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NEMO SINE

Application of nanostructured sensors for Cultural Heritage monitoring and protection

Dr. Gabriele Varani

g.varani@biosensor.it

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Introduction to the problem

- A huge percentage of the recent cultural heritage can be found in movies, photographs, posters and slides produced between 1895 and 1970 were made using ***cellulose derivate*** .
- More than 75 years of visual and audio memories are in serious danger to be lost due to the natural instability of cellulose acetate.
- The degradation produces ***Acetic Acid*** (vinegar effect), in an autocatalytic process.
- Thus, it is important to have sensors able to detect the presence of acetic acid and to control its concentration over time in order to be able to take preventive actions for ***human health*** and ***heritage preservation***.

State-of-the-art

In past decades, some ***gas sensors*** for the determination acetic acid have been developed:

Solution	***Issues***
Quartz crystal microbalance (QCM) based sensors, coated with polyaniline (PANI)	Irreversible changes of signal response were observed over time. They needed ***very frequent recalibration***.
Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (***MEH-PPV***) based films can be used as fluorescent probes for acetic acid vapor.	These sensors require a ***high-intensity light source*** for photoluminescence (PL) excitation and show ***low sensitivity.***
Considerable attention in recent years has been directed to sensors for toxic gases based on ***Metal Oxide Semiconductors*** (MOS).	The most common metal oxide semiconductors sensitive to gasses are n-type semiconductors, thus, they demand ***high operating temperatures*** that limits their use at room temperature.
Among many others, ***Zinc Oxide*** (ZnO) is a unique material, which possesses specific semiconducting ,optical properties, and good biocompatibility.	The photoluminescence of ZnO is very attractive for sensor development operating at ***room temperature*** . ZnO can be exploited as a selective analytical transducer, which enables to enhance the analytical signal, increase detection sensitivity and signal-to-noise ratio.

Aim of the work

- Our purpose is to realize a novel ***ZnO/PANI*** nanocomposite based photoluminescence sensors for the determination of ***acetic acid*** vapors at ***room temperatures***.

- Moreover the integration of the ZnO/PANI nanocomposites with an ***portable optical system*** for application in ***vinegar analysis*** and in ***cultural heritage*** protection.

ZnO deposition and formation of ZnO-PANi composite*

- PANI was synthesized by oxidative- chemical deposition method. The 1 mg/ml of ZnO nanorod (ZnO-NR) colloidal suspension in water was mixed with pure aniline. 50 mM and 100 mM aniline concentrations were used for composite preparation.

- Twenty microliters of the ZnO-PANI composite solution were deposited on the prepared glass substrate (10mm*10 mm) by drop casting method.

Characterization of the sensing layer:

- X-ray diffraction spectroscopy (XRD);
- Scanning Electron Microscope (SEM);
- High Resolution Transmission Electron Microscopy (HRTEM)

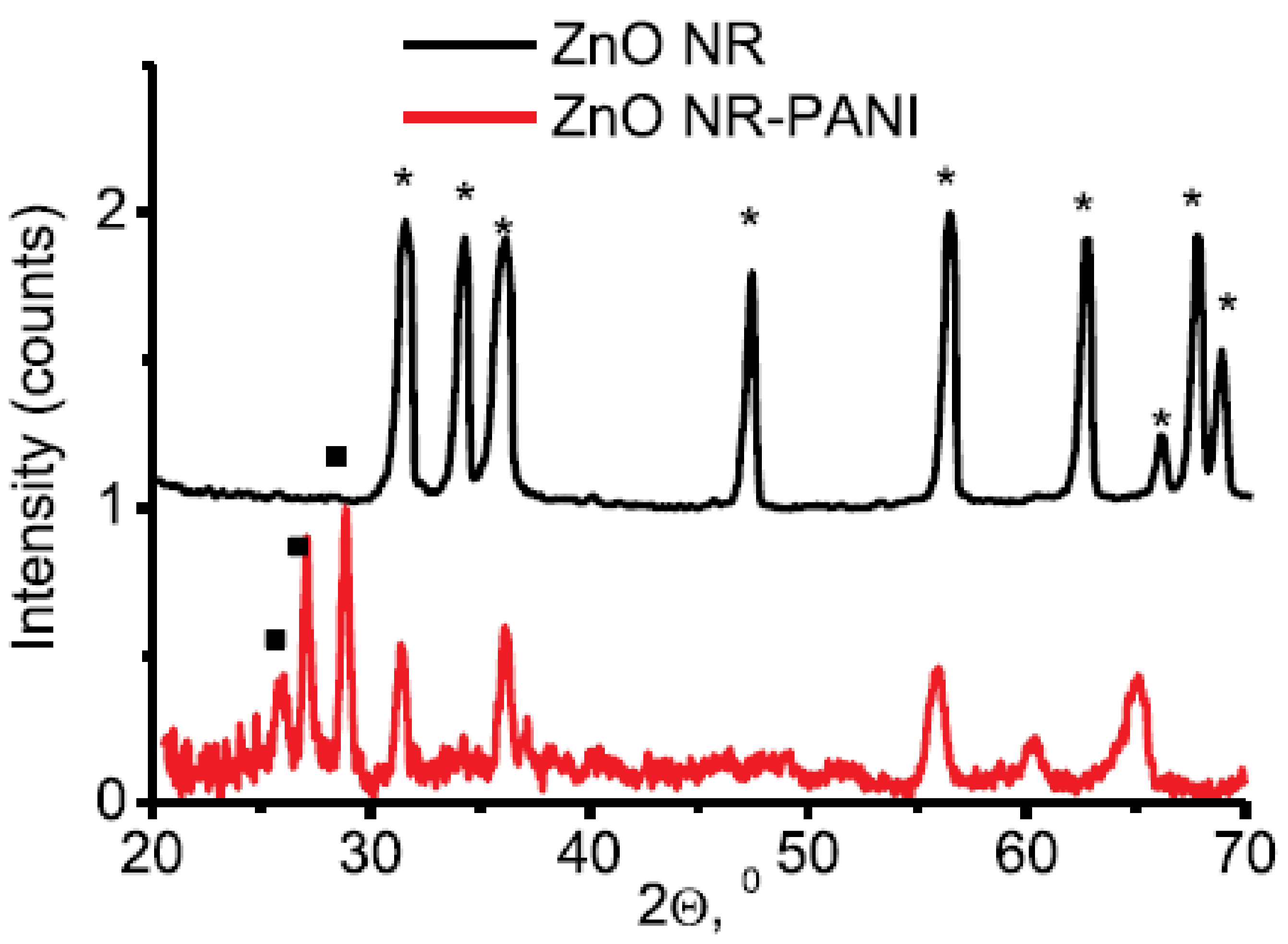
*Mehmet Turemis, Daniele Zappi, Maria Teresa Giardia, Giovanni Basile, Almira Ramanaviciene, Aleksandrs Kapralovs, Arunas Ramanavicius, Roman Viter, ***ZnO/polyaniline composite based photoluminescence sensor for the determination of acetic acid vapor***, Talanta 211 (2020) 120658.

X-ray diffraction spectroscopy (XRD)

- All the experiments performed with composite material obtained by 100 mM aniline coating. The 50 mM concentration of aniline didn't provide conformal coating.

- ZnO and PANI peaks are marked as * and ■, respectively)

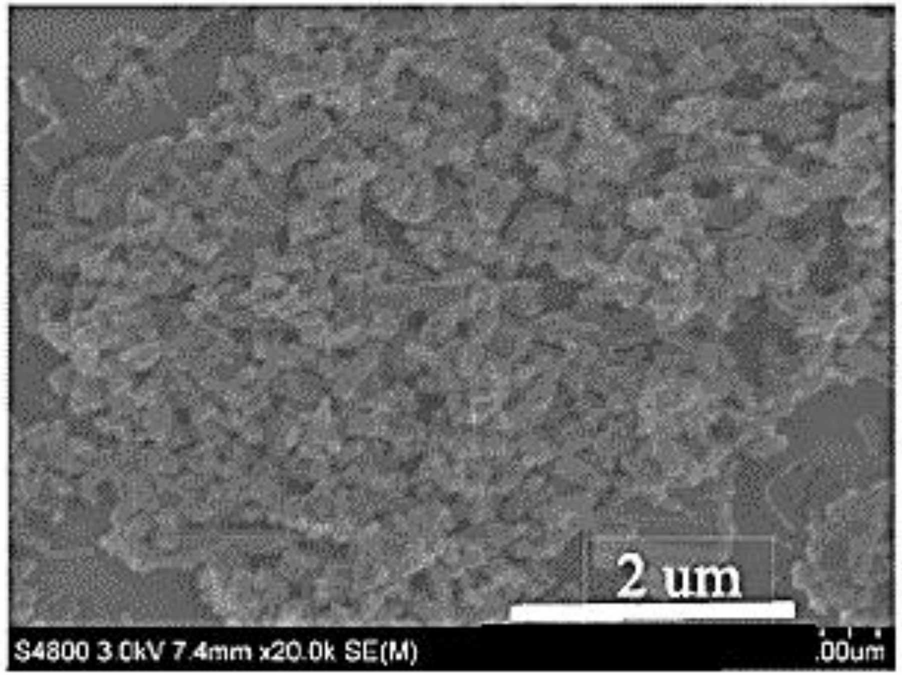
- Peaks of ZnO at 55.88, 60.2 and 64.88 are shifted due to forming of ZnO/PANI composite structure.

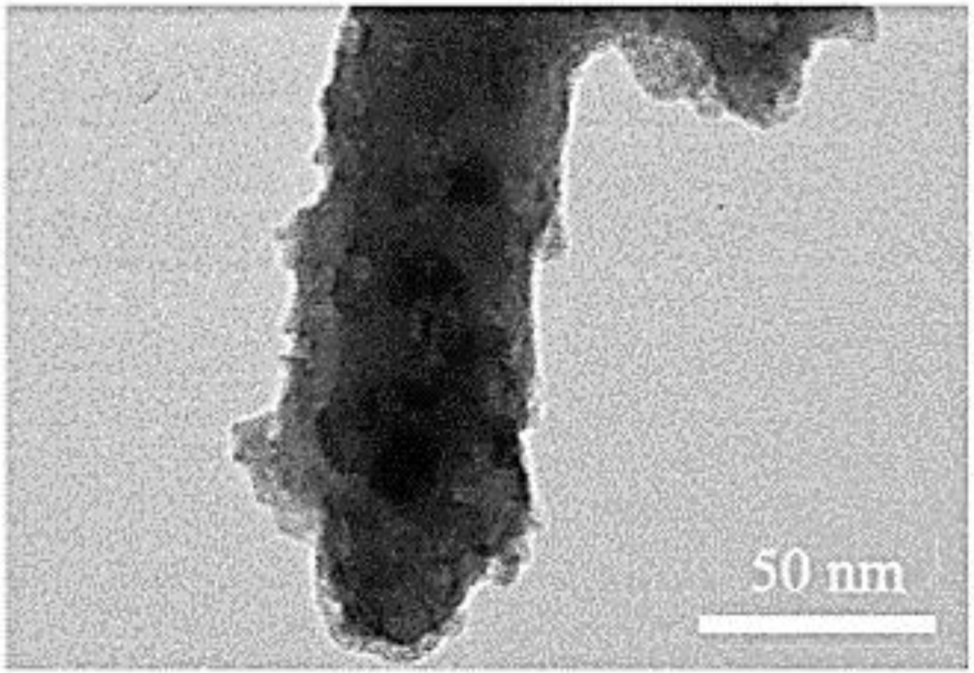


Scanning Electron Microscope(SEM) and High Resolution Transmission Electron Microscopy(HRTEM)

- Scanning electron microscopy (SEM) image of the ZnO/PANI on a glass substrate shows a uniform distribution of nanostructure grains of about 60–90 nm diameter and 400–600 nm length.
- HRTEM image of the ZnO/PANI indicate conformal coating of PANI. The average thickness of the PANI coating layer, estimated from HRTEM image was7 ± 3 nm.

SEM

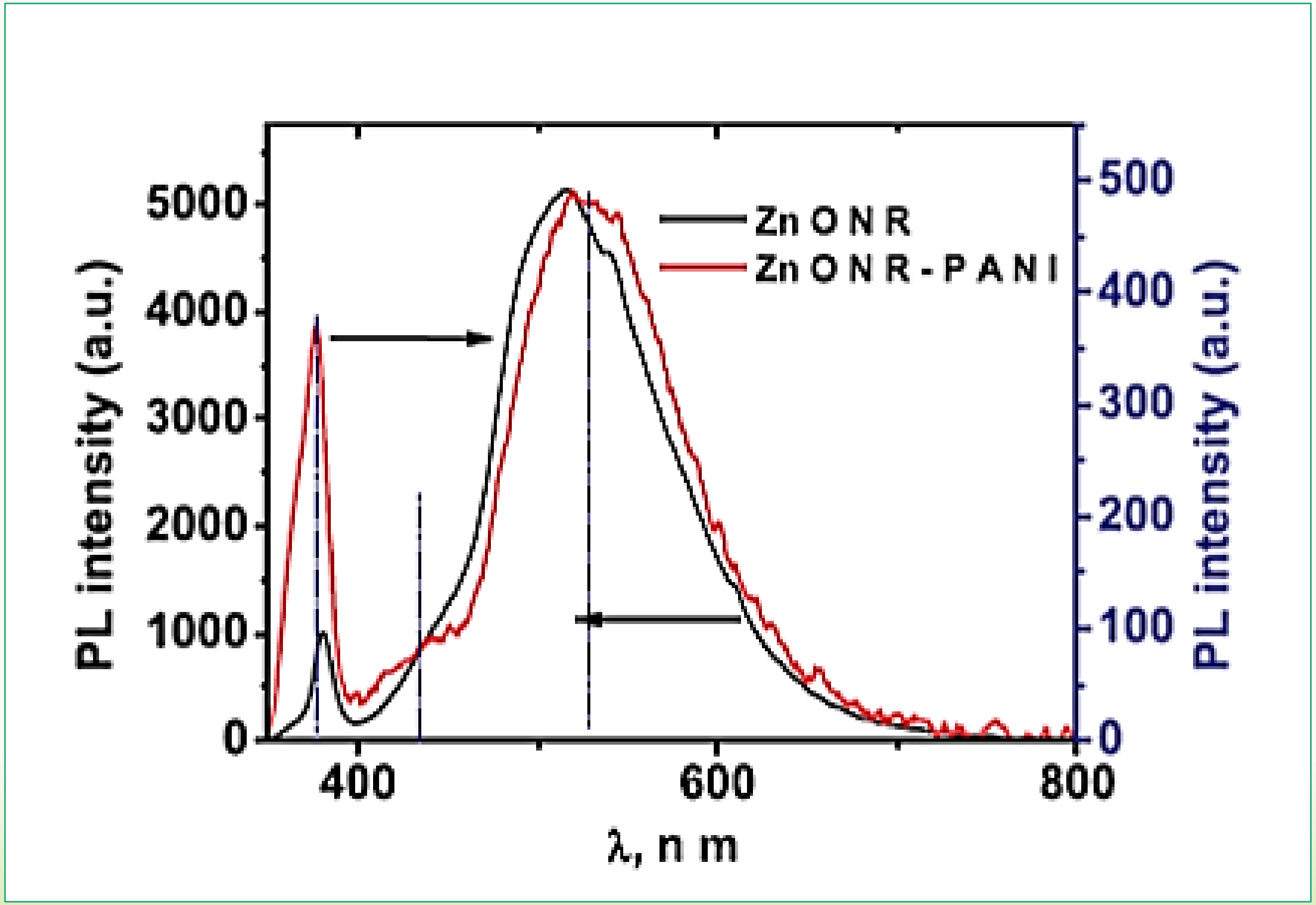




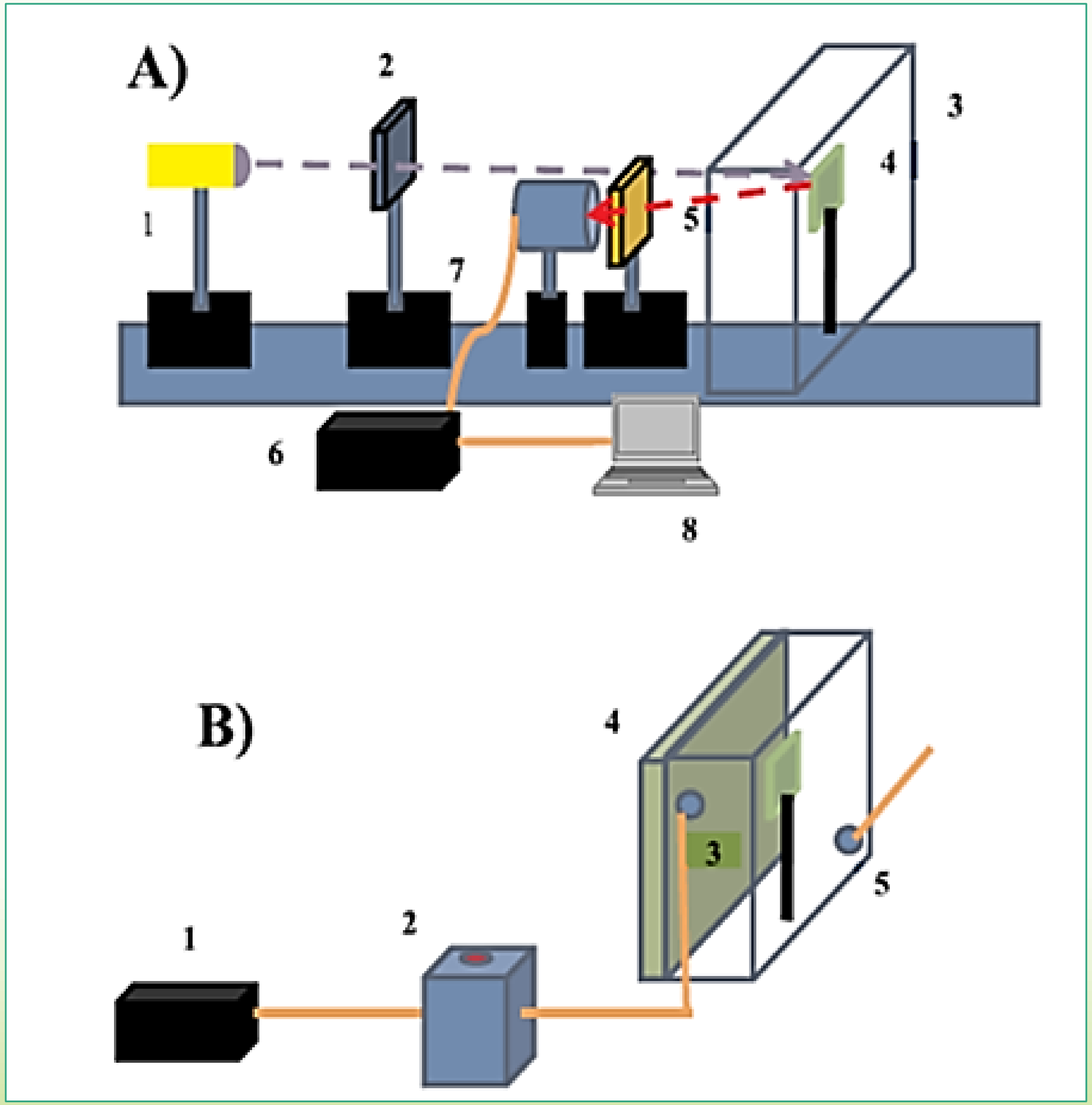
HRTEM

Optical properties: Photo Luminescence Spectra (PL)

- PANI deposition results in a decrease of intensity of ZnO-based PL.
- Sufficient decrease of PL emission might be related to absorption of the emitted light by PANI.
- Peak shifts are observed in UV and visible region, suggesting the formation of composite with charge transfer between PANI and ZnO.
- At 380 nm and 520 nm wavelengths, where obtained the best PL performance.



Experimental Set-up for gas sensing (concept)



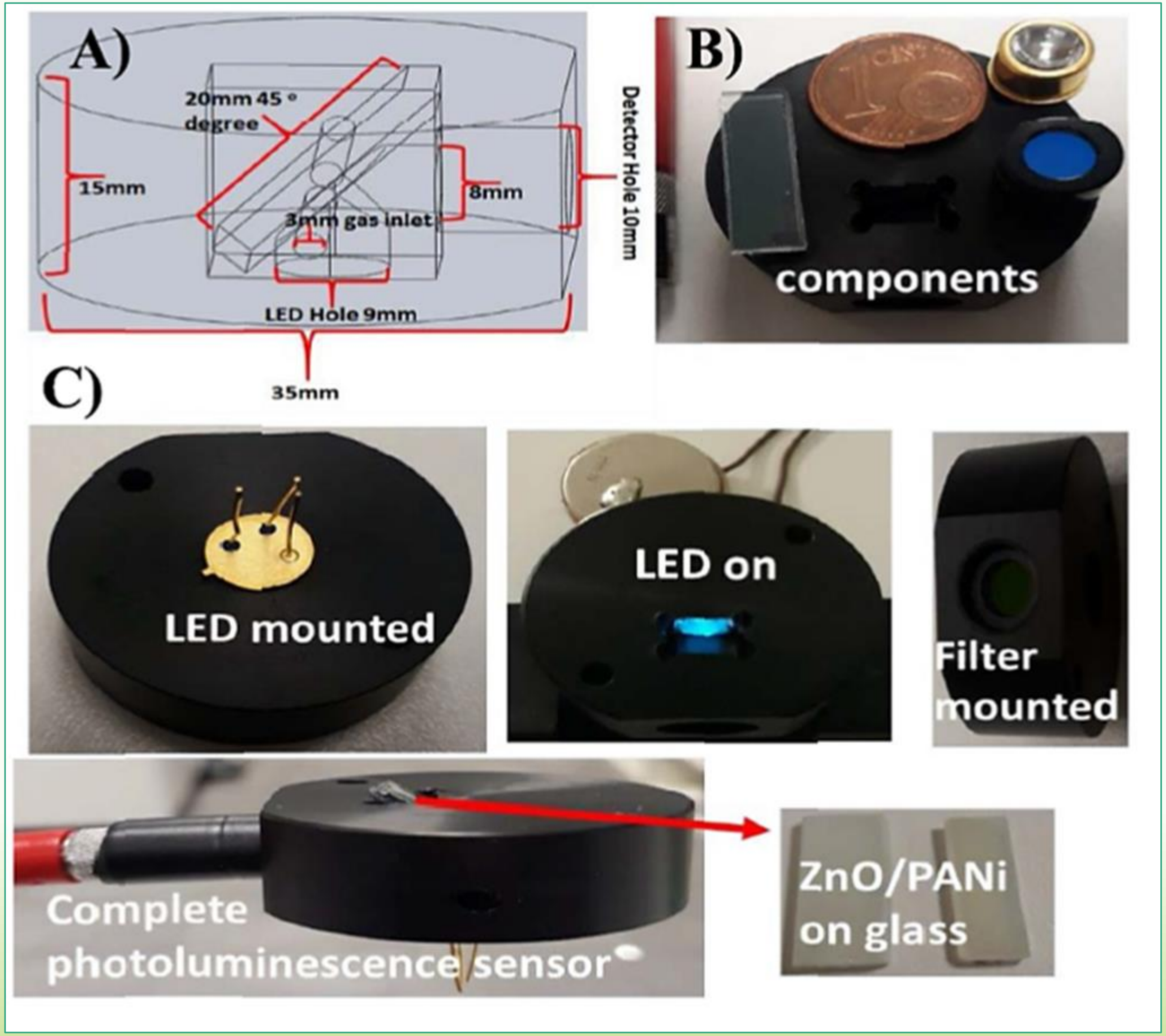
Schematic set-up

- (1)Light emitting diode (LED);
- (2)Band pass filter;
- (3)Gas chamber;
- (4)Sample holder;
- (5)Long pass filter;
- (7)Fiber optic spectrometer equipped with lens;
- (6)Detector;
- (8)Computer;

Gas supply system

- (1)Air pump;
- (2)Buffer volume;
- (3)Inlet chamber;
- (4)Measurements cell:
- (5)Outlet;

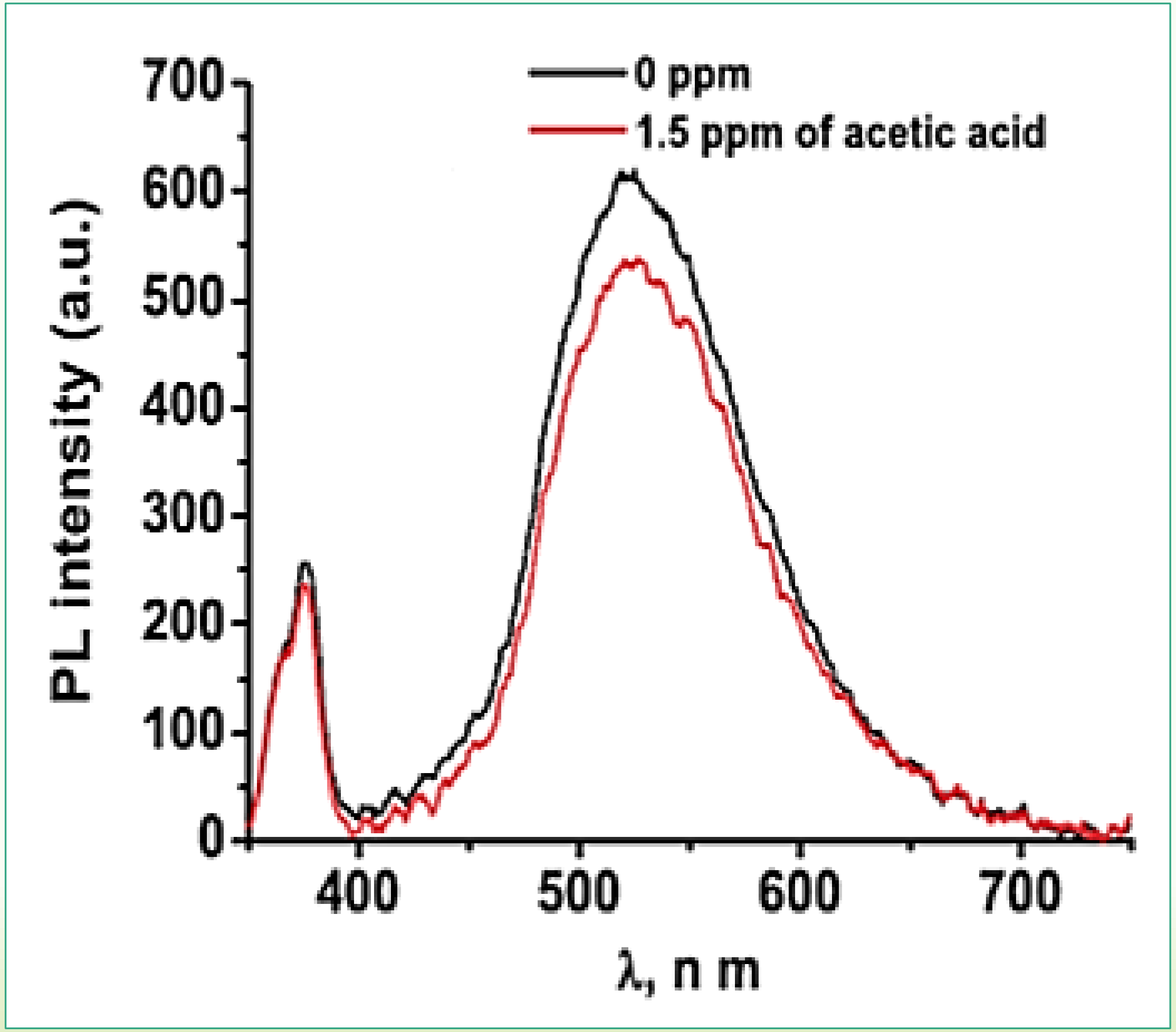
Experimental Set-up for gas sensing (platform)



- A) Drawings of the measurement chamber indicating the angle of measurement of photoluminescence by the fiber optic spectrometer;
- B) parts of the developed sensor array;
- C) in order from left: LED mounted on measurement cell, measurement cell when UV LED turned on, filter mounted on measurement cell, complete sensor assembly with glass plate deposited ZnO/PANI sensing layer.

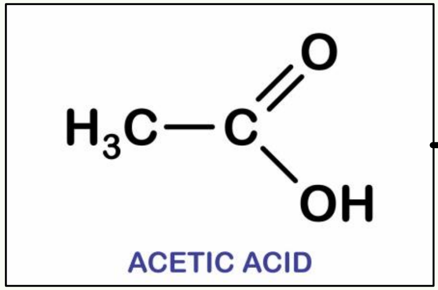
PL Spectra of Acetic acid injection

- The presence of acetic acid into the measurement cell resulted in the ***decrease of the PL intensity*** of ZnO/PANI nanocomposites.

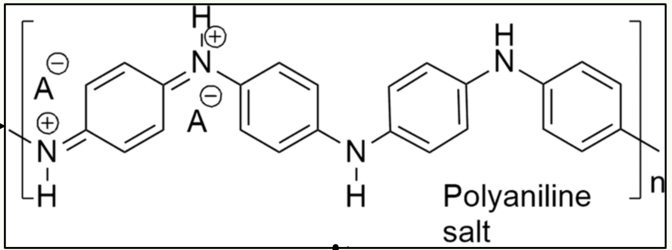


Mechanisms of action for the ZnO/PANi composite layer

Theory of **High specific surface area** of the ZnO-PANi layer



Absorption and chemisorption



Porous composite layer with enhanced superficial interaction with the gas vapour.

Photo-oxidation by ZnO-PANi

p/n junction theory

Decrease of activation energy and enthalpy

Formation of p/n junction between HCl p-type doped polyaniline and n-type ZnO semiconductor

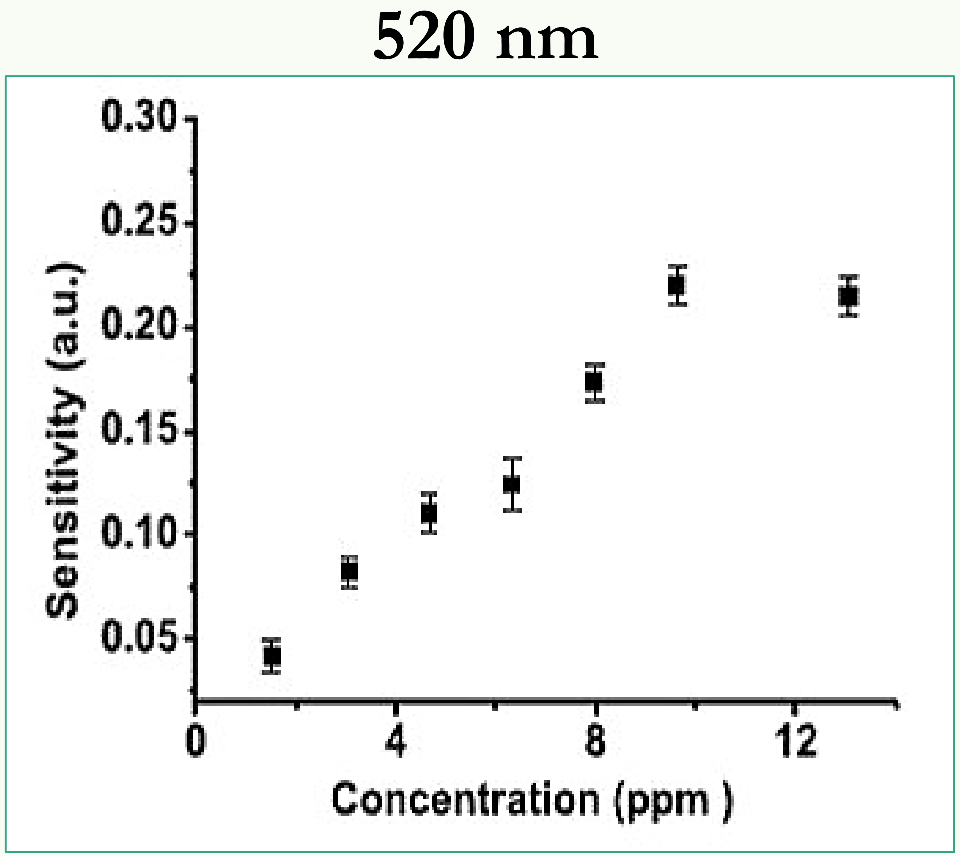
Formation of various molecula adsorption site on PANi surface with eencreased sensitivity compared to pure ZnO and pure Polyaniline

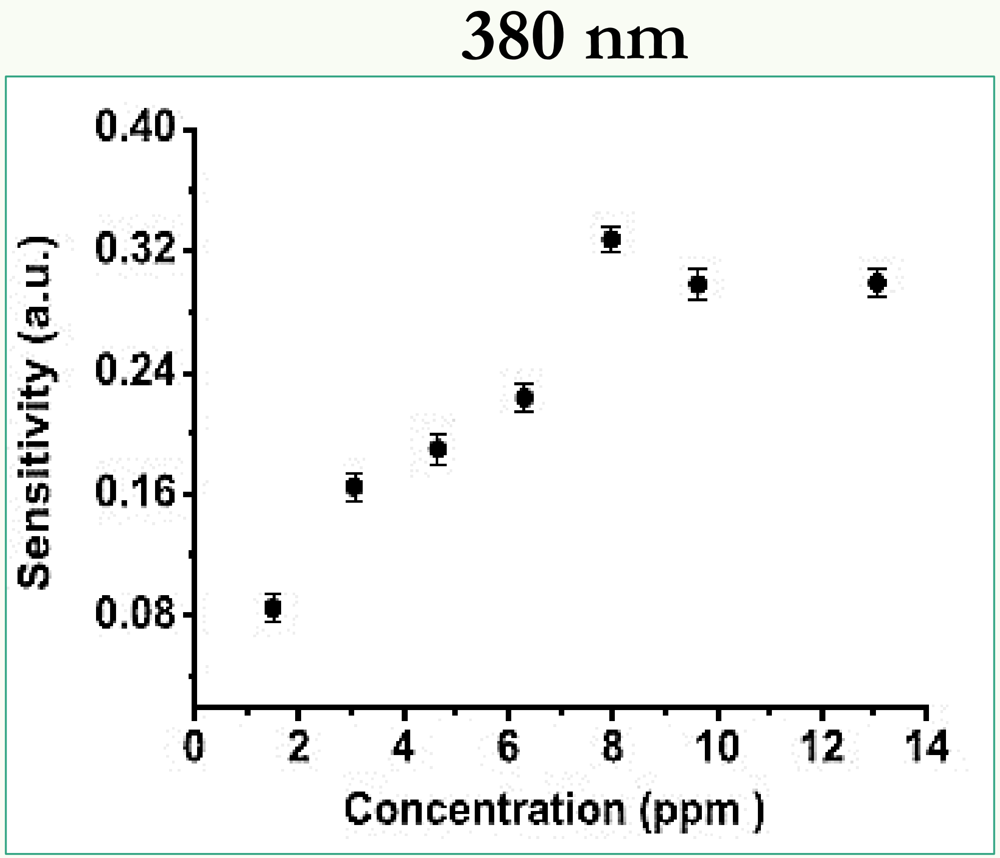
AA detection

Interaction betwen NH2-groups and the target

Electric field on the surface and consequently move of the electrons from emission centres to the surface with decrease of the PL intensity.

Calibration curves at 520 and 380 nm





$$\begin{cases} S = \frac{I_0 - I_c}{I_0} \\ LOD = \frac{3\sigma}{K} \end{cases}$$

Sensitivity

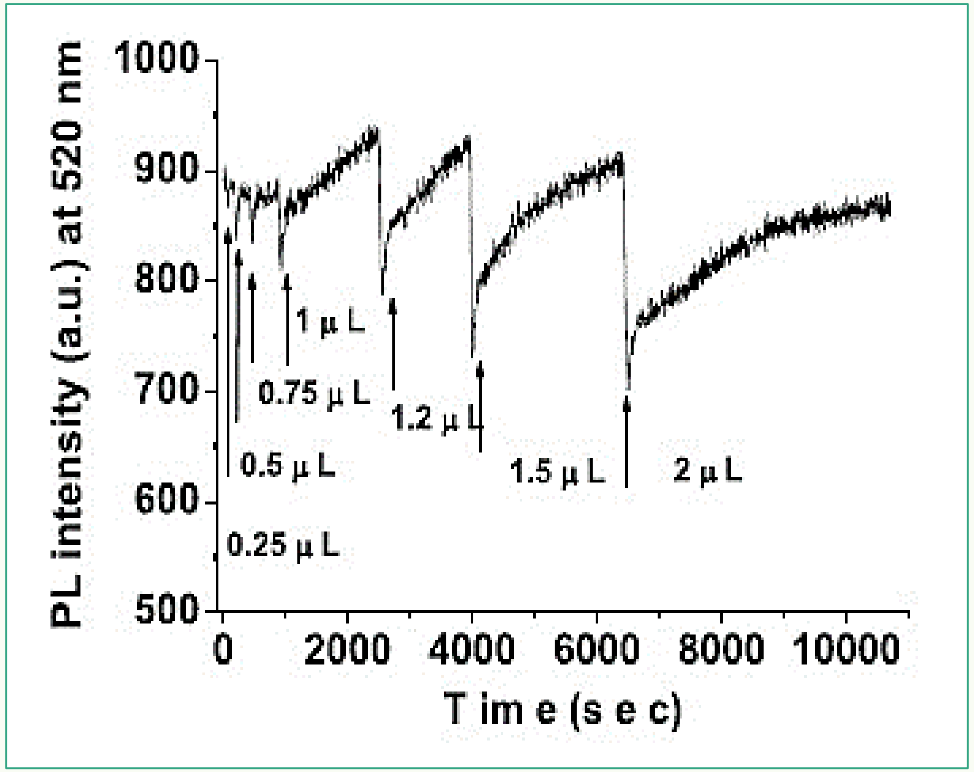
Limit of detection

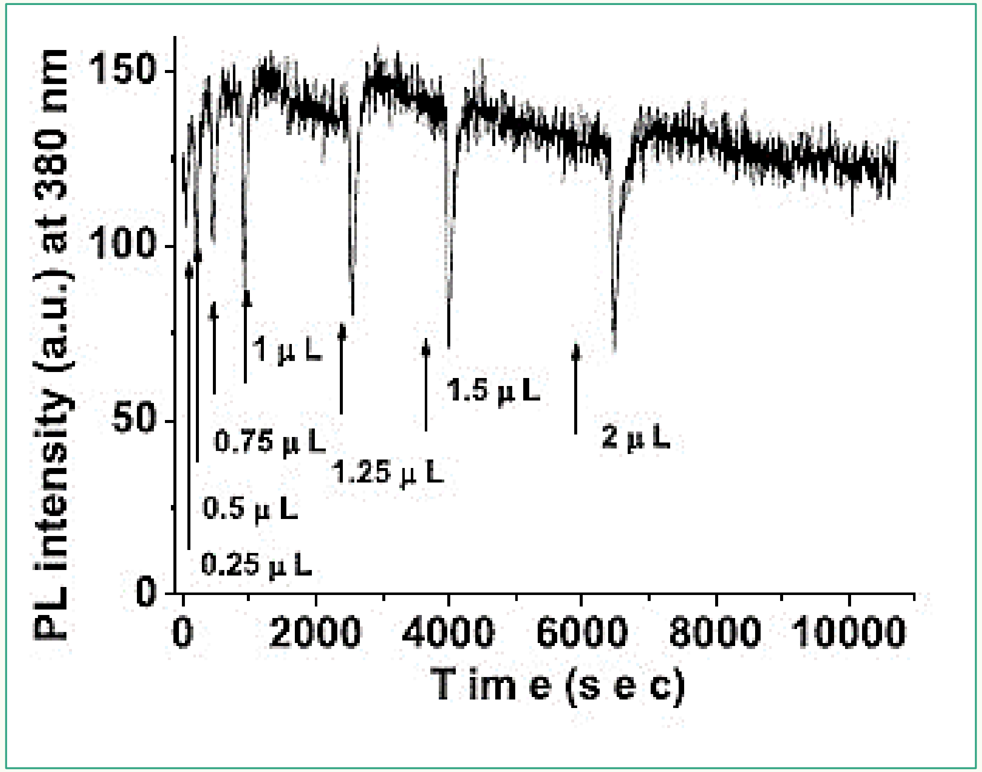
- The calibration curve of the ZnO gas sensor depicts the linear behavior of the sensor response at the measured range of the acetic acid concentrations (**1-13 ppm**)

1.2 ppm (at 520 nm); **2ppm** (at 380 nm)

Evaluation of sensor response towards acetic acid

- The kinetic study of adsorption/desorption of acetic acid on the surface of ZnO/PANI shows that the intensity of the PL emission peaks decreased when the acid concentration has increased.





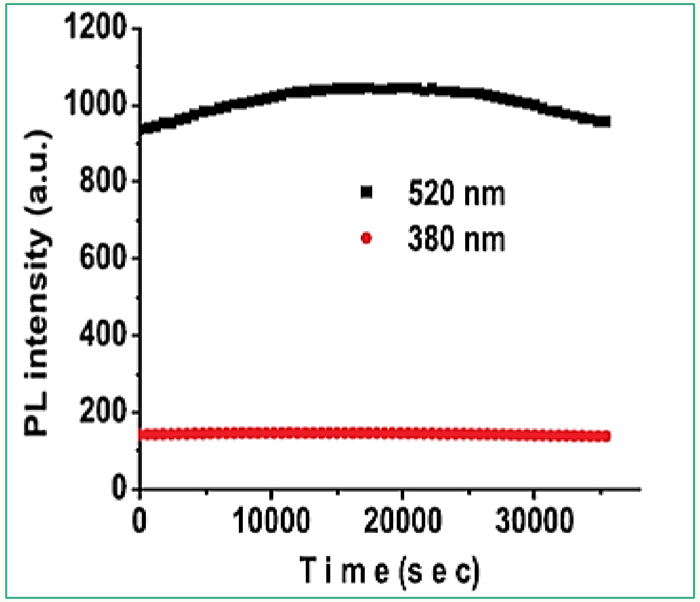
- The sensor signal was partially reversible. Recovery time of the sensor increases proportional to the acetic acid concentration in the tested range.
- The larger recovery times are likely due to the slow rate of diffusion and desorption of acetic acid from the sensing surface.

Stability, Repeteability and Selectivity of the sensor

Stability

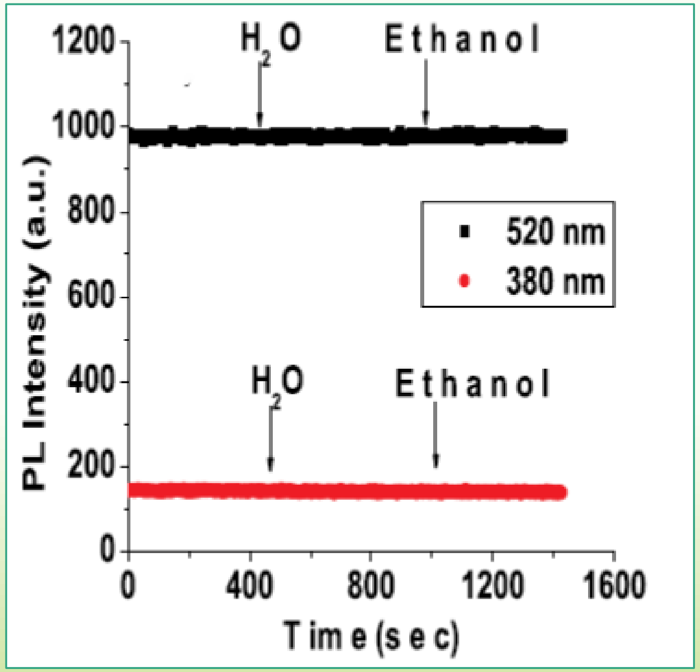
Long term → Sensor exposed to 5ppm of AA , 25°C could be used up to 30 days (retain 90% of initial PL response)

Operational stability → Over 10h of measurements the sensor is stable in the range 1-13 ppm of AA. For concentration > 20ppm the signal drops up to 20%



Reproducibility Repetability → PL measurements for differents layers prepared indipendently in differents days gave Relative Standard Deviations (RDS) of ±0.6 each 5ppm.

Selectivity → The sensor was exposed to water vapors and 100 ppm ethanol. No signal changes were observed.



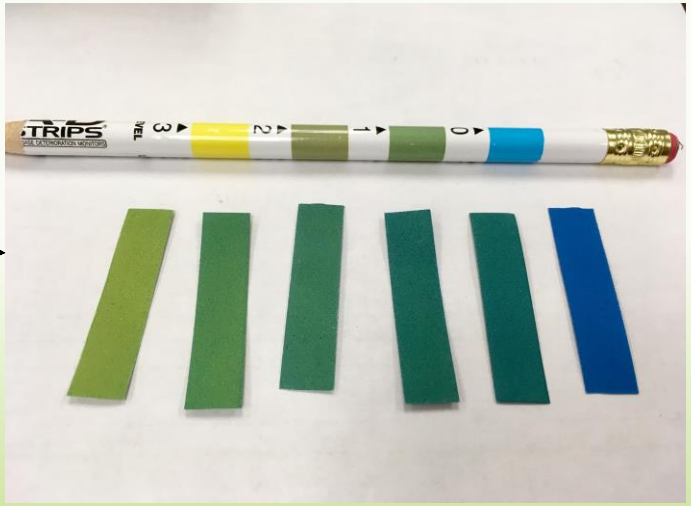
Real Sample Analysis

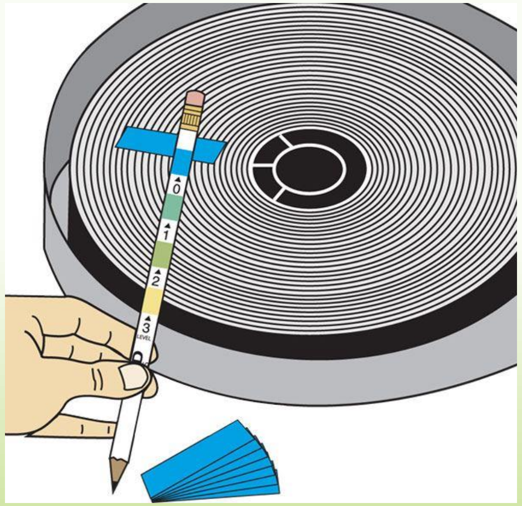
- The proposed method was applied for the determination of acetic acid concentrations in ***two commercial vinegar samples*** and produced by ***film samples***.

Samples	Value found with A-D strips	Value found with described sensor system	Recovery
Vinegar (Cirio; Label value 6%)	–	5.7% ± 0.4	94.7%
Vinegar (Panorama; Label value 7%)	–	6.4% ± 0.5	92.1%
Film 1 (No deterioration)	0 (< 1 ppm)	Nr	–
Film 2 (Deterioration started)	1 (1–2 ppm)	1,5 ppm ± 0.3	–
Film 3 (Actively degrading)	2 (6–8 ppm)	7,6 ppm ± 0.8	–

Nr.: Not revealed.

- The acid concentration of the commercial vinegar samples was found to be around 6–7%.
- Acetic acid gas arising from ancient films was in good agreement with the results obtained with ***A-D strips***.
- A-D strips are filter paper soaked with a pH colorimetric indicator. The degradation level is evaluated by comparing the color of the strips with a provided color reference.





In collaboration with: **Nadja Wallaszkovits** (Austrian Academy of Sciences);**Ana Ramos** (Universidade NOVA de Lisboa); **Andrea de Polo Saibanti** (Fratelli Alinari); **Juan Ignacio Lahoz Rodrigo** (Institut Valencià de cultura); **Kerstin Herlt** (DFF-Deutsches Filminstitut & Filmmuseum);**They were used in the context of the European Project NEMOSINE**.

Comparison with other sensors

Sensing layer	Pr-doped ZnO	poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene	Y-doped SnO2	Ni^{2+} –doped ZnO	CBF containing CTAB and SNARF-1	ZnO/PANi composite
Analyte	Acetic acid	Formic acid	Acetic acid	Acetic acid	Acetic acid	Acetic acid
Technique	Resistive	PL	Resistive	Resistive	PL	PL
Linear/Working range	20–400 ppm	0–2500 ppm	10–500 ppm	0.001–10 ppm/ 10–1000 ppm	3–65 ppb	1–10 ppm
LOD	N.R	348 ppm	Not reported	0.001 ppm	3ppb	1.2 ppm
Operating temperature	200–375 °C	R.T	300 °C	310 °C	RT	R.T
Response time	37–51s	18s	4–7s	4s	N.r.	30s
Recovery time	48-40s		8–11s	27s	N.r.	215–360s
Partial selectivity over	Methanol, DMF	Nr	Ammonia, DMF Methanol	Benzene Toluene	SO_2	Ethanol

- The developed ZnO/PANI-based sensors showed ***good sensitivity*** comparing to ZnO-based gas sensors, based on resistive metal oxide nanostructures.

- The resistive sensors working with fast response and recovery time but at high temperature. Thus they ***consume more energy*** and ***cannot be used to detect gases at archives (due to the explosive nature of nitrocellulose films) .***

- In monitoring of cellulose degradation, the key parameters are operation at ***room temperature*** and ***fast response***.

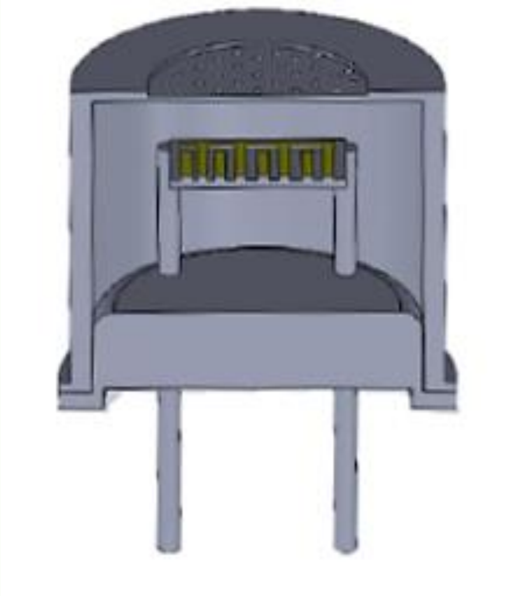
Conclusions

- The results presented in this work show for the first time that ***ZnO/ PANI-based nanocomposites*** are good candidates for the ***determination of acetic acid at room temperature*** based on photoluminescence measurements.
- The results of the photoluminescence and measurements of these composites exposed to the ***acetic acid vapors*** show that ***photoluminescence decrease with increasing the samples concentration***.
- The developed ZnO/PANI-based sensor showed ***good sensitivity*** to acetic acid in the range of ***1–13 ppm***, with acceptable ***response*** and ***recovery times*** suitable for the monitoring of acetic acid.
- A new miniaturized sensing system based on ZnO/PANI sensing layer prototype was developed. The prototype combines ***LED (UV)*** and a ***fiber optic*** measurements system with ***photoluminescence ZnO/PANI sensing element***.
- The developed sensor can be of practical interest for ***monitoring vinegar*** and for the ***protection of the cultural heritage*** against acetic acid production during ***the degradation of acetate cellulose films***, since their storage is an important task related to protection and conservation of cultural heritage.

Future perspectives

- We are now applying these developed sensible nanomaterial to integrate them in ***MOS technology***.

- The first results obtained makes us hopefull that this integration is possible and it will led to a new generation of ***miniaturazied acetic acid sensors for Cultural Heritage protection and preservation***.



Work in progress: D.Zappi, G.Varani, G.Basile, M.T.Giardi, ***Development of sensor array for acetic acid determination***. (Not yet submitted).

Contacts

Web page

http://www.biosensor-srl.eu/

Cordis website-Giovanni Basile

https://cordis.europa.eu/partners/web/giovannibasile

E-mails

g.basile@biosensor.it
info@biosensor.it
d.zappi@biosensor.it
g.varani@biosensor.it
mt.giardi@biosensor.it

You can find us on :

- Facebook
- Twitter
- Instagram

Biosensor Srl
Via degli Olmetti, 44
00060 Formello (Roma)
Italy
Tel. +39 06 9075116

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