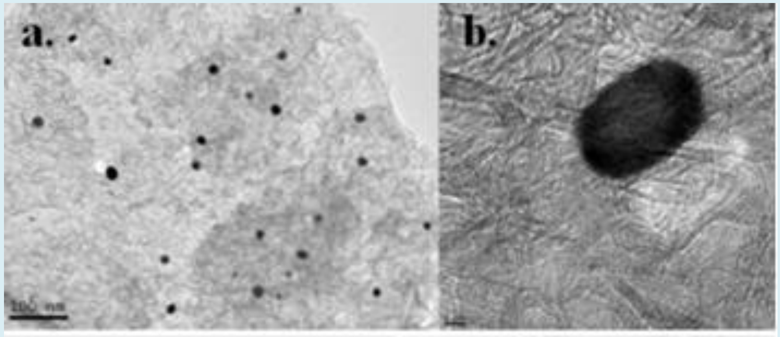
- ❑ Au(x)/MgO- catalyst, where x = 1, 2 or 3 wt%
- ❑ Ag(x)/MgO-catalyst, where x = 1,2 or 3 wt%
- ❑ Pt(x)/MgO-catalyst, where x = 1,2 or 3 wt%

- ❑ AuAg(x)/ MgO-catalyst, where x = 1:1 or 1.5:1.5 wt%
- ❑ AuPd (x)/ MgO-catalyst, where x = 1:1 or 1.5:1.5 wt%
- ❑ AuCu (x)/ MgO-catalyst, where x = 1:1 or 1.5:1.5 wt%
- ❑ AuPt (x)/ MgO-catalyst, where x = 1:1 or 1.5:1.5 wt%

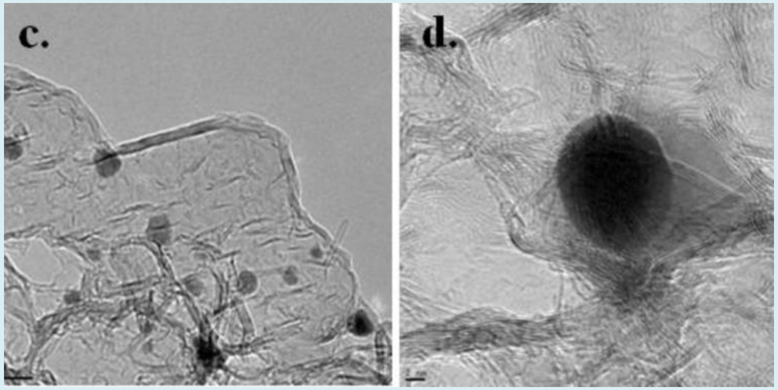
Methane; (carbon source)
1000 ^{o}C- synthesis temperature (60 minutes)

Purification in HCl (30 minutes)
Drying - 120 ^{o}C (overnight)

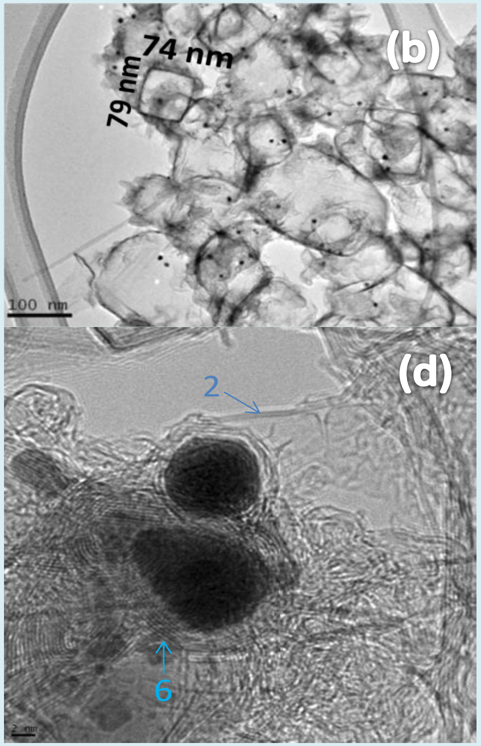
TEM/HRTEM images (3 wt.% metal)



Graphene-gold nanoparticles (5-35 nm; 22 nm)



Graphene-silver nanoparticles (5-200 nm; 35 nm)



Graphene-platinum nanoparticles (2-10 nm; 8 nm)

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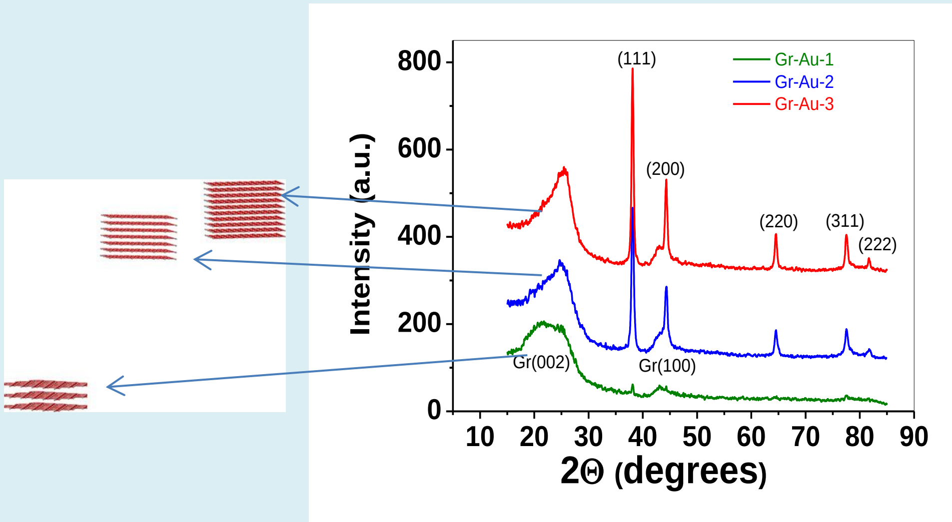
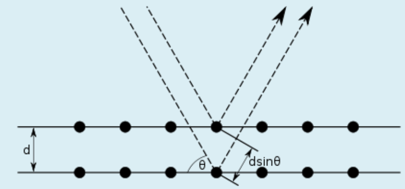
XRD study



XRD patterns of Gr-Au-x nanocomposites



Bragg's law: nλ = 2d sinΘ

d-spacing:
Graphite = 0.335 nm

Gr-Au-3 = 0.349 nm
Gr-Au-2 = 0.358 nm

Scherrer equation: τ = Kλ/βcosθ

τ = the mean size of the crystalline domains

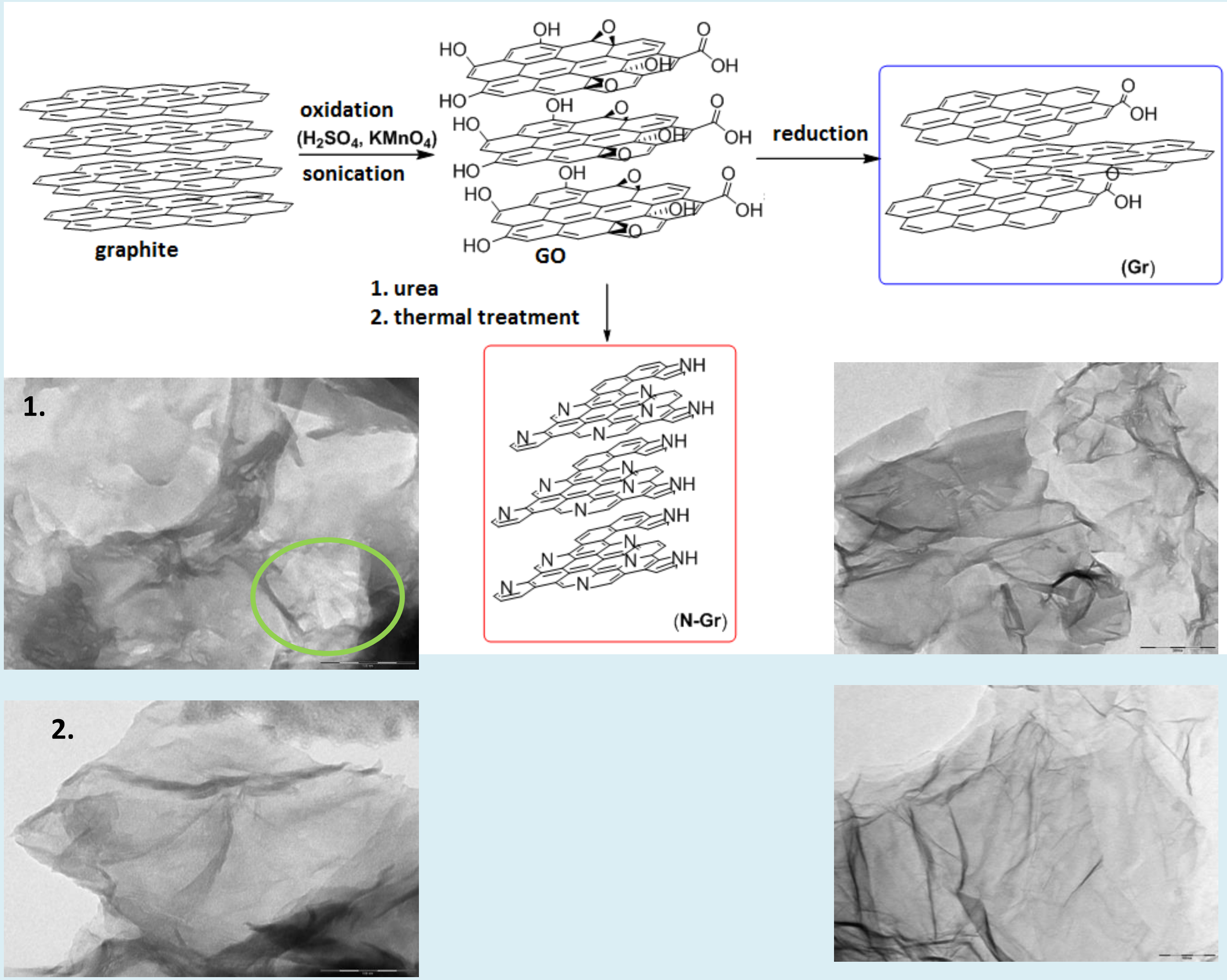
where *K* is the shape factor, λ is the x-ray wavelength,
β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle

Gr-Au-3
τ (graphene): 2.2 nm (6 graphitic layers)

Gr-Au-2
τ (graphene): 1.6 nm (4 graphitic layers)

S Pruneanu et al, International Journal of Nanomedicine 2013(8) 1429–1438

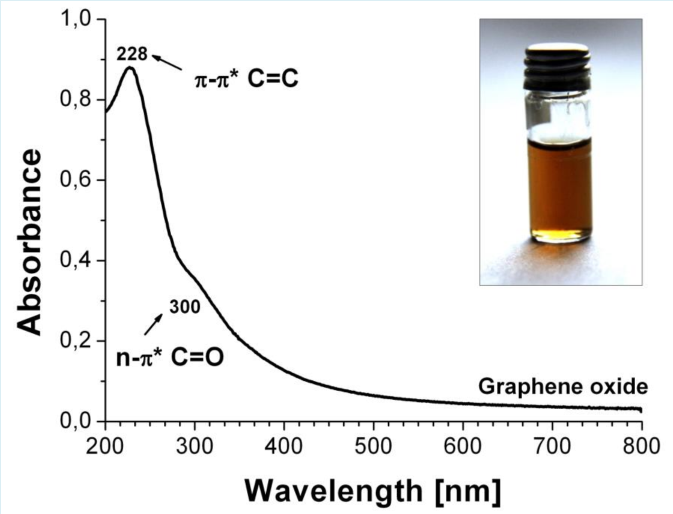
B) Chemical synthesis (top-down)

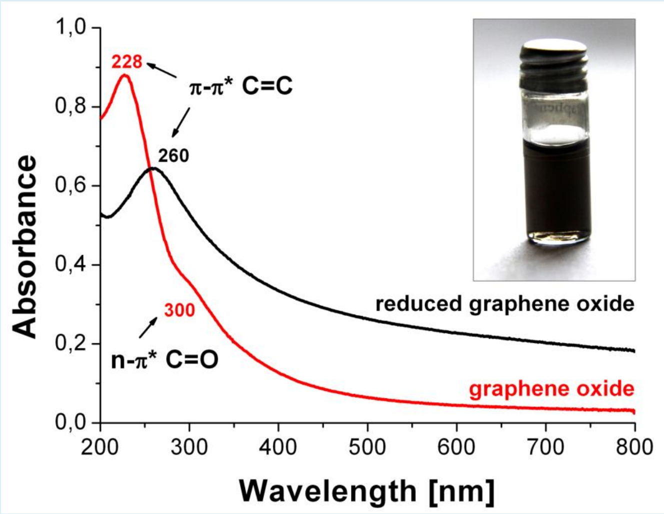


Chemical reduction

Thermal reduction
300º Ar

C. Socaci et al., Sensors and Actuators B 213 (2015) 474–483



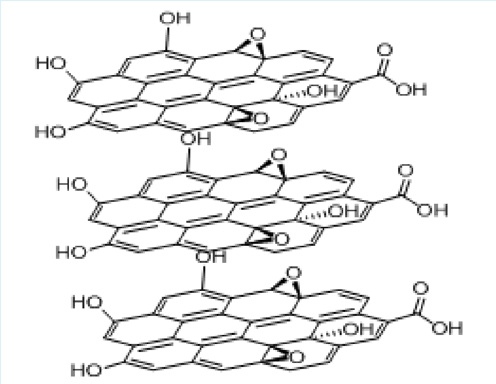


$$A(\lambda) = \varepsilon_m(\lambda) \cdot d \cdot C$$

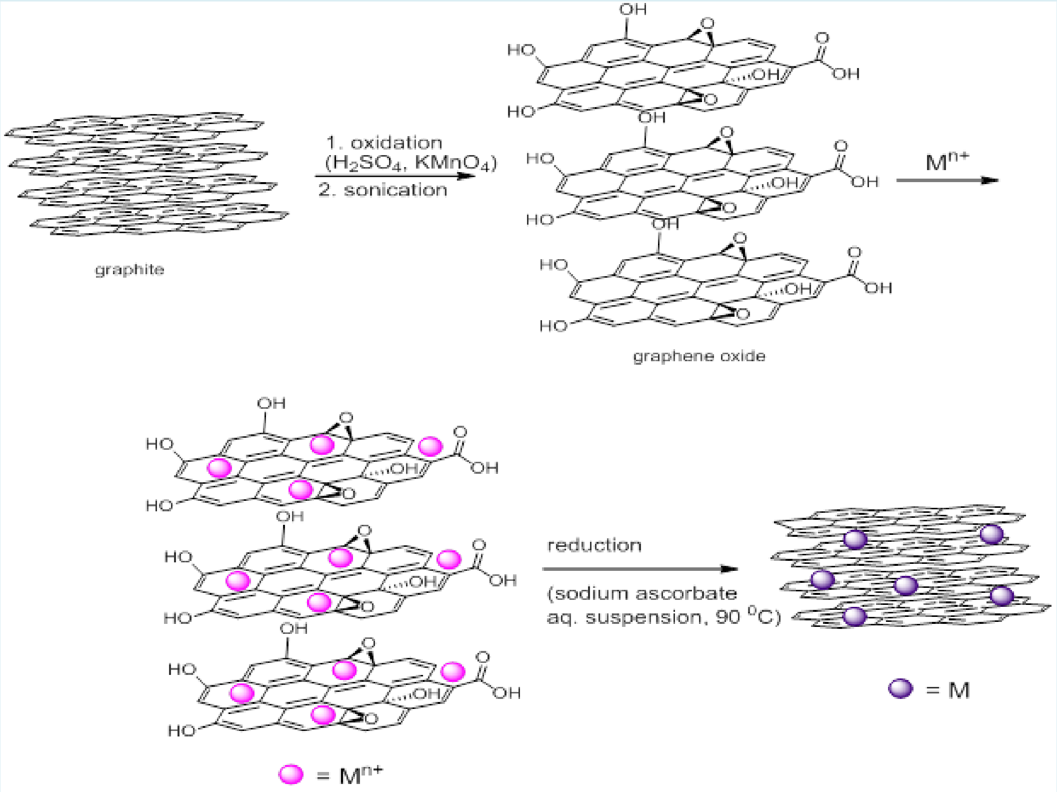
$$\varepsilon_{228\ nm} = 0.88\ mL \cdot mg^{-1} \cdot cm^{-1}$$
$$\varepsilon_{700\ nm} = 0.04\ mL \cdot mg^{-1} \cdot cm^{-1}$$

d-spacing:
GO = 0.75 nm

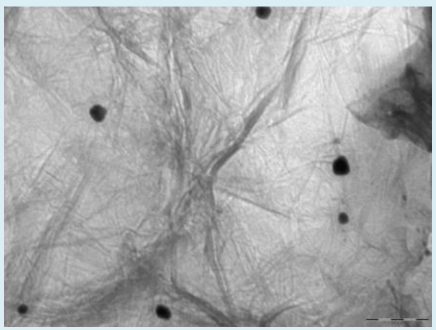
RGO = 0.36 nm
N-Gr = 0.35 nm

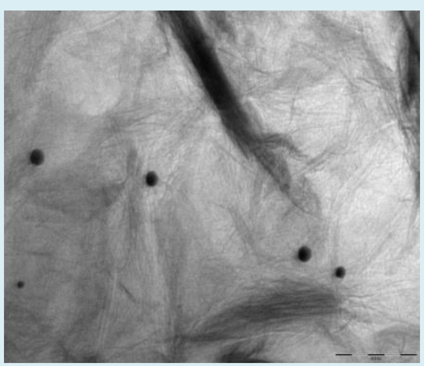


Graphene-metallic nanoparticles starting from graphite

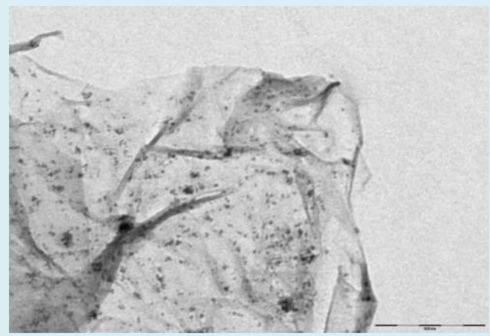


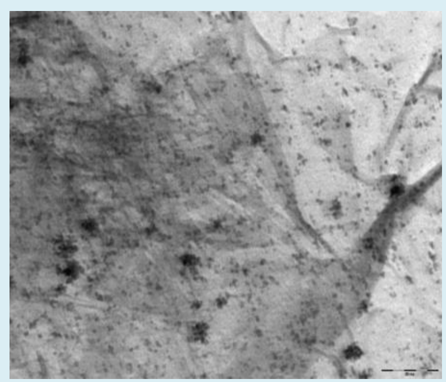
Graphene/AuNPs
(10 – 40 nm)



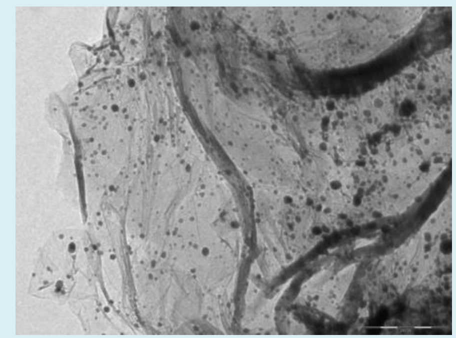


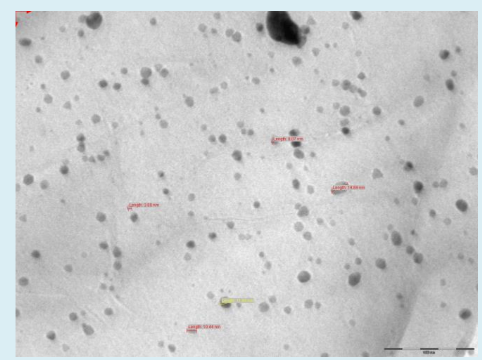
Graphene/PtNPs
(5 – 10 nm)





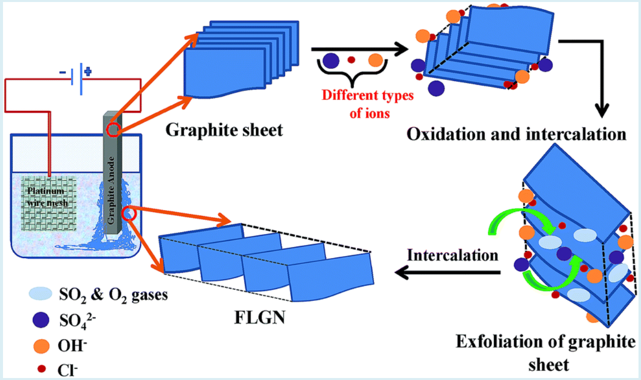
Graphene/Au-PdNPs
(5 – 20 nm)



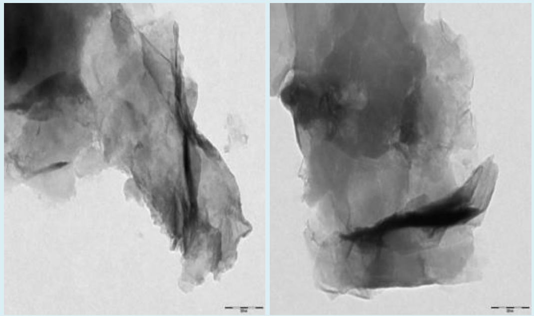


C. Electrochemical graphene/graphene-porphyrin synthesis *(top-down)*

- Electrochemical exfoliation of graphite- in acidic solution



- Electrolyte: mixture of strong acids (sulfuric : nitric)
- low voltage (2-3 V)
- few hours
- **wash, filtrate and dry**

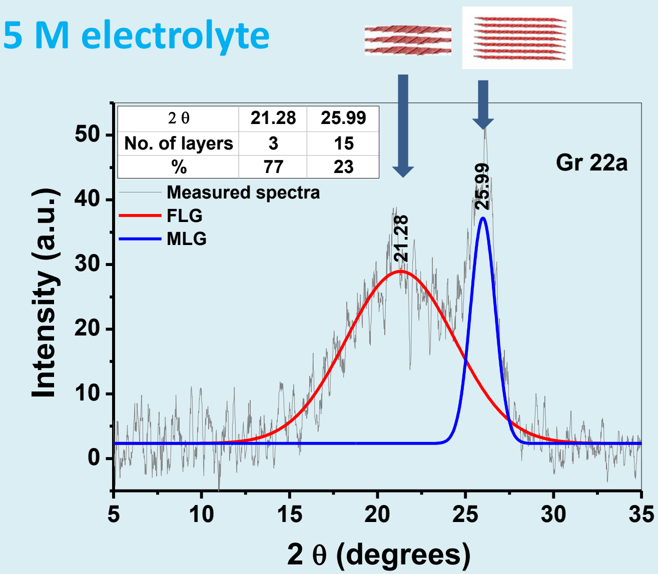


TEM images of graphene

XRD study

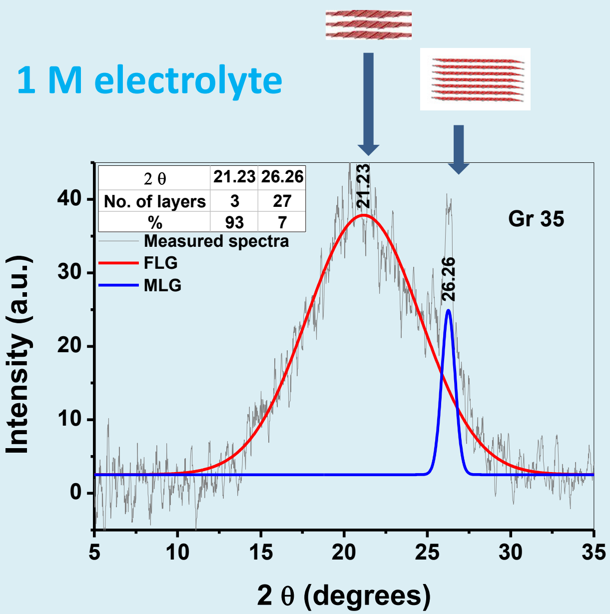
immediately after preparation: mixture of few-layer and multi-layer graphene

0.5 M electrolyte



XRD pattern of graphene

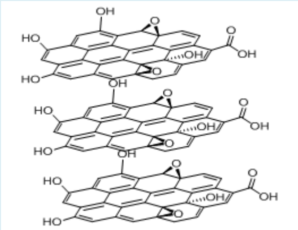
1 M electrolyte



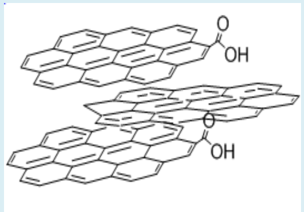
XRD pattern of graphene

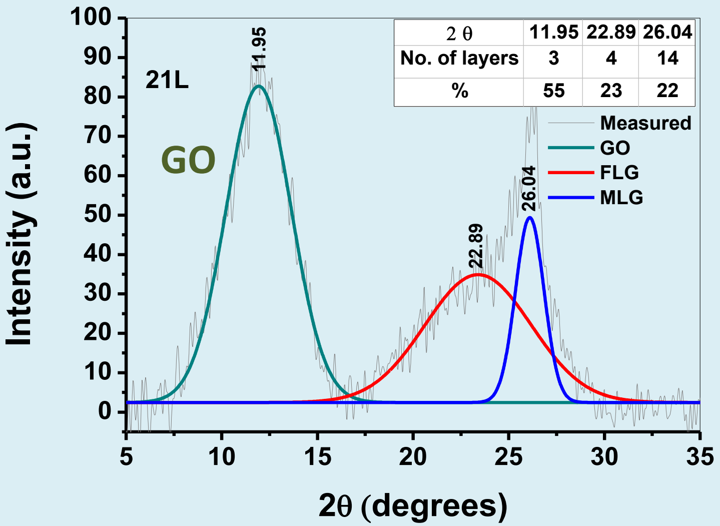
after few days: mixture of graphene oxide, few-layer and multi-layer graphene

GO

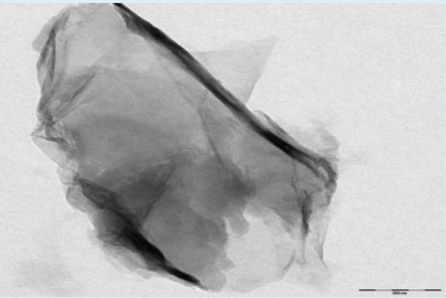


GR





XRD pattern of the mixt material



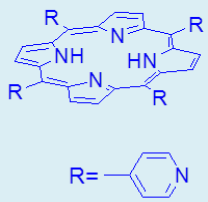
TEM image of the mixt material

d-spacing:

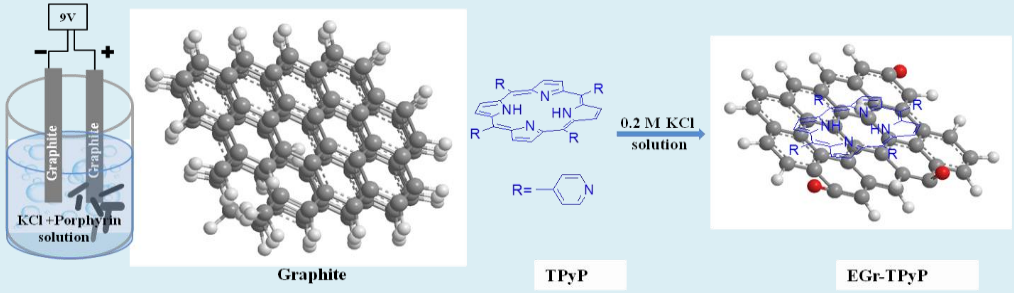
GO = 0.75 nm
(insulating; good biocompatibility with living systems)

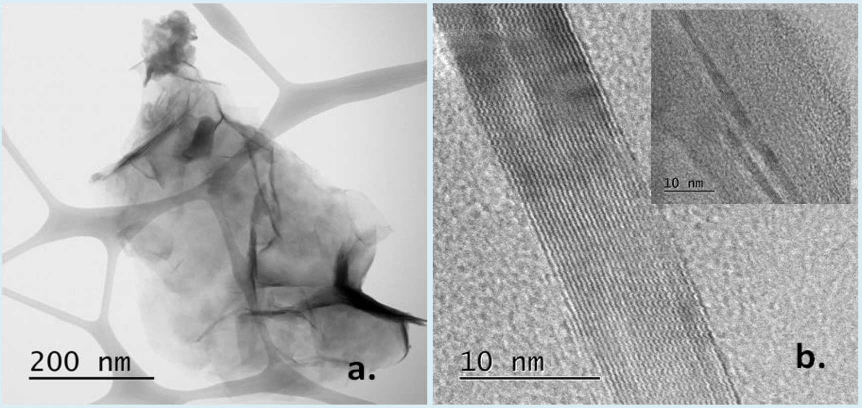
GR = 0.36 nm
(highly conductive; poor biocompatibility with living systems)

- Electrochemical exfoliation of graphite - in neutral solution

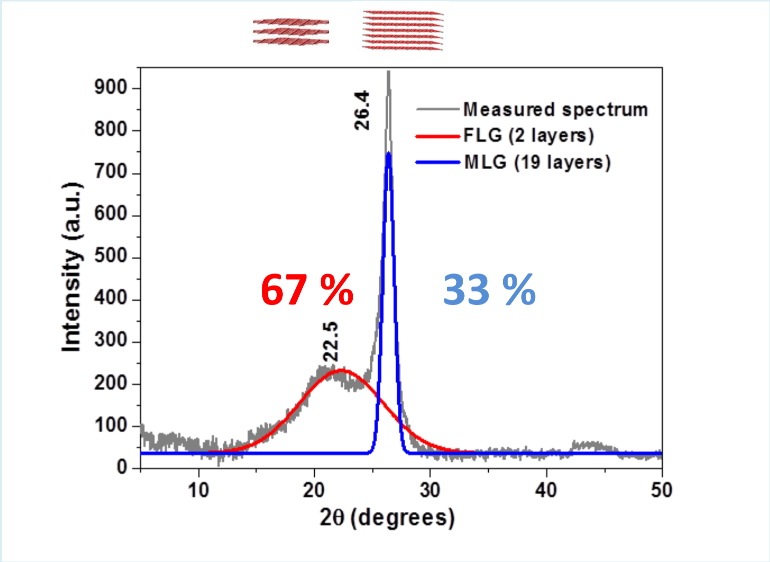


6 x 10^{-6} M TPyP in 0.2 M KCl
Bias: 9 V





TEM/AFM images of EGr-TPyP composite

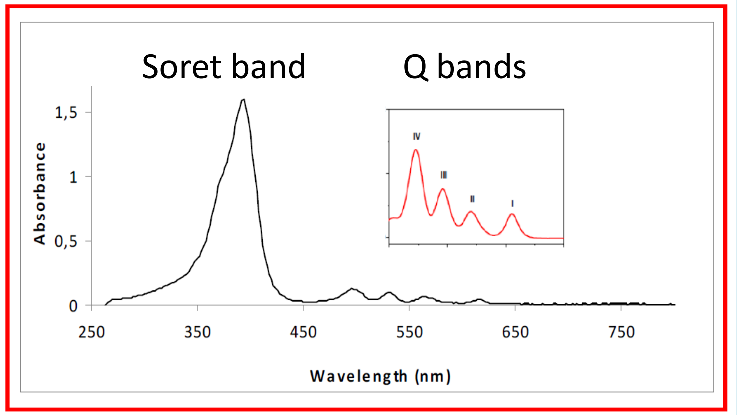


XRD pattern of EGr-TPyP composite

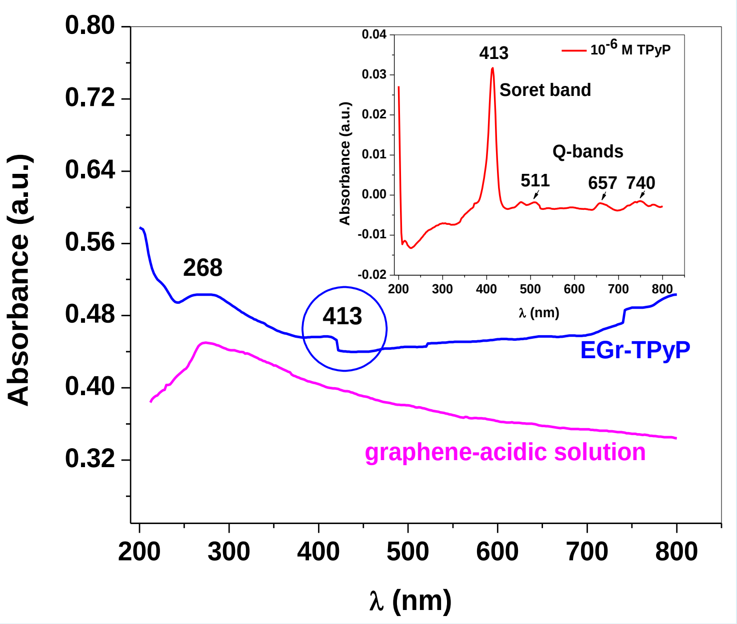
UV-Vis characterization

➢ Porphyrins display extreme intense bands, the **so-called Soret or B-bands** in the **380–500 nm range** with molar extinction coefficients of $10^5\ M^{-1}\ cm^{-1}$

➢ In the **500–750 nm range**, their spectra contain a set of weaker, but still considerably intense **Q bands** with molar extinction coefficients of $10^4\ M^{-1}\ cm^{-1}$

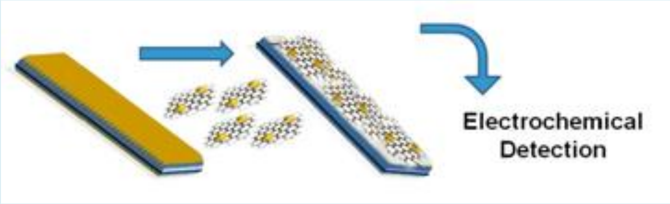


UV-Vis spectrum of porphyrin



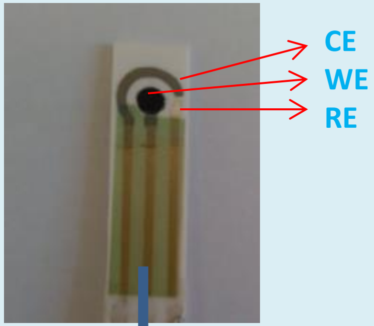
UV-Vis spectrum of EGr-TPyP composite

2. Electrochemical detection of catechol



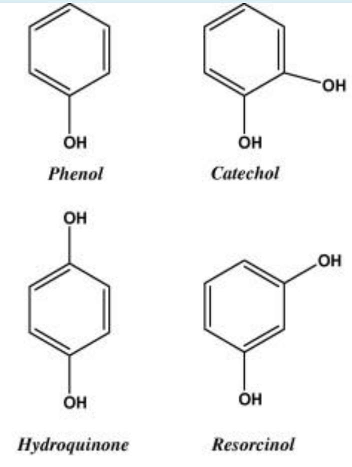
EGr-TPyP/GC

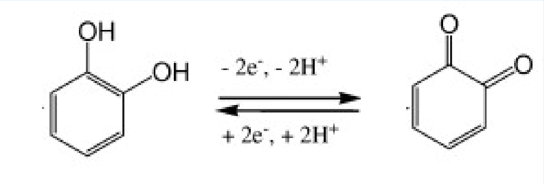
Screen-printed electrode



- ❑ **Increases the active surface area (50 - 100 %)**
- ❑ **Improves the transfer of electrons**

Phenols





- catechol undergoes reversible oxidation to quinone by a transfer of two electrons and two protons

- ➢ Phenolic compounds are a class of chemical compounds consisting of a hydroxyl functional group (–OH) attached to an aromatic ring

- ➢ Phenols can have two or more hydroxyl groups bonded to the aromatic ring(s) in the same molecule

- ➢ Phenol, catechol, and hydroquinone, are urinary end-products of the metabolism of benzene, nutrients, drugs, and endogenous substances.

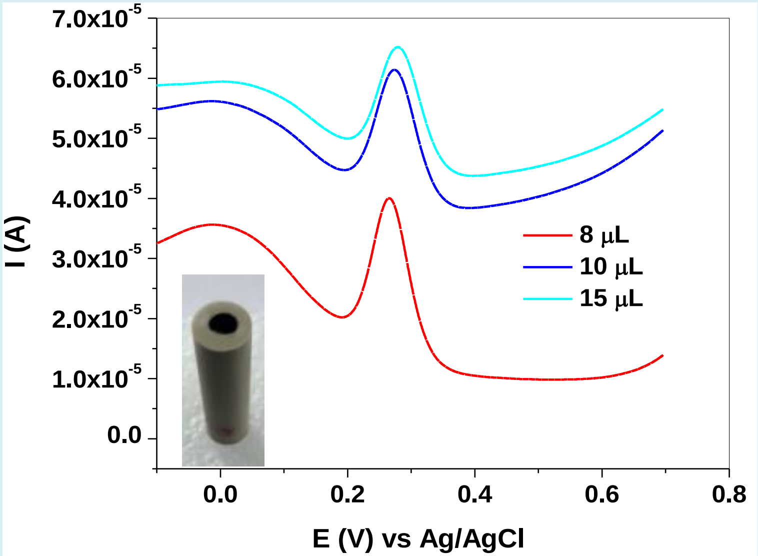
- ➢ Phenol, catechol, and hydroquinone may have a role in the carcinogenicity of benzene and in mechanisms that lead to leukemia.

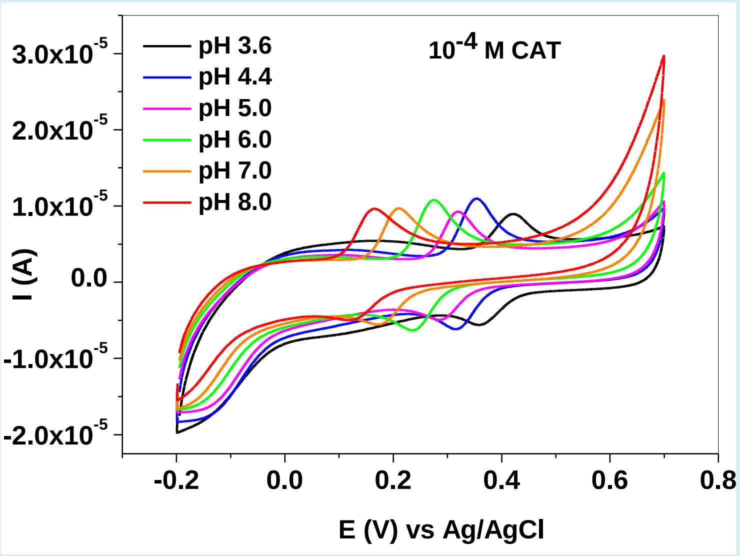
- CAT and HQ are widely used in industrial applications such as cosmetics, pesticides, flavoring agents, antioxidant, dyes and pharmaceutics
- They are highly toxic to both the environment and humans, even at very low concentrations.
- The high toxicity and low degradability has made CAT and HQ important contaminants, which are considered as environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU)
- Therefore, it is very important to develop simple and rapid analytical methods for the determination of CT and HQ.
- In this respect there is the need of rapid, low-cost, and possibly direct methods to quantify these phenolic metabolites.

According to Romanian regulations, CAT concentrations $< 4.5 \times 10^{-7}$ M are normal
Alert values: $> 10^{-5}$ M

Optimization of experimental conditions

graphene dispersion in DMF 1 mg/mL

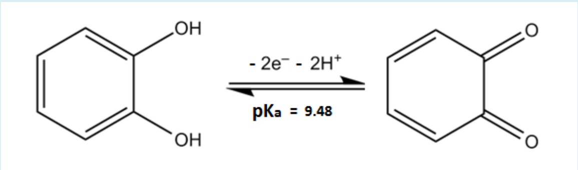




SWVs recorded with GC electrodes modified with various volumes of EGr-TPyP solution in pH 6 PBS solution containing 10^{-4} M catechol; scan rate 10 mVs^{-1}.

CVs recorded with EGr-TPyP/GC electrode in pH varying solutions (from 3.6 to 8); Optimum pH was selected to be pH 6

$I_{cap} = C \times dV/dt$ - 3×10^{-5} - 6×10^{-5} A



Glassy carbon vs EGr-TPyP/Glassy carbon

quasi-reversible redox process

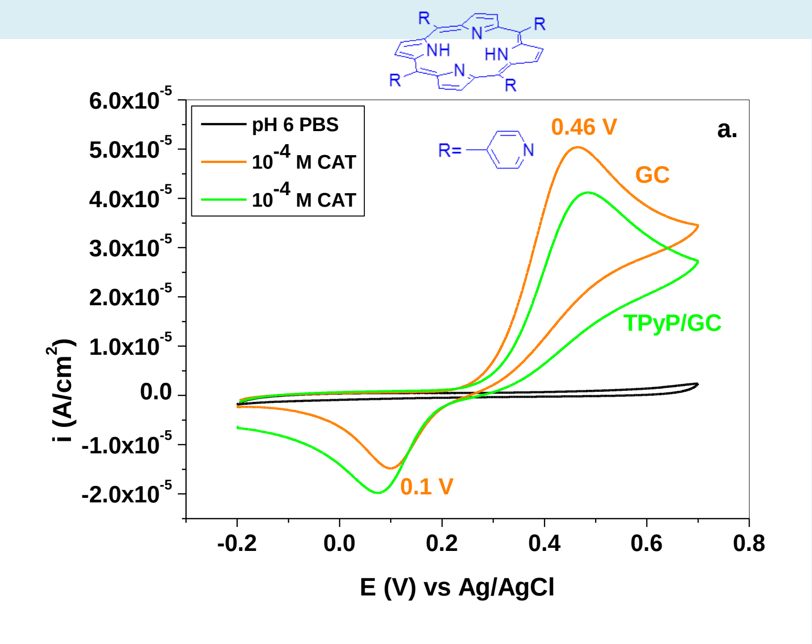
ΔE_{peak} = 380 mV (>> 60 mV)

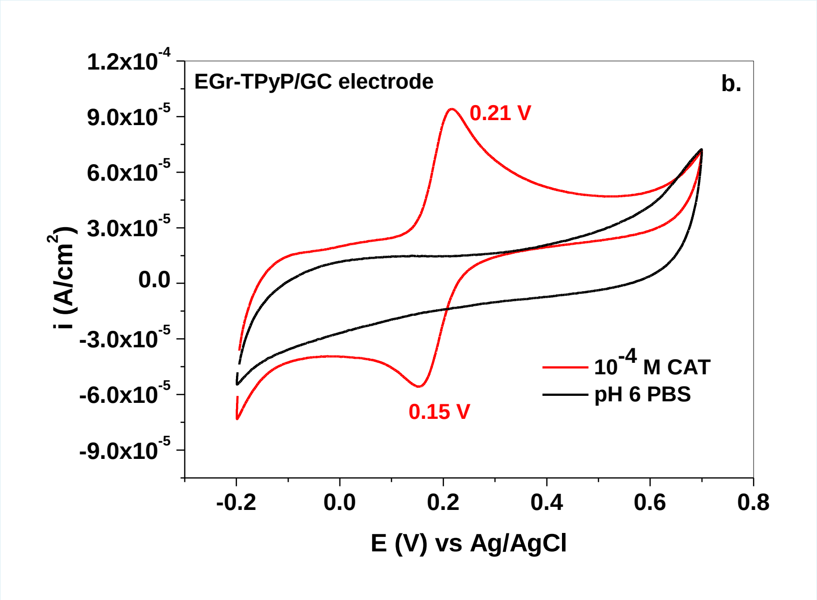
$I_{pa} >> I_{pc}$

reversible redox process

ΔE_{peak} = 60 mV

$I_{pa} = I_{pc}$

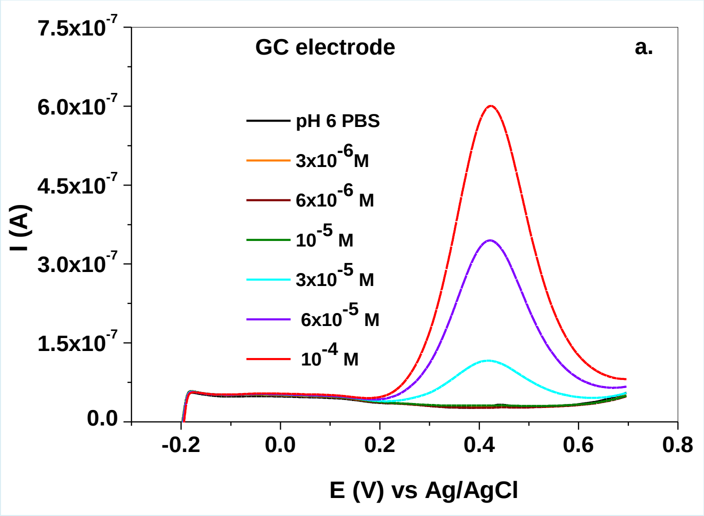




Active area (GC) = 0.028 cm^2

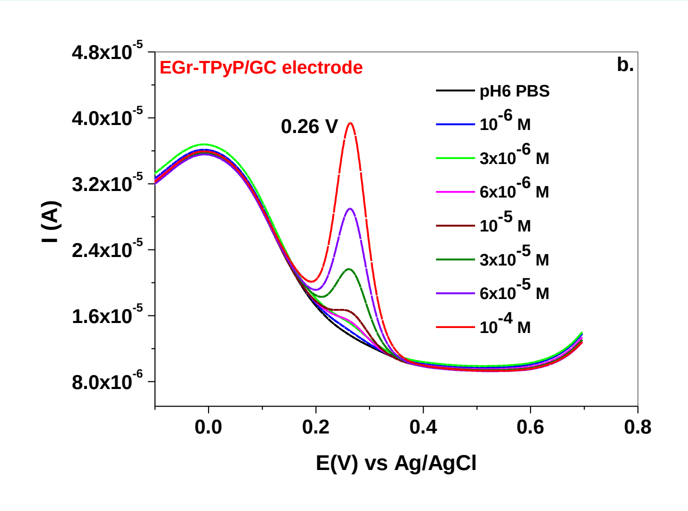
Active area (EGr-TPyP/GC) = 0.081 cm^2

GC electrode

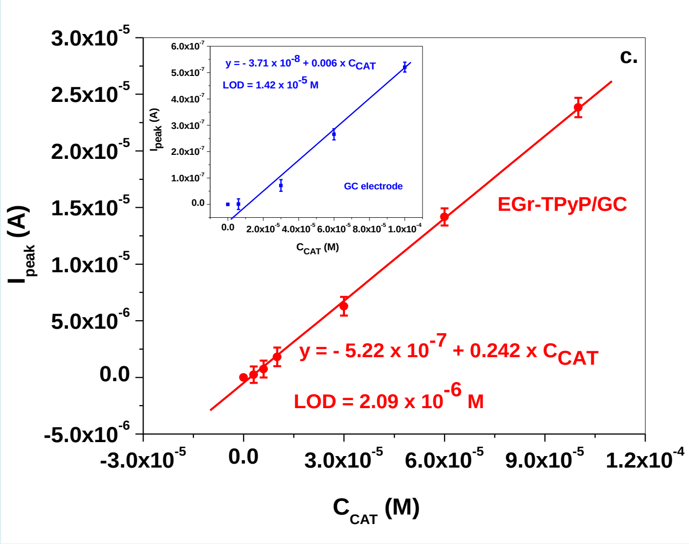


SWV recorded in the presence of CAT

EGR-TPyP/GC electrode



SWV recorded in the presence of CAT



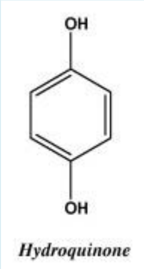
GC electrode

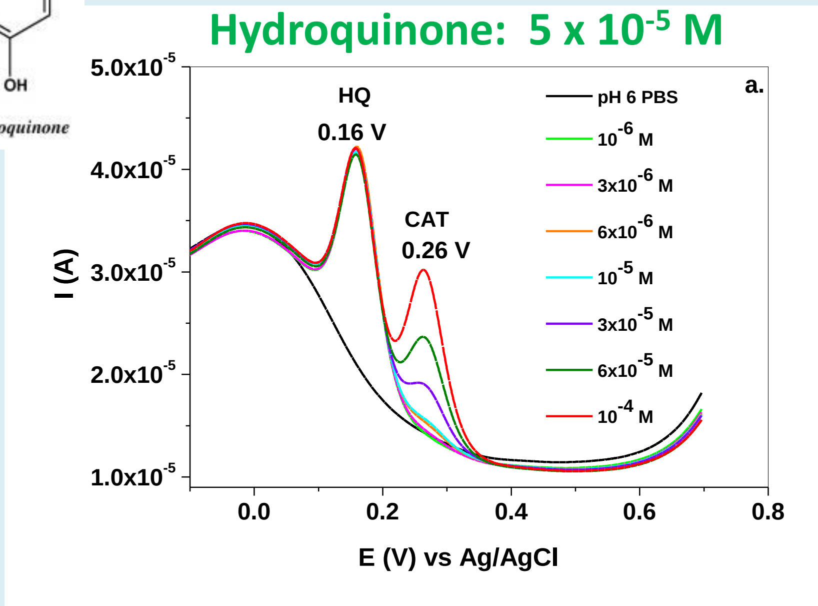
Linear range: 10^{-5} - 10^{-4} M
Sensitivity: 6 mA/M
LOD = 1.42×10^{-5} M

EGR-TPyP/GC electrode

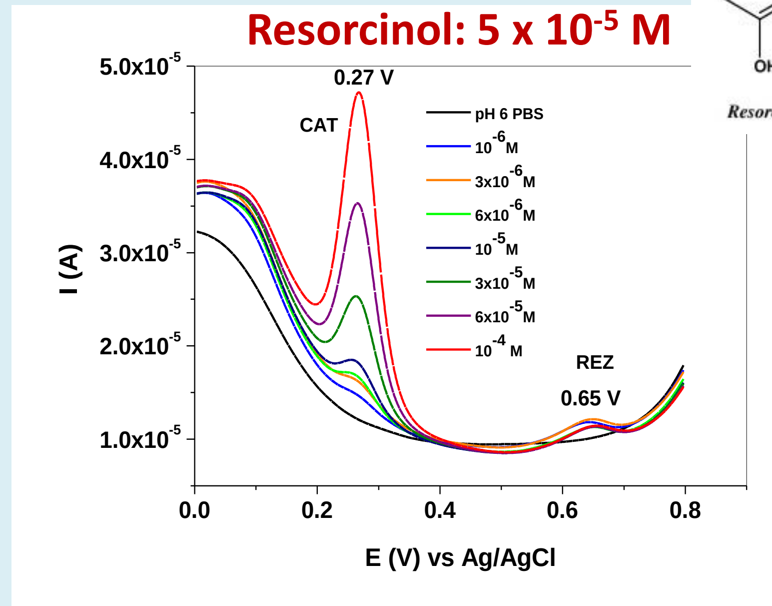
Linear range: 10^{-6} - 10^{-4} M
Sensitivity: 242 mA/M
LOD = 2.09×10^{-6} M

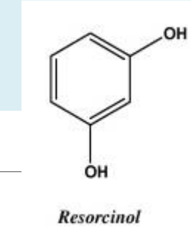
EGR-TPyP/GC electrode





SWV recorded in the presence of HQ and CAT





SWV recorded in the presence of REZ and CAT

- ➢ The reactivity of the aromatic ring activated with an OH group > when the OH group is in the ***ortho or para positions*** (the highest electron density is located on both ***ortho and para*** positions).
- ➢ Hydroquinone and catechol have the aromatic ring activated, while the resorcinol ring is not activated.

Interfering species

Hydroquinone: 5 x 10^{-5} M

Linear range: 10^{-6} - 10^{-4} M

Sensitivity: 110 mA/M

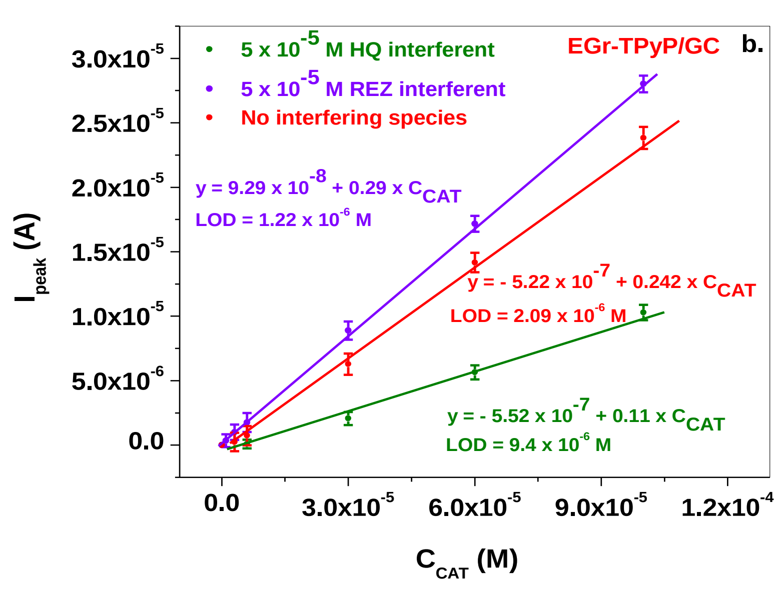
LOD = 9.4 x 10^{-6} M

Resorcinol: 5 x 10^{-5} M

Linear range: 10^{-6} - 10^{-4} M

Sensitivity: 290 mA/M

LOD = 1.22 x 10^{-6} M



No Interfering species

Linear range: 10^{-6} - 10^{-4} M

Sensitivity: 242 mA/M

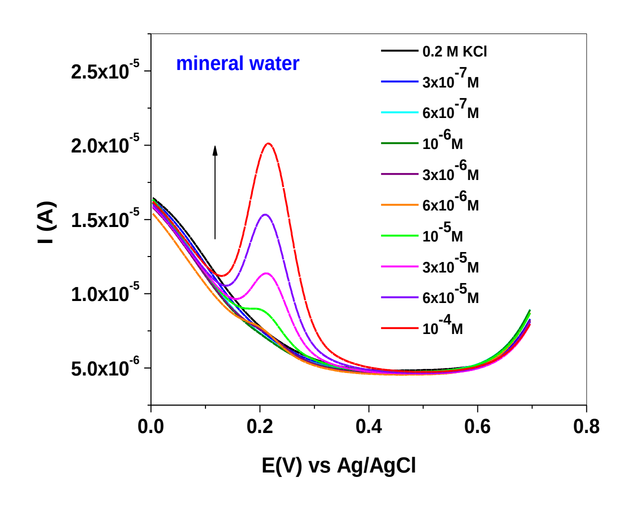
LOD = 2.09 x 10^{-6} M

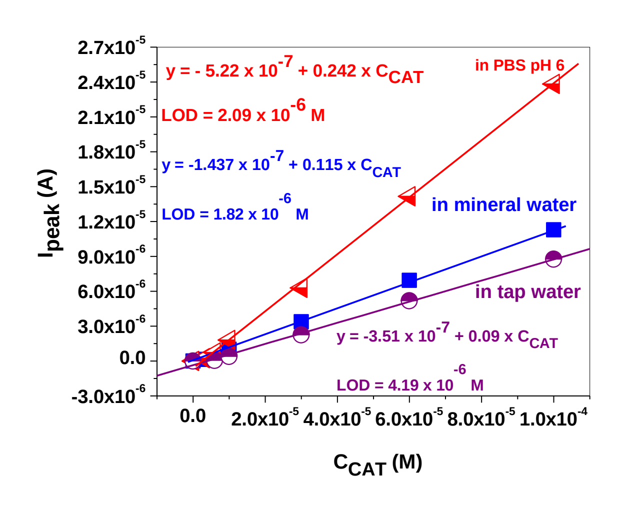
Analysis of CAT in a relevant environment

two drinking water sources:

- tap water (the pH was adjusted to pH 6)
- commercial mineral water (pH 5.9) containing known quantities (mg/L) of interfering species:

23.59 Na^+; 4.75 K^+; 60.14 Mg^{2+}; 191.2 Ca^{2+}; 11.12 Cl^-; 13.57 SO_4^{2-}.





No interfering species

Linear range: 10^{-6} - 10^{-4} M

Sensitivity: 242 mA/M

LOD = 2.09×10^{-6} M

In mineral water:

Linear range: 6×10^{-6} - 10^{-4} M

Sensitivity: 115 mA/M

LOD = 1.82×10^{-6} M

In tap water:

Linear range: 6×10^{-6} - 10^{-4} M

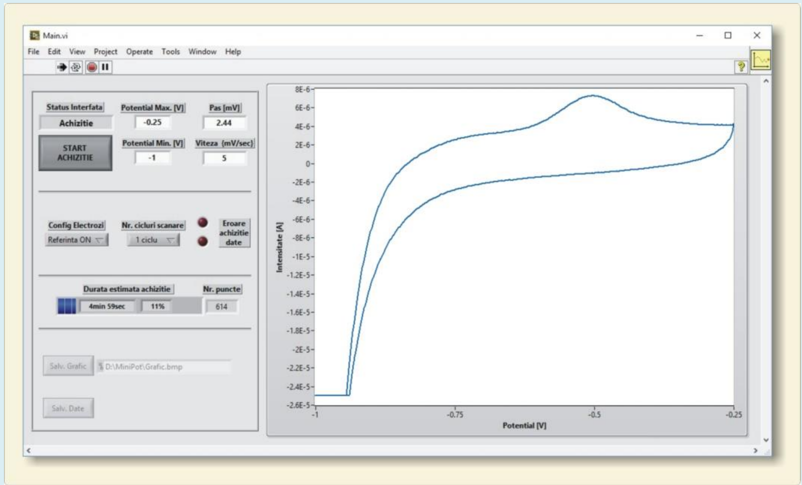
Sensitivity: 90 mA/M

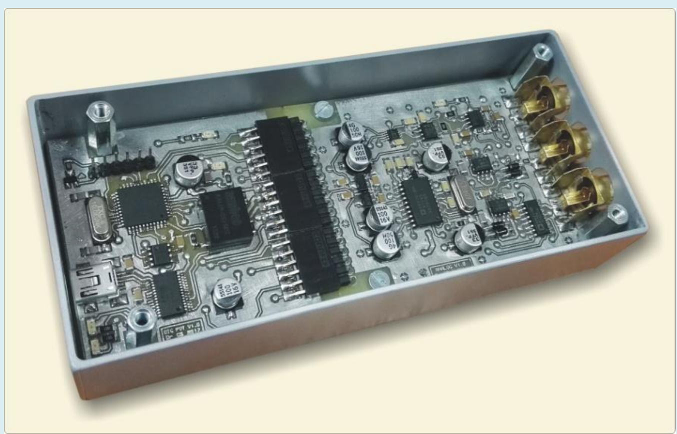
LOD = 4.19×10^{-6} M

Table 2. Determination of catechol in mineral and tap water

EGr-TPyP/GC	Added (M)	Found (M)	Recovery %	RSD (%)
Mineral water	10^{-5}	0.95×10^{-5}	**95**	7.21
	3×10^{-5}	3.3×10^{-5}	**110**	7.22
	10^{-4}	1.04×10^{-4}	104	3.15
Tap water	10^{-5}	0.97×10^{-5}	**97**	4.49
	3×10^{-5}	2.96×10^{-5}	98	5.07
	10^{-4}	1.03×10^{-4}	**103**	6.48

Sensor device is under construction…





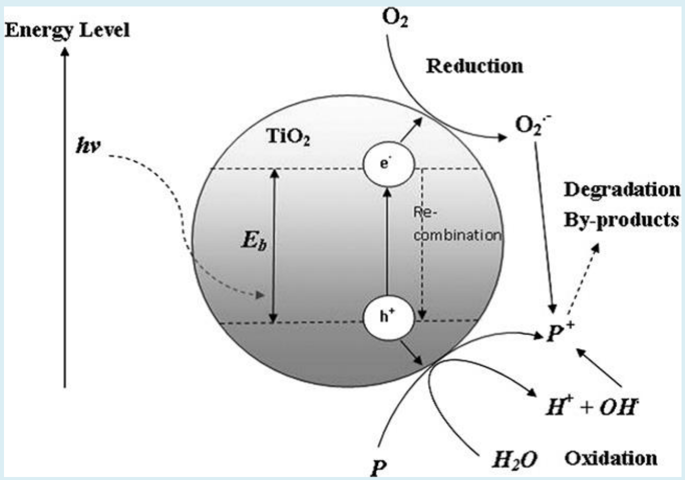
For detection of:

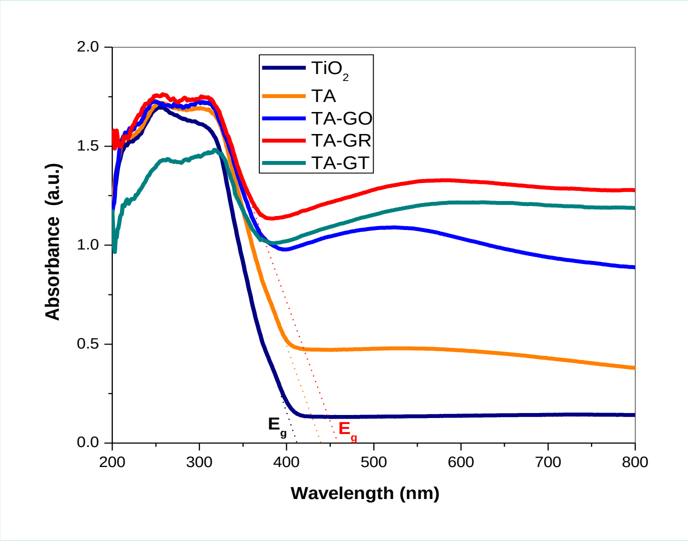
- heavy metal ions (Pb2+)
- phenols (catechol, hydroqinone)
- neurotransmitters (dopamine)

3. Photodegradation of pollutants with graphene-TiO2 based materials

Graphene-TiO_2/Ag composites

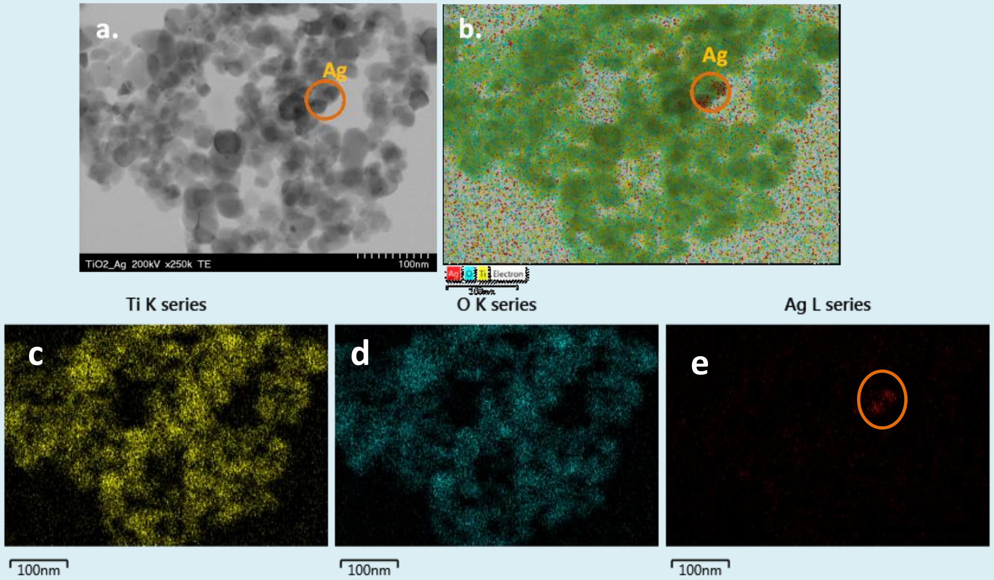
TiO_2	3.26 eV – wide band-gap semiconductor
TA- TiO_2/Ag	3.09 eV
TA- GO	3.06 eV
TA- GR	3.04 eV
TA - GT	3.05 eV



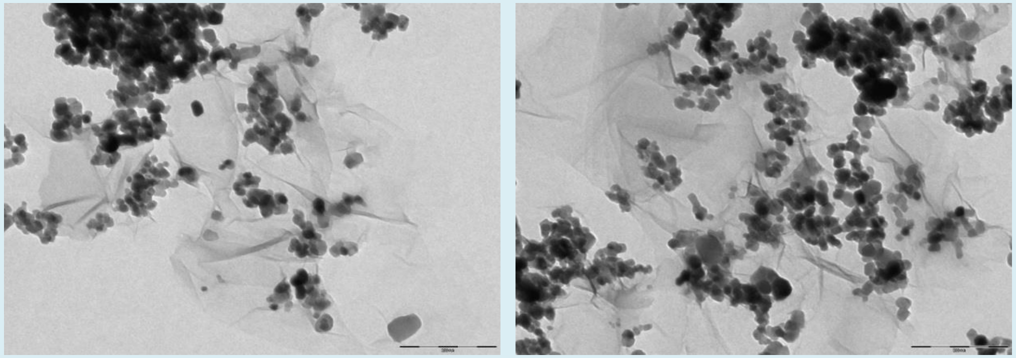


UV-Vis spectra of graphene-TiO2 based materials

Shift of the absorption edge towards visible range



TEM/EDS mapping of TiO_2/Ag



TEM images of graphene-TiO_2/Ag

NANOGENTOOLS Autumn School
October 2017

Amaranth

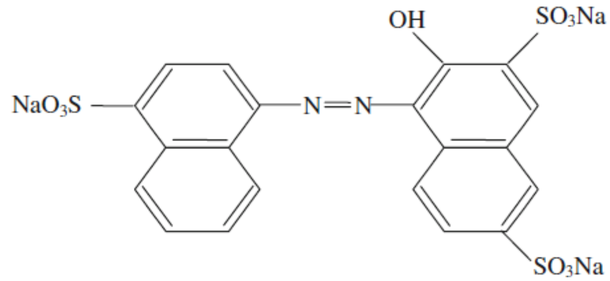
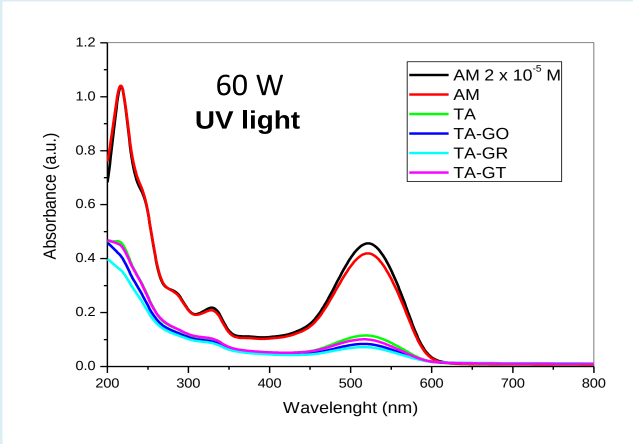


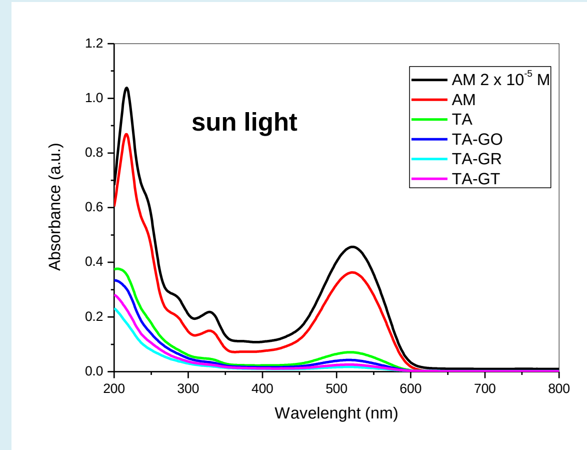
Fig. 1 Structure of amaranth

- Is a purple azo dye used to color: food, cosmetics, paper, wood, leather
- Coloring agent for jam, jellies (**E123- food additive**)
- In USA it is legally prohibited (since 1976)

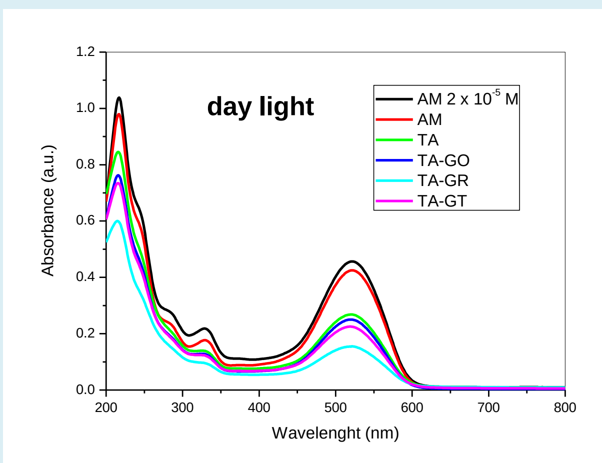
- In Romania is legally used (since 2002)
- Prolonged intake can result in tumors and allergy

UV-Vis investigation





4 mg of photo-catalysts (TA, TA-GO, TA-GR and TA-GT) - in 20 ml of amaranth solution (2 x 10^{-5} M)



After two hours

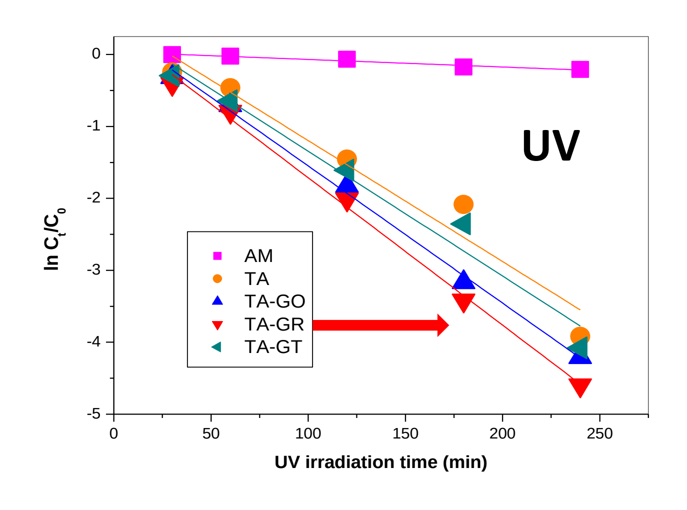
Reaction kinetics

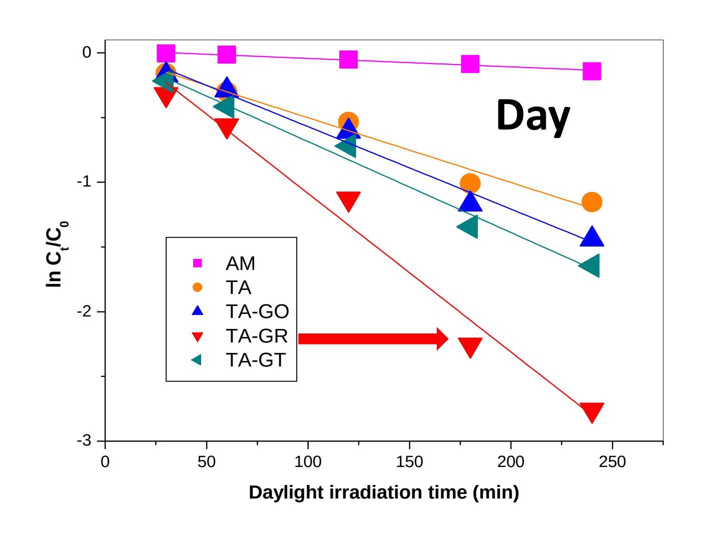
First order reaction- the rate *depends linearly* on the concentration of only one reactant (*a unimolecular reaction*)

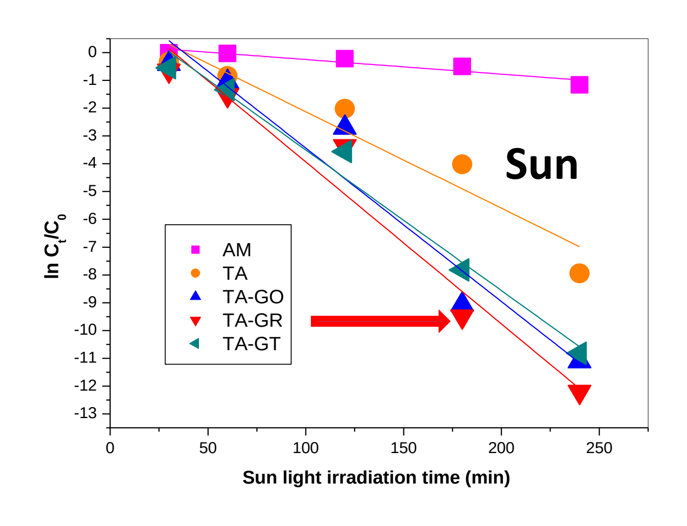
$$Rate = -\frac{dC}{dt} = kC$$

the reaction rate;
k is the first order rate constant

or $$ln\frac{C}{C_o} = -kt$$







first order rate constant

Samples	UV k (min^{-1})	Sun k (min^{-1})	Day k (min^{-1})
AM	**0.0010**	**0.0052**	**0.0006**
TA	**0.0168**	**0.0347**	**0.0050**
TA-GO	**0.0191**	**0.0552**	**0.0063**
TA-GR	**0.0204**	**0.0583**	**0.0122**
TA-GT	**0.0173**	**0.0505**	**0.0070**

HPLC analysis

	Sun light		
	30 min	**2 h**	**4 h**
TA	**77%**	**12.8%**	**0.04%**
TA-GO	**69**	**7.3**	**0**
TA-GR	**55**	**2**	**0**
TA-GT	**59.2**	**3.2**	**0**

Conclusions

- Novel method for graphene/graphene-porphyrin synthesis – **electrochemical exfoliation of graphite**

- Substrates modified with graphene-TPyP- **highly sensitive to the electrochemical detection of catechol – but NOT selective**

- Additional work - **to eliminate the influence of interfering species**

- Graphene-TiO_2 nanoparticles composite – **excellent material for pollutants degradation**

Funding Projects

Partnership-230/2014
TE- 5/2015
PED 101/2017
PED 102/2017
PED 103/2017
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Thank-you