



COMMON SENSE

MARINE SENSORS - MARINE MONITORING

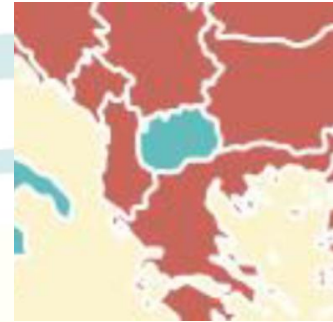
pH and pCO₂ NANOSENSOR

Partner FTM-UCIM

FINAL DISSEMINATION EVENT

BARCELONA, 26 – JANUARY - 2017



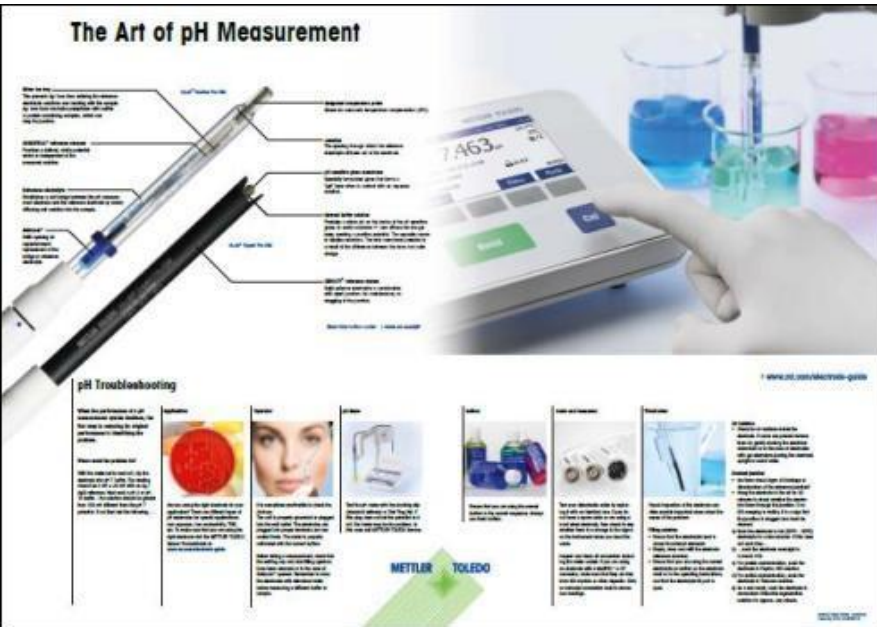


- Speaker: Prof. Anita Grozdanov,
Faculty of Technology and Metallurgy,
University Ss Cyril and Methodius in Skopje
- Expertise Area: Polymer Nanocomposites
and Nanosensors
- Why CS ?
- CS research task contribute to the improvement
of my skills for Design and Development of
Nanosensors based on Polymer Nanocomposites
To make wider the network of
coworkers.

Role on CS: *Coordinator of the
Macedonian research team*



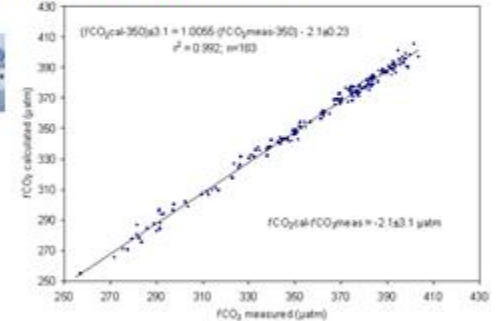
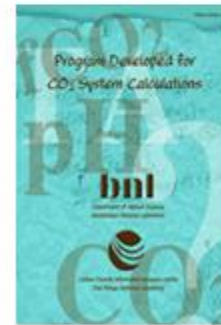
- State of the art at initial stage



pCO₂ detection

Indirect measurement - 1

ORNL/CDIAC-105 - Program Developed for CO₂ System Calculations



Relationship between fCO₂ measured and fCO₂ calculated from TALK and pH

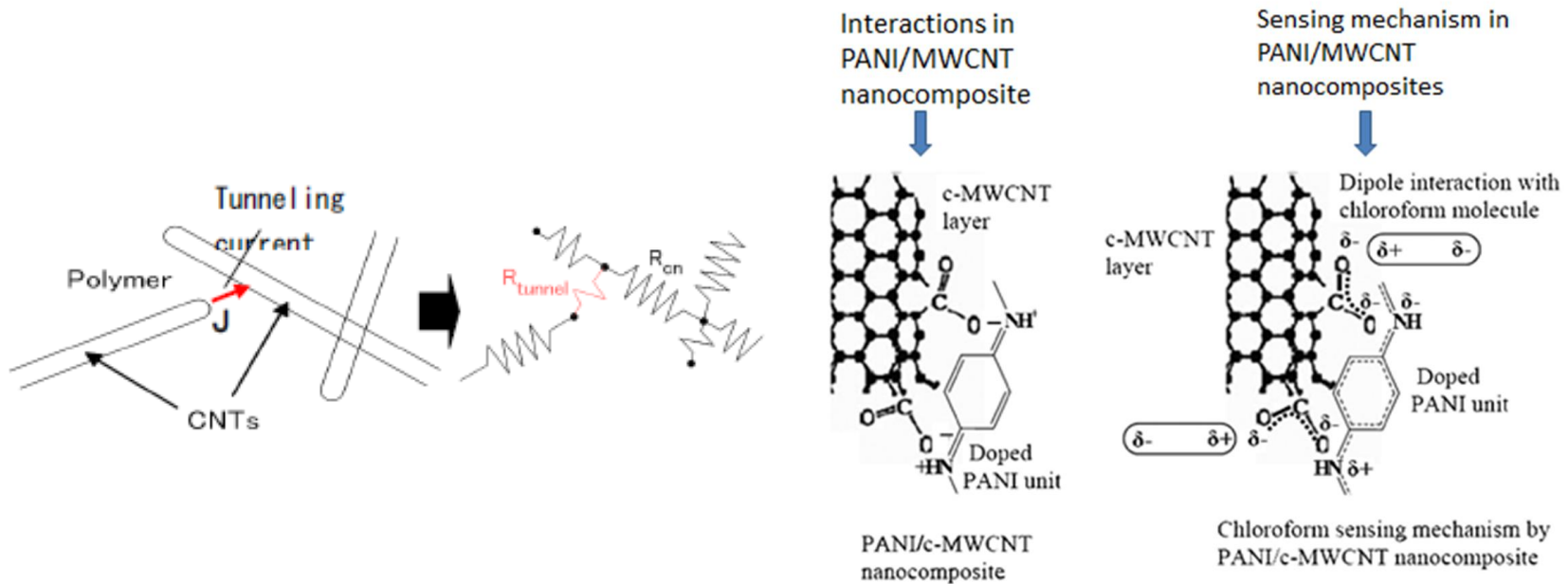
<http://cdiac.ornl.gov/oceans/co2rprt.html>

- Needs identification!
- Low cost sensor
- 3 S nanosensor
- (Sensitivity, Stability, Selectivity)



This project has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No 614155.

“3 S nanosensor (Sensitivity, Stability, Selectivity) “



- Using the synergy effect of conductive polymer matrix – Polyaniline and conductive filler – CNT & G, resistivity and sensitivity should be increased and improved.

Plan implementation



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- Based on **electronic** properties of carbon nanotubes are:
 - **metallic** or
 - **semiconducting** → f (diameter, chirality of graphitic rings)
- The unique properties of carbon nanotubes have led to their use as:
 - sensors,
 - actuators,
 - field-emitting flat panel displays,
 - energy, and gas storages.
- **Greater adsorptive capacity**
due to larger surface-area-to-volume ratio → high sensitivity
- CNT-based sensors detect:
 - the nature of gases
 - their concentrations

CNT surface area ~1587 m²/g

“based on change in electrical properties induced by charge transfer with the gas molecules (e.g., O₂, H₂, CO₂) or in mass due to physical adsorption”



- Plan implementation

Technical contribution



Experiment	Percent of nanostructure	Film or electrolyte	Time
KG-1 P	1	Film	40
KG-2 P	1	E	40
KG-3 P	2	Film	40
KG-4 P	2	E	40
KG-5 P	3	Film	40
KG-6 P	3	E	40
KG-7 P	1	Film	60
KG-8 P	1	E	60
KG-9 P	2	Film	60
KG-10 P	2	E	60
KG-11 P	3	Film	60
KG-12 P	3	E	60

<http://graphene.mk>

Experiment	Percent of nanostructure	Film or electrolyte	Time
KC-1 P	1	Film	40
KC-2 P	1	E	40
KC-3 P	2	Film	40
KC-4 P	2	E	40
KC-5 P	3	Film	40
KC-6 P	3	E	40
KC-7 P	1	Film	60
KC-8 P	1	E	60
KC-9 P	2	Film	60
KC-10 P	2	E	60
KC-11 P	3	Film	60
KC-12 P	3	E	60



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FTM-UKIM Task: **NanoSensors for autonomous pH & pCO₂**

measurements

For pH sensor, nano-composite film, based on Polyaniline, Graphene (G) and multi-walled carbon nanotubes (MWCNTs) was developed using two types of deposition:

- G & MWCNT Deposited on Electrode (Film)
- G & MWCNT Dispersed in Electrolyte

Phase 1: Preparation and characterization of nanocomposite films

NC Systems:
pH: PANI/G
pCO₂: PANI/MWCNT/PVDF/G



Phase 2: Preparation of Screen Printed Electrode

NC sensor as a tablet



Phase 3: Field Testing

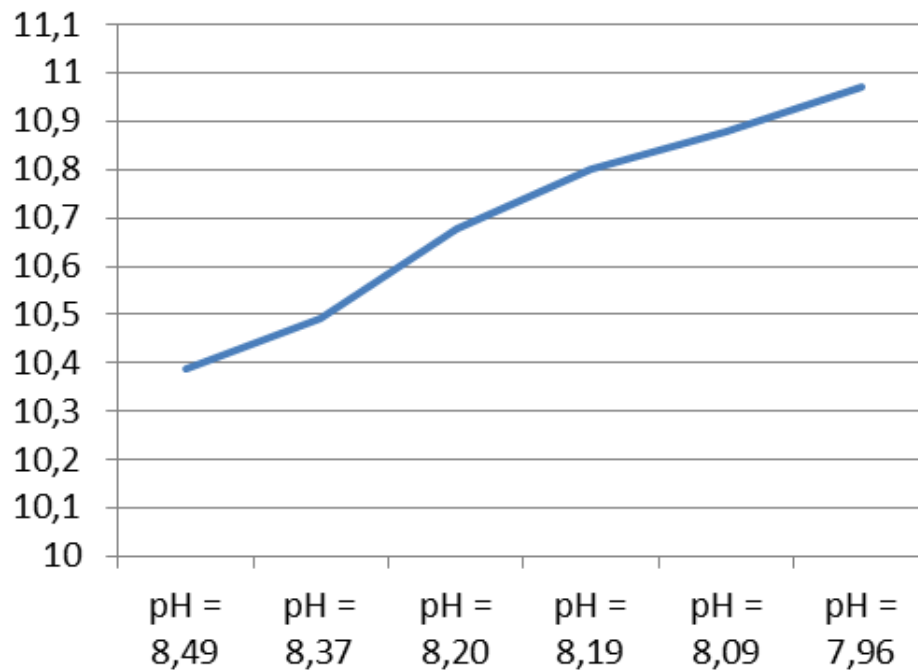


This project is
Programme 8
under grant agreement

Table 3. Validation test of SPE-MWCNT nanosensors in simulated sea water (changing pH ; controlling pH and R)

Sample: 3wt% MWCNT/PANI	T=20,3°C		R [MΩ]		
	1 min	2 min	4 min	5 min	8,5 min stabilized
pH = 8,49	8,49	9,53	10,32	10,380	10,386
pH = 8,37	8,28	9,32	10,49	10,494	10,494
pH = 8,20	10,4				
pH = 8,19	10,6				
pH = 8,09	10,6				
pH = 7,96	10,6				

8,5 min stabilized



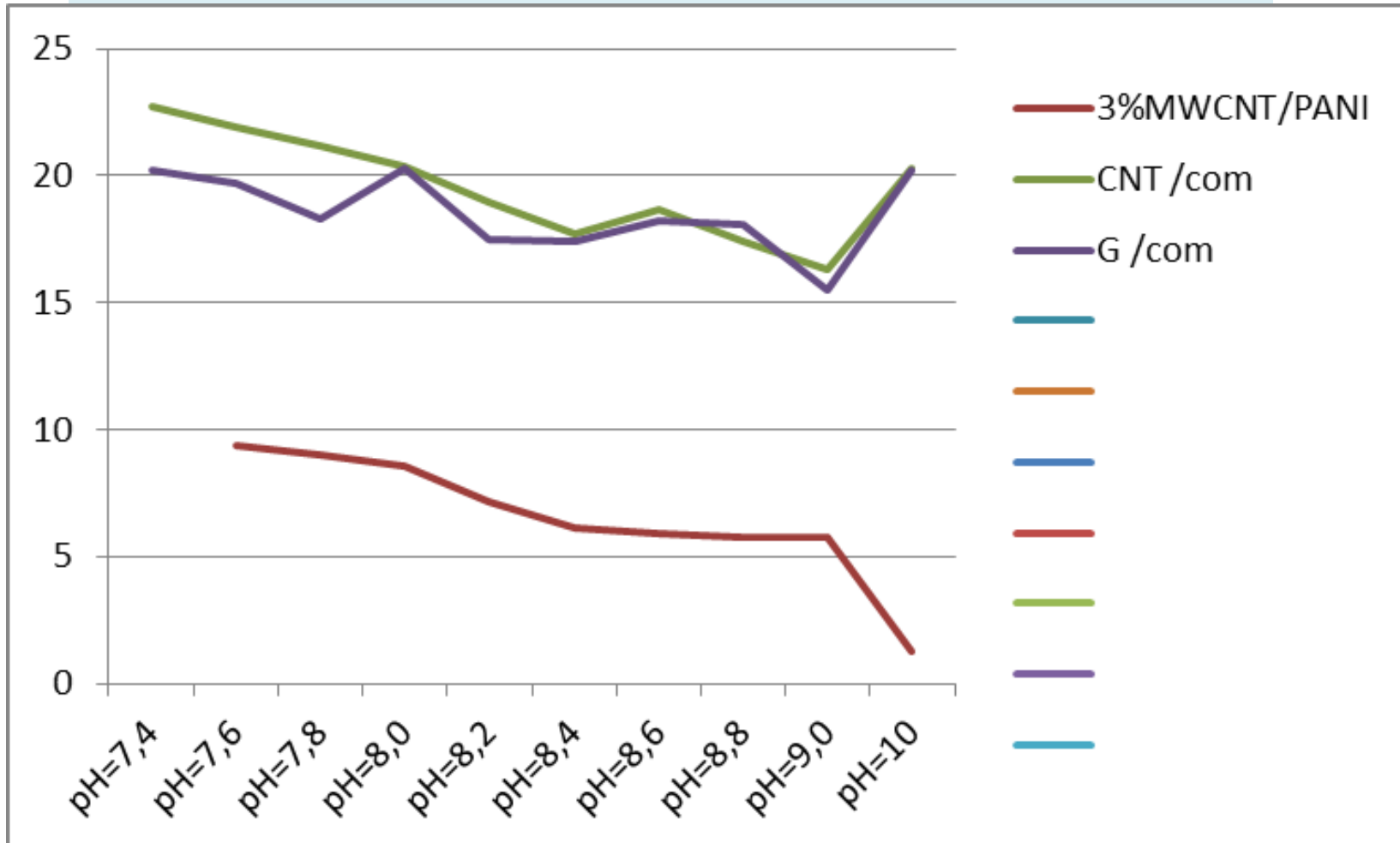
— 8,5 min stabilized



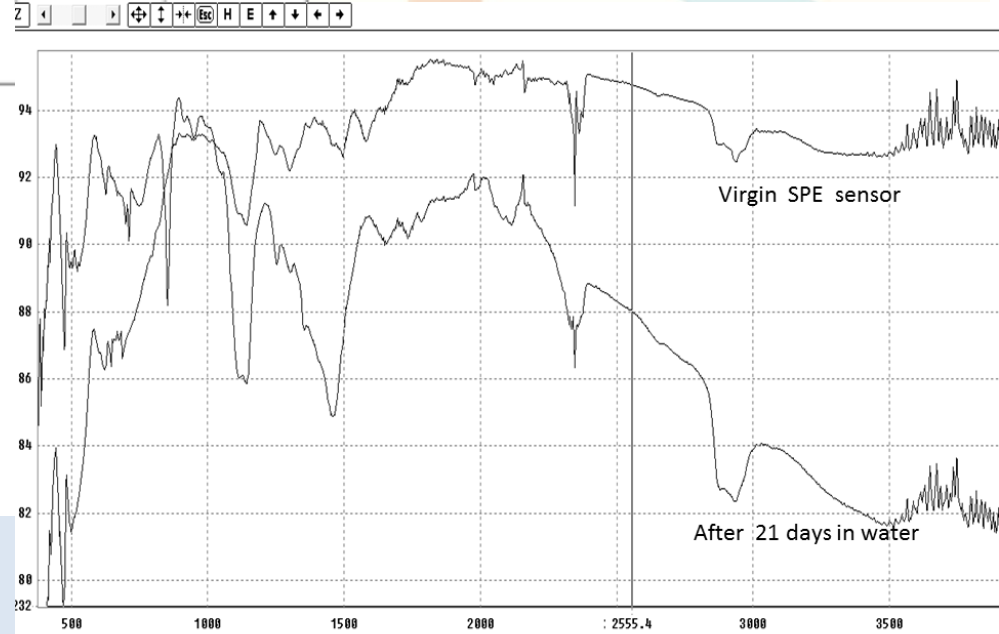
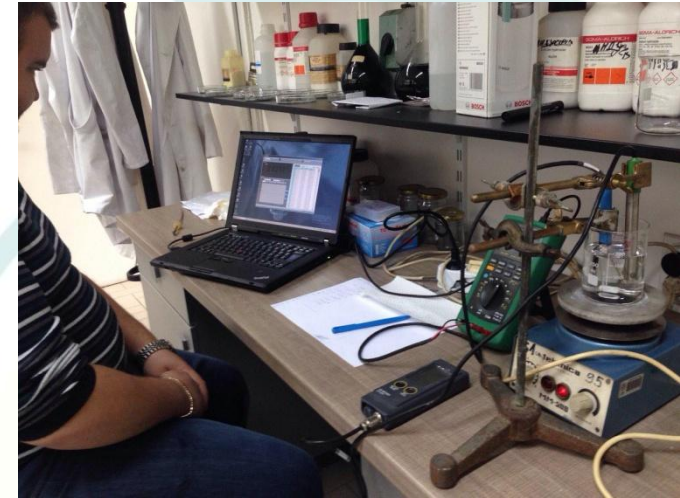
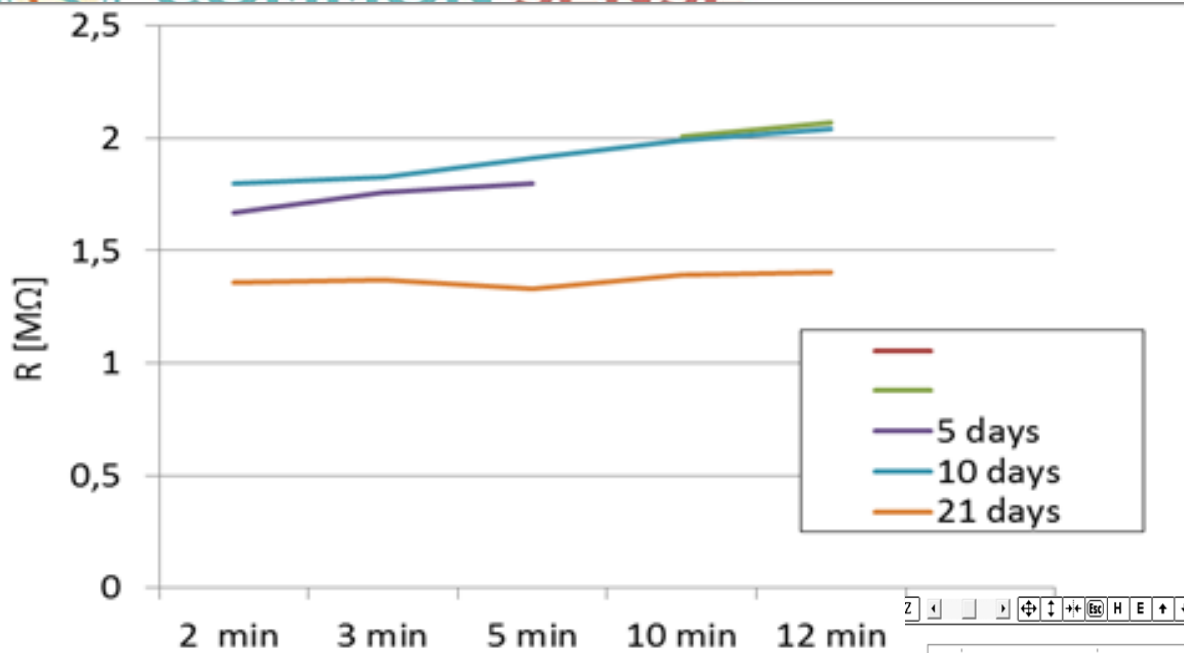


Electrical conductivity after treatment of the SPE-G and SPE-MWCNT nanosensors at pH range : 7,4 to 9,0 (~ pH of the sea water)

RESULTS



Achieved results vs Initial



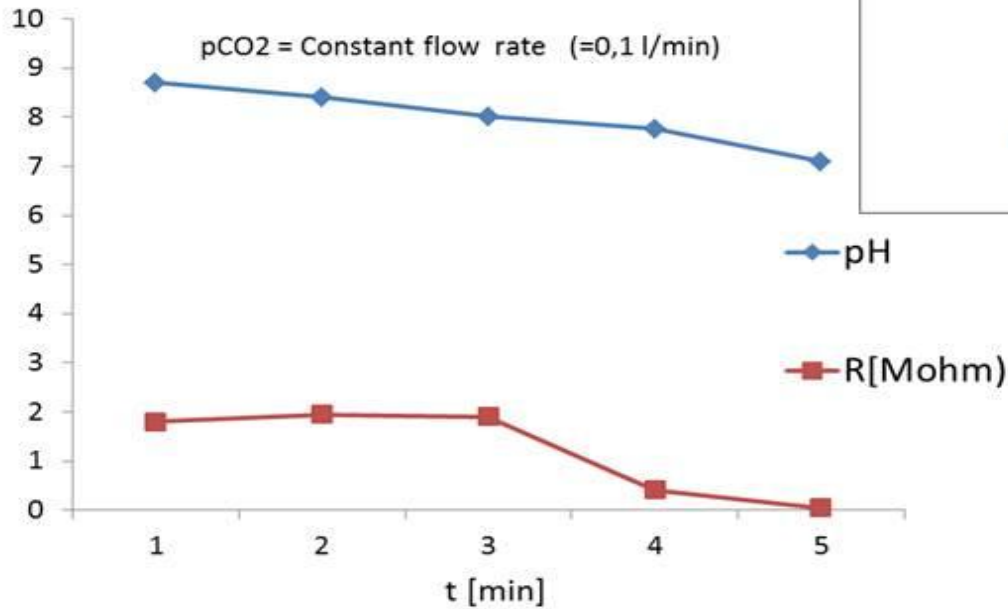
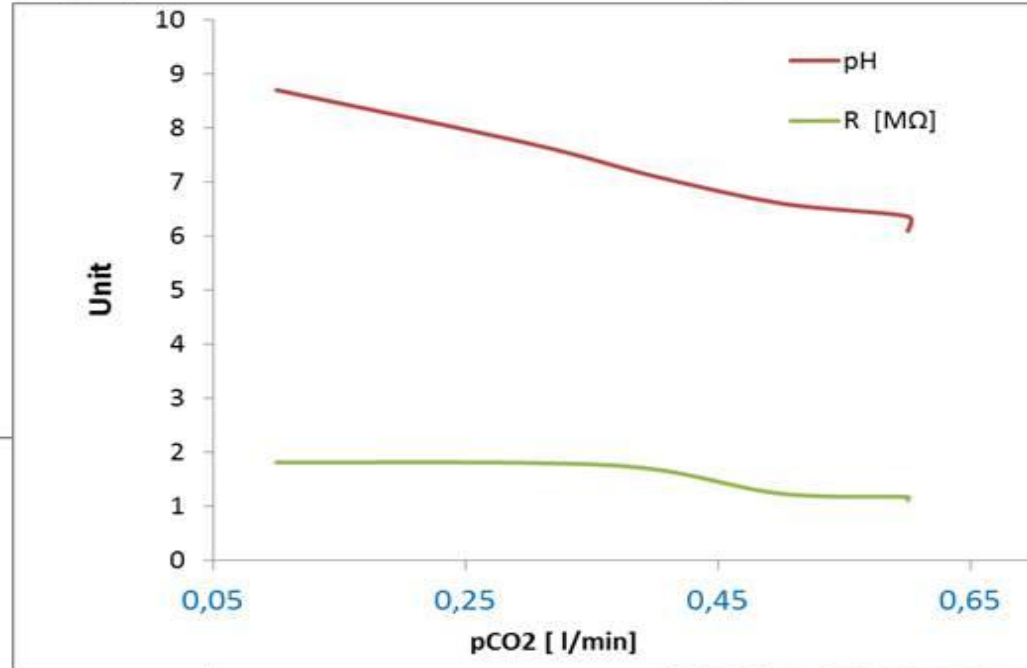
Stability of SPE-MWCNT nanosensors in sea water at pH = 8,4 (Lucrino, It)



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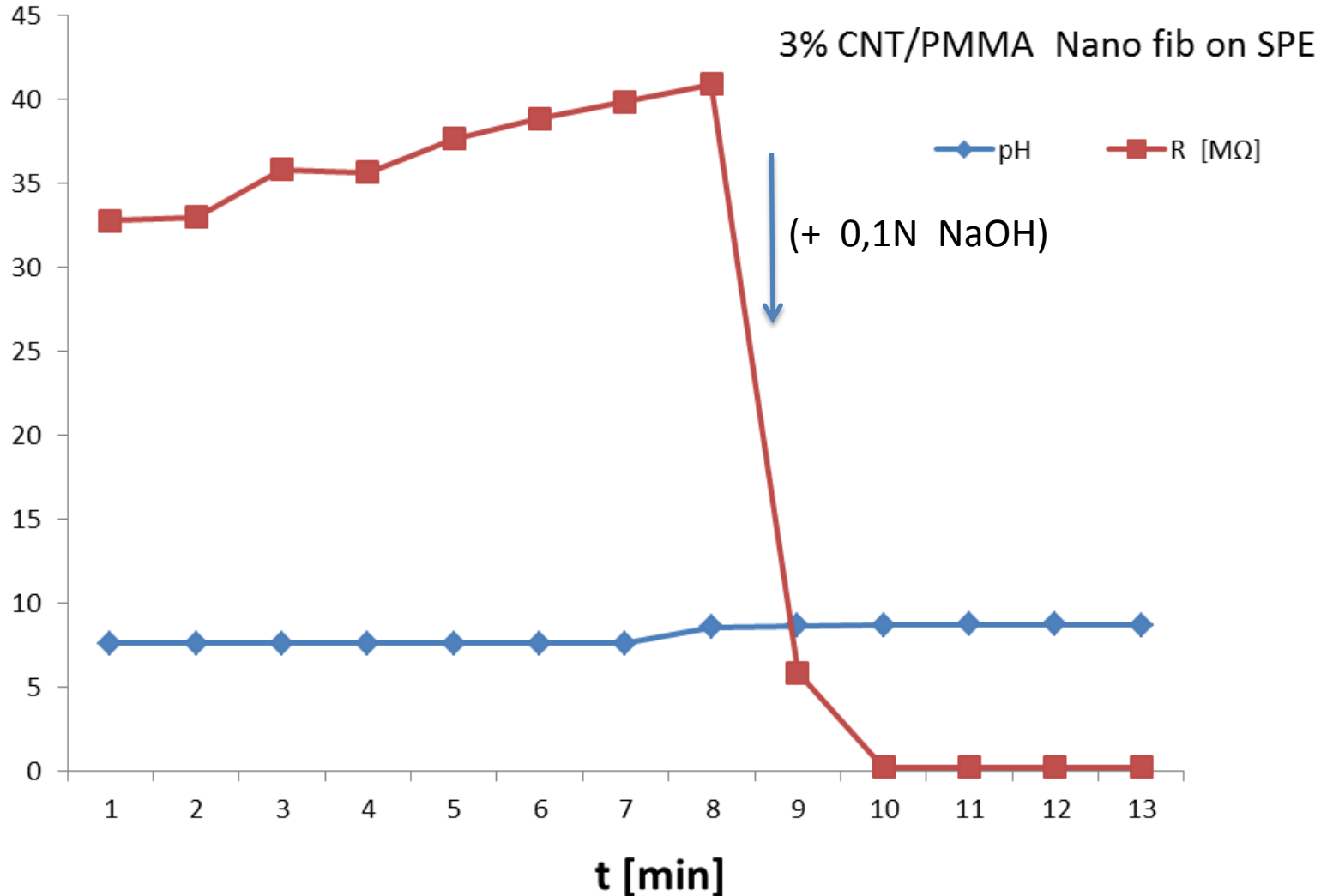
2016 June, pCO₂ testing (in simulated sea water)



Testing (Conductivity measurements) of SPE-Nano fiber 3% MWCNT/PMMA nanosensors in Lucrino-sea water (changing pH ; controlling pH and R)

Achieved RESULTS

(2016 June ; pH testing in Sea-Lucrino water)

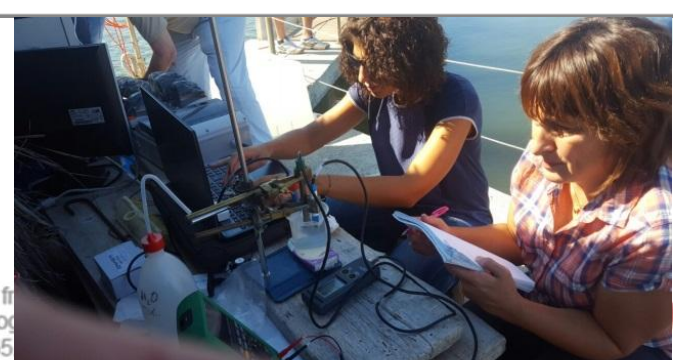
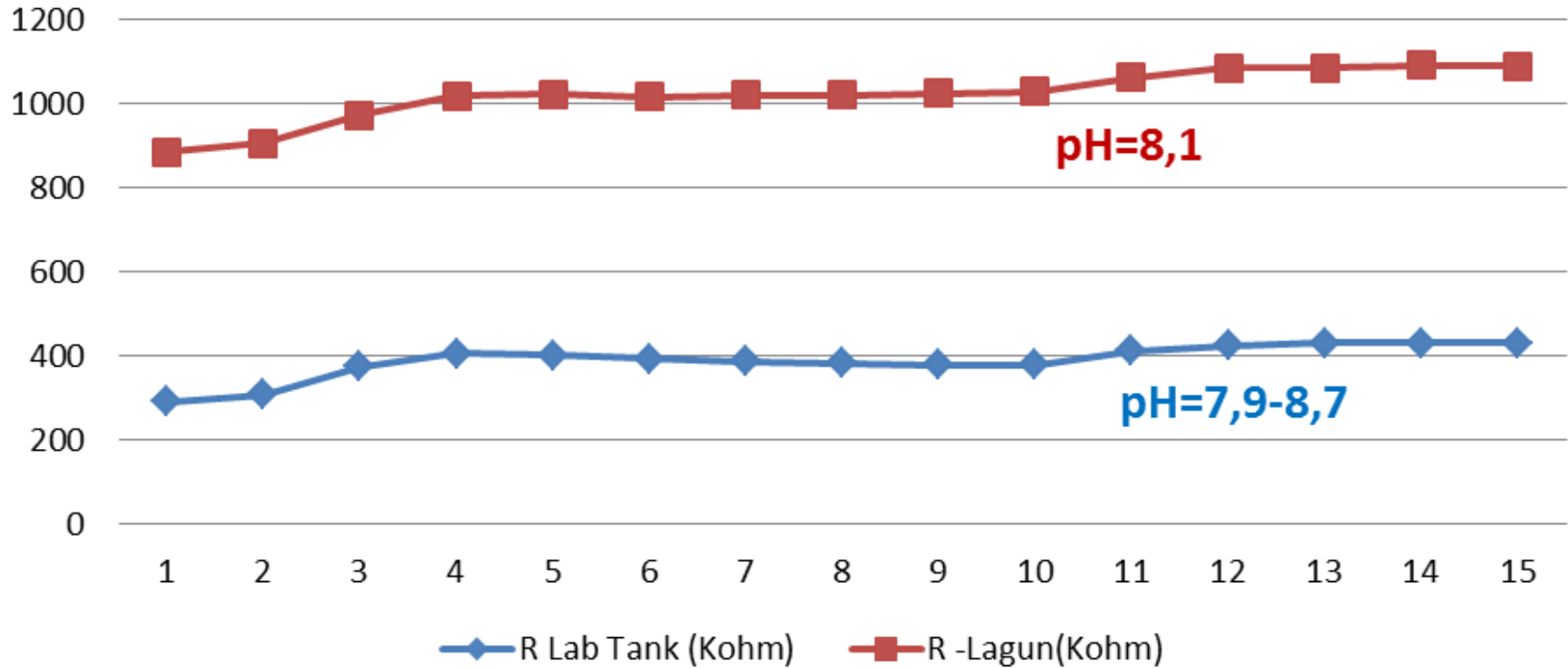


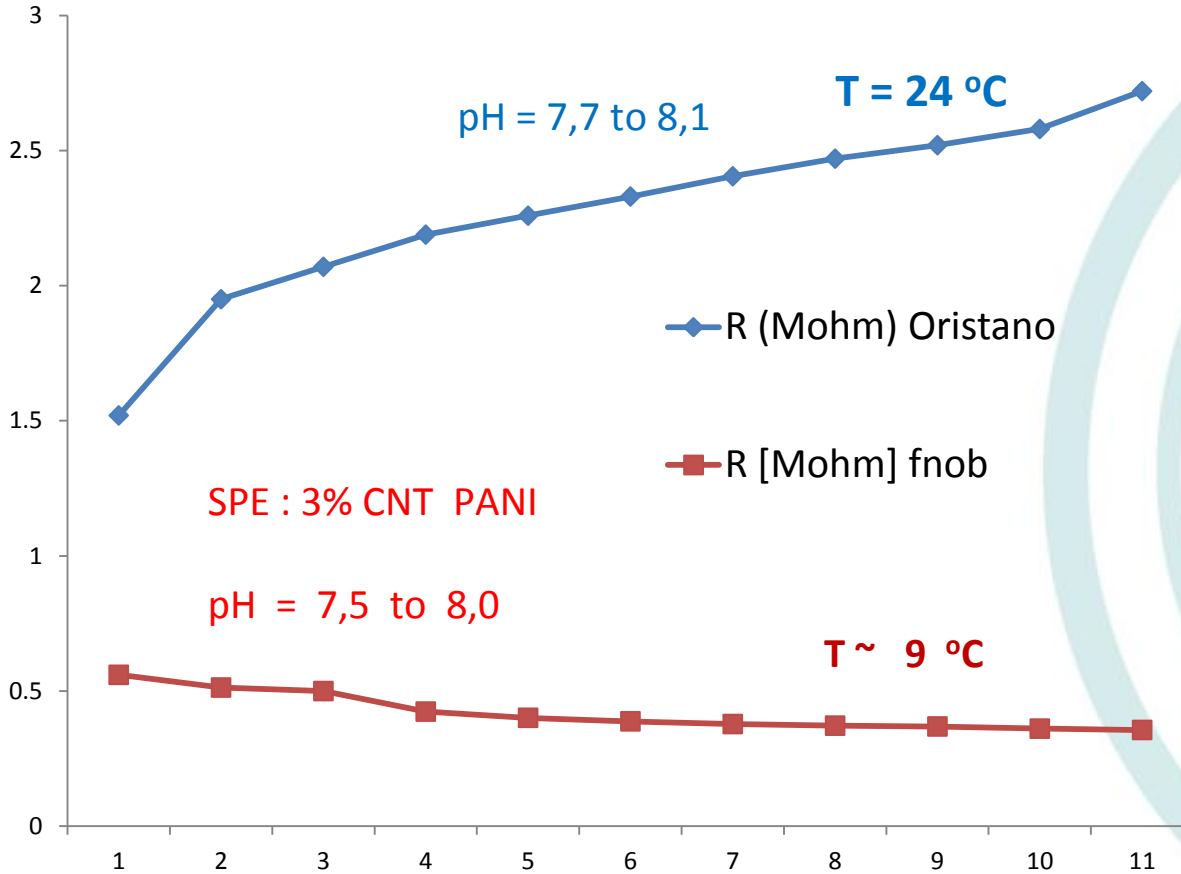
ORISTANO LAGUNA TESTING

For SPE of 3% G/PANI Nanocomposite

Status M36
Description of technical activities

Comparison of Lagun and Lab Tank testing



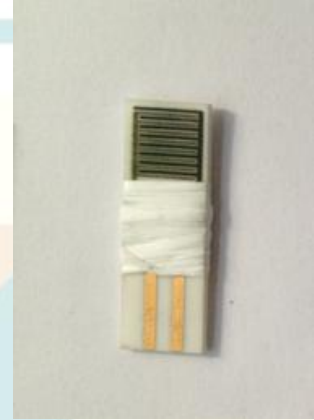


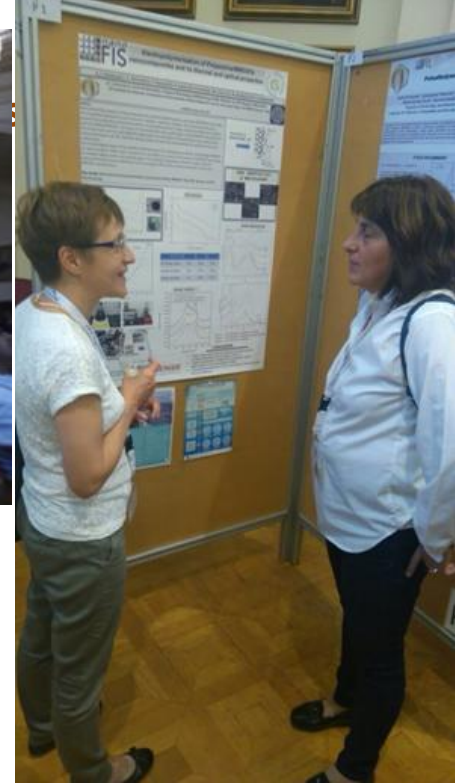
Testing in FNOB, 25.01.2017



Highlights of developed technology and TRL

- ✓ New nanocomposite based pH and pCO₂ sensor
 - ✓ Detection based on resistivity changes
 - ✓ Remarkable smaller dimensions
 - ✓ Overpassed mechanical fragility
 - ✓ Cost effective
 - ✓ Easy operation
 - ✓ Fast recovery (15 min) of the SPE nanocomposite sensor
 - ✓ Utilises an a electronic measuring that combine several measurement functions in one
- TRL : 5





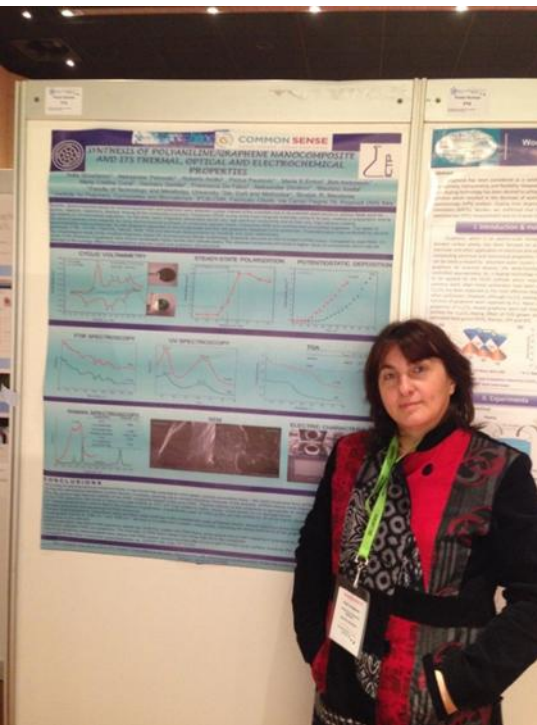
Promotion of COMMON SENSE

Presentations in

1. Nano & Material Conferences

2. Trinity Hall, Cambridge ,
15 December 2015

3. DG Research and Innovation Officers
E.C.- Mr. Kostas Gilos, Head of Unit
Ms. - Tania Friederichs, Policy Officer





Synthesis and characterization of nanocomposites based on PANI and carbon nanostructures prepared by electropolymerization

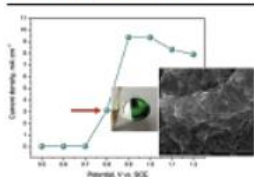
Aleksandar Petrovski^a, Perica Paunović^a, Roberto Avolio^b, Maria E. Erriço^b, Mariacristina Cocca^b, Gennaro Gentile^b, Anita Grozdanov^{a,c}, Maurizio Avella^b, John Barton^c, Aleksandar Dimitrov^a

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^cTrinity National Institute, University College Cork, Dún Laoghaire, T12 R5C2, Cork, Ireland

HIGHLIGHTS

- Nanocomposites of PANI with carbon nanostructures were prepared for sensing applications.
- By cyclic voltammetry conductive films of PANI (green signal on cathodic phase) obtained 0.75 V.
- Using 4 Probe method, nanocomposite PANI/CNS solids was tested for sensing application.
- Micro-structural properties of nanocomposites were studied by SEM, TGA and Raman analysis.

GRAPHICAL ABSTRACT



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Nanocomposites
Raman spectroscopy
Thermogravimetry

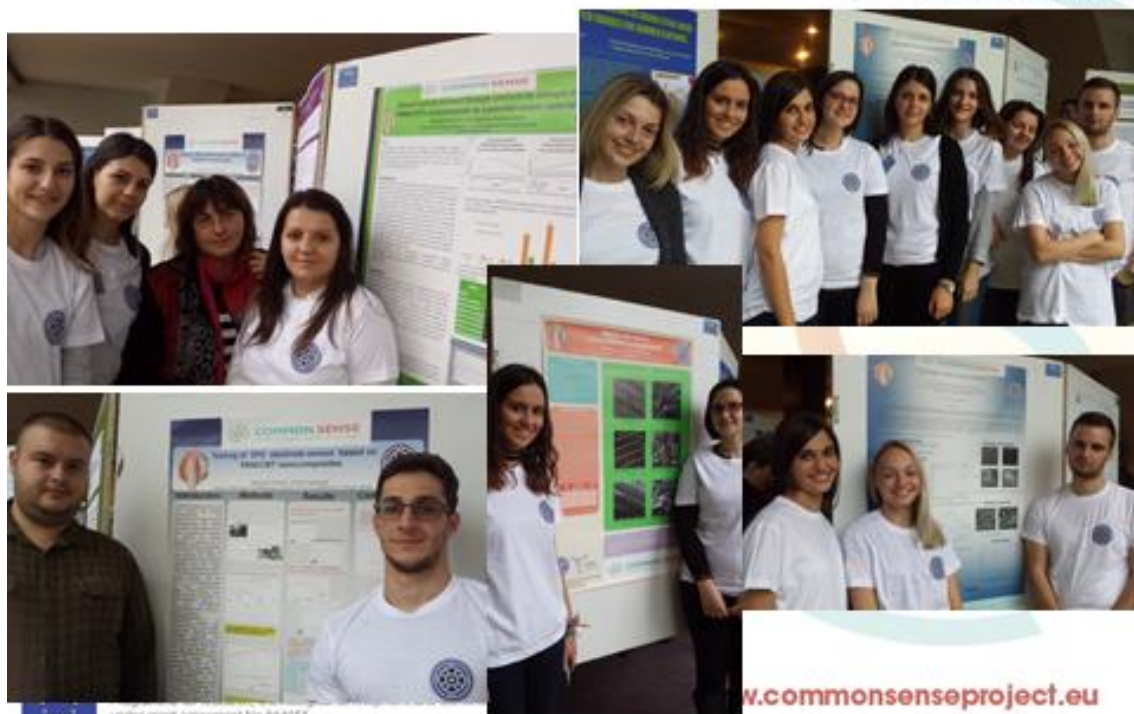
ABSTRACT

Nanocomposites based on polyaniline (PANI) and carbon nanostructures (CNS) (graphene (G) and multiwall carbon nanotubes (MWCN B)) were prepared by in situ electrochemical polymerization. CNS were inserted into the PANI matrix by dispersing them into the electrolyte before the electro-polymerization. Electrochemical characterization by means of cyclic voltammetry and steady state polarizations were performed in order to determine conditions for electro-polymerization. Electro-polymerization of the PANI based nanocomposites was carried out at 0.75 V vs. saturated calomel electrode (SCE) for 40 and 80 min. The morphology and structural characteristics of the obtained nanocomposites were studied by scanning electron microscopy (SEM) and Raman spectroscopy, while thermal stability was determined using thermal gravimetric analysis (TGA). According to the morphological and structural study, fibrous and porous structure of PANI based nanocomposites was detected well entangling both G and MWCNTs. Also, strong interaction between spatial structure of PANI with carbon nanostructures via π-π stacking was detected by Raman spectroscopy. TGA showed the increased thermal stability of composites reinforced with CNS, especially those reinforced with graphene.

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KNOWLEDGE TRANSFER – STUDENT’S CONGRESS 05.11.2016 Belgrade

Status M40
Description of technical activities



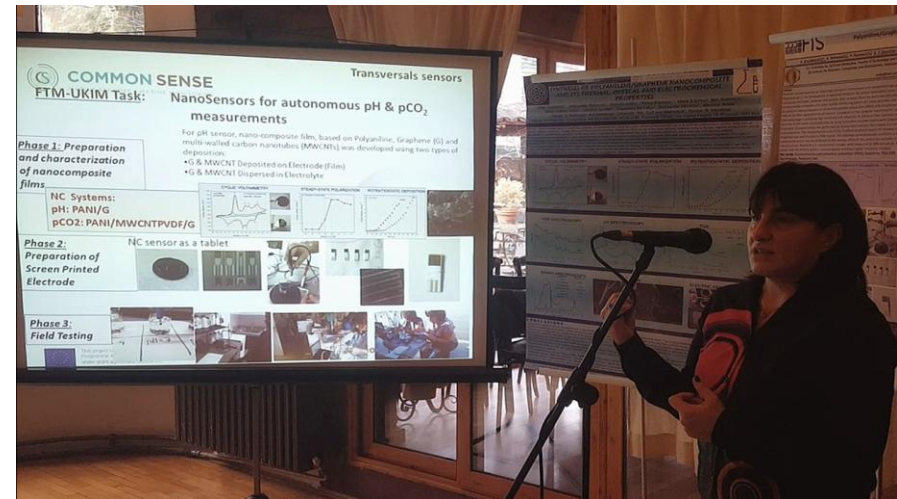
under grant agreement No 614155.

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1st . Public Dissemination Event



Guests: Min of EDU&SCI,
SMEs, Rectorate, IPR-Low Office,
Colleagues, Technical faculties
14 Decembar 2016



2nd . Public Dissemination Event

✓ With SME, Companies and ENV-Ministry
in February, 2017



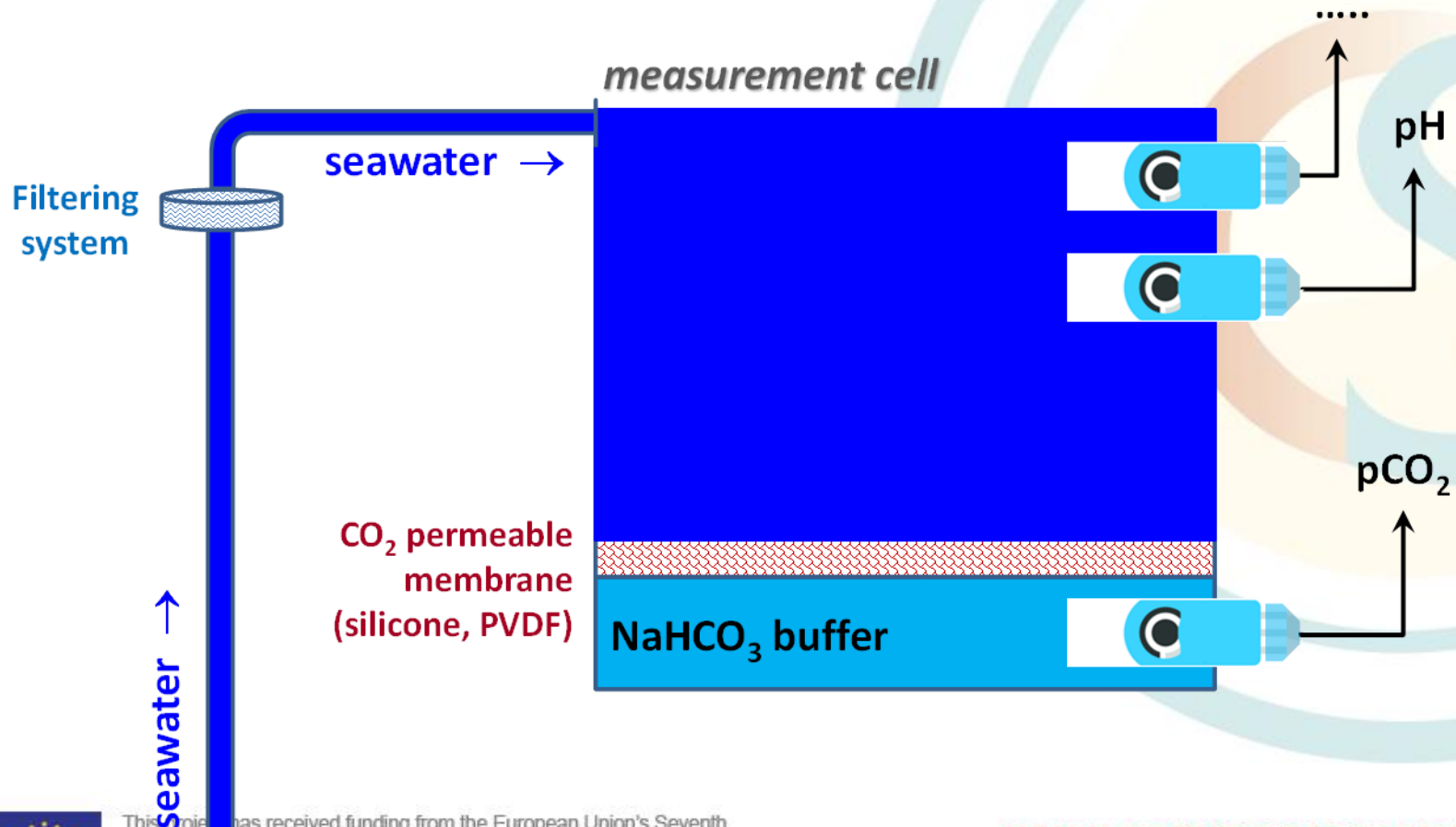
This project has received funding from the European Union's Seventh

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EXPLOITATION

FURTHER WORK





COMMON SENSE

MARINE SENSORS - MARINE MONITORING

Thank you for your Attention

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