NEW MAGNETIC POLYMERIC COMPOSITE ELECTRODE MATERIAL FOR AMPEROMETRIC NITRITE SENSOR

G.M. Ispas[1,2], I. Crăciunescu[1], S.A. Porav[1], R. Turcu[1], D. Gligor[2]

[1]National Institute for Research and Development of Isotopic and Molecular Technologies, 67-103 Donat, 400293 Cluj-Napoca, Romania

[2]Department of Environmental Analysis and Engineering, "Babes-Bolyai" University, 400294 Cluj-Napoca, Romania

E-mail: george.ispas@itim-cj.ro

Abstract

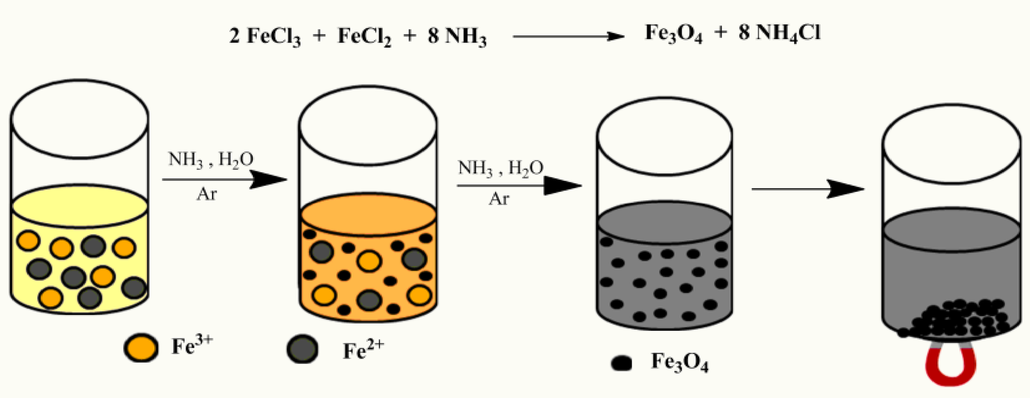
New modified electrode materials, based on a combination of hybrid nanocomposites such as magnetic nanoparticles, inorganic polymer, like silica and organic polymer like poly acrylic acid (pAac) ((MNPs-SiO2 and MNPs-SiO2-pAAc) were studied. The as prepared magnetic polymeric composite materials present high potential applicability as electrochemical sensors for quantitative measurements of nitrite from different kind of real samples.

The electrochemical properties of the synthesized materials were investigated. By electrochemical measurements was proved that this electrode presents electro catalytic effect towards nitrite oxidation and can be used for nitrite detection. By comparing with other electrodes, the electro catalytic effect of MNPs-SiO2-pAAc is better, because the nitrite oxidation peak appears in this case at a potential closer to 0 mV vs. Ag/AgCl/KClsat, which is favourable to avoid interferences in amperometric nitrite detection in real samples

Synthesis

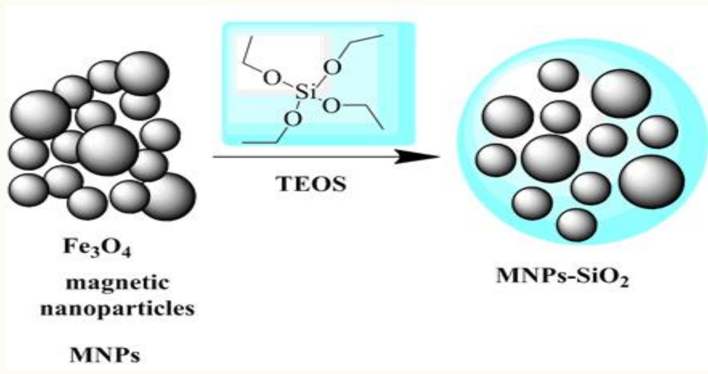
1st step

Synthesis of Fe_3O_4 by co-precipitation method (**MNPs**)



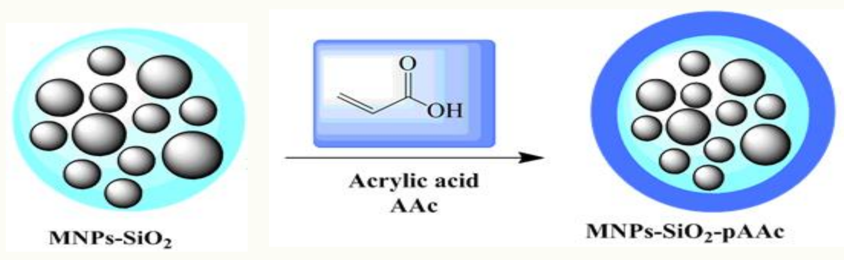
2nd step

Coating of MNPS with SiO_2 shell (**MNPs-SiO$_2$**)



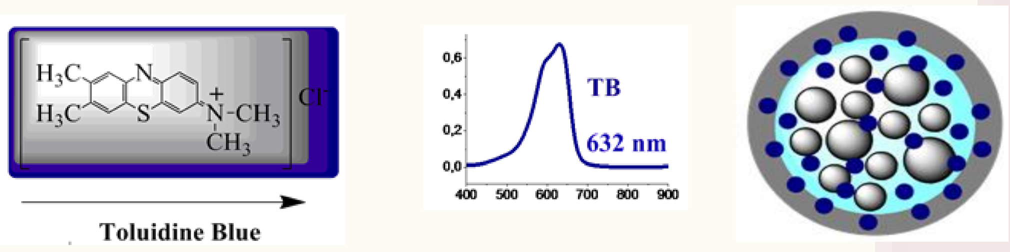
3th step

Coating of MNPs-SiO$_2$ with poly acrilic acid (pAAc)



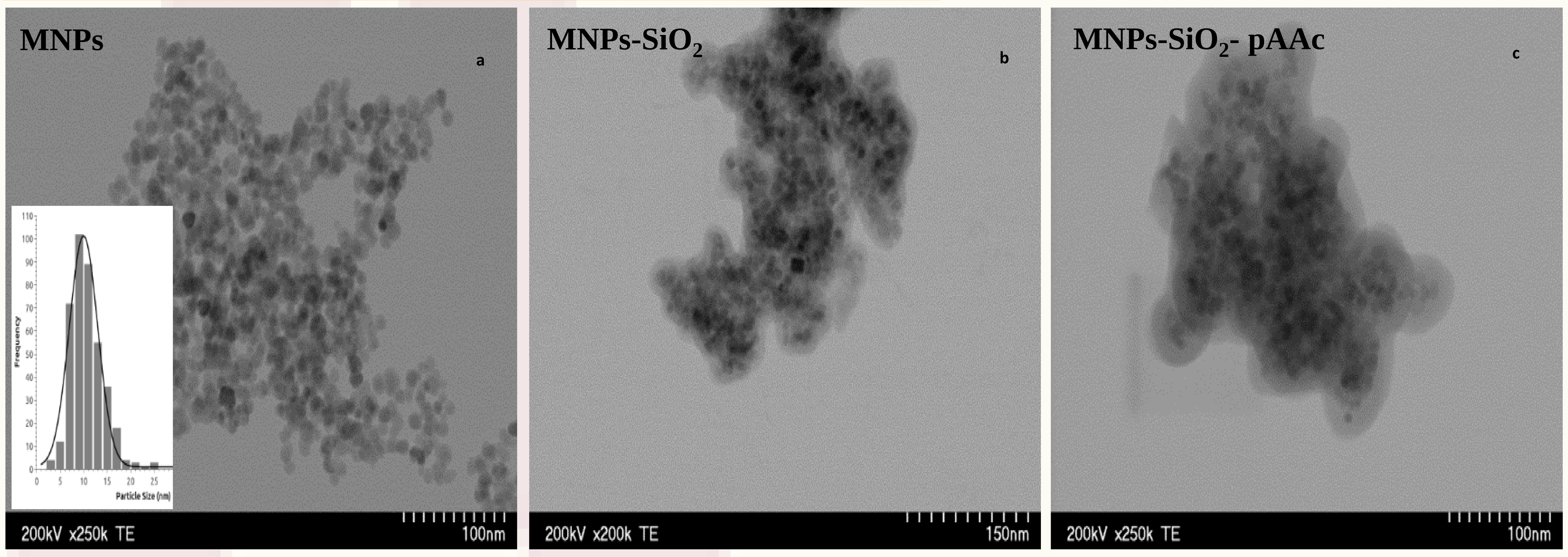
4th step

TB adsorption on MNPs-SiO$_2$- pAAc

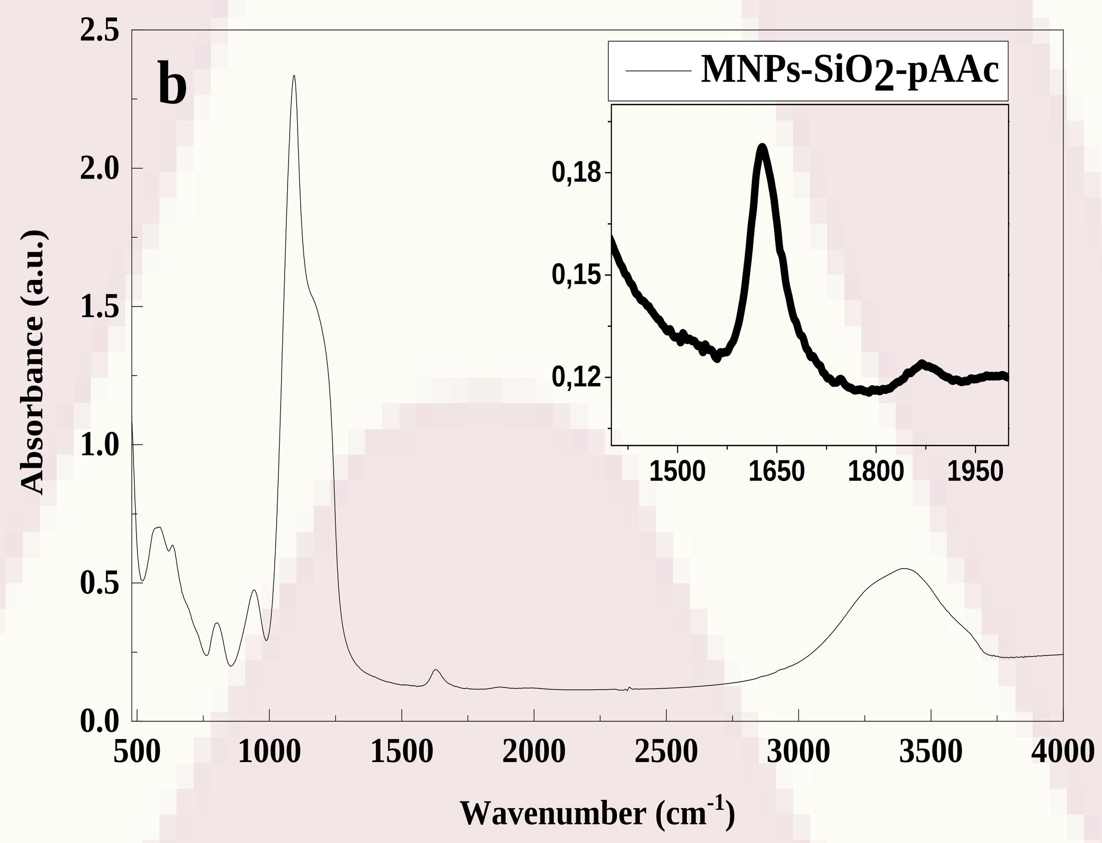


Characterization

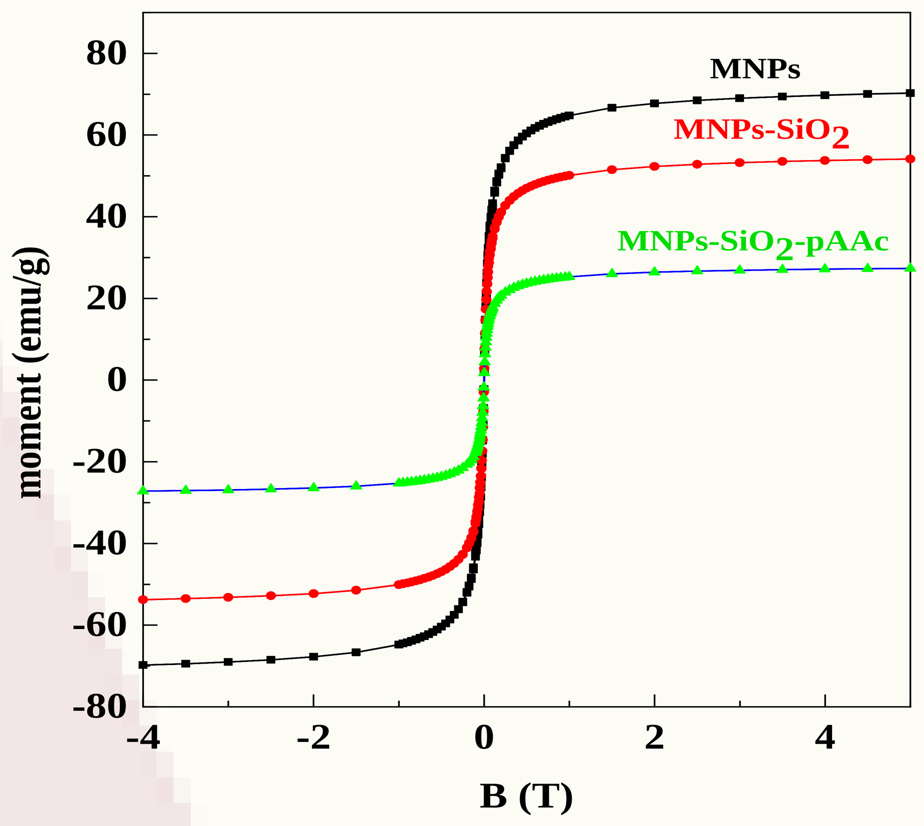
Morphological characterization by TEM



Structural characterization by FTIR



Magnetic characterization



Electrocatalytic process

$TBH^+ + NO_2^- \rightarrow TBH^+ \bullet NO_2^-$

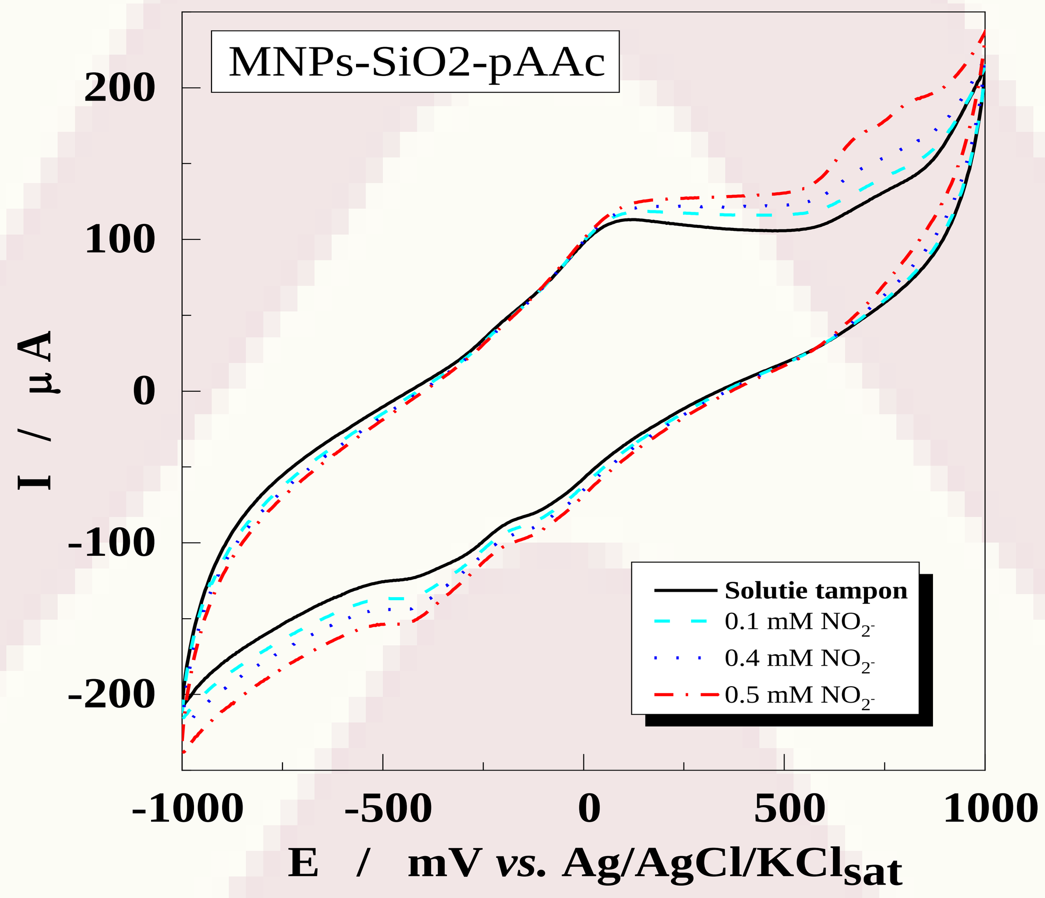
$TBH^+ \bullet NO_2^- + H_2O \rightarrow TBH^+ \bullet NO_3^- + 2H^+ + 2e^-$

$TBH^+ \bullet NO_3^- \rightarrow TBH^+ + NO_3^-$

Detection of nitrite in real samples

Water		Soil (solution)			
1	2	1 (0-20 cm/depth)	2 (20-40 cm/depth)	3 (0-20 cm/depth)	4 (20-40 cm/depth)
0.680 (mg/L)	0.704 (mg/L)	1.93 (mg/kg)	1.83 (mg/kg)	2.103 (mg/kg)	1.737 (mg/kg)

Electrochemical characterization



- The nitrite oxidation peak appears in this case at a potential closer to +100 mV *vs.* Ag/AgCl/KCl$_{sat}$
- The main analytical parameters are: sensitivity: 10.79 mA/M (R/N = 0.999/5); linear domain: 0.08–1 mM; detection limit 20 µM.
- The possible interference were studied in determination of nitrite. The results showed that 100-fold SO_4^{2-}, CO_3^{2-}, Cl^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+} had no effect on the current responses of 0.1 mM nitrite

Conclusions

- ✓ New modified electrode materials, based on a special combination of hybrid nanocomposites such as MNPs, magnetite (Fe_3O_4), inorganic polymer (SiO_2) and an organic polymer (pAAC) were studied.
- ✓ The organic polymer like hydrogel-type polymer (pAAc) poly acrylic acid was used to obtain a polymeric shell of cross-linked poly acrylic hydrogels with a favourable hydrogel structure and thicknesses which is perfectly suitable for adsorption of a relatively high concentration of Toluidine Blue (TB).
- ✓ As could be seen from the morphological measurements (TEM/SEM), MNPs-SiO$_2$-pAAc have very well-controlled properties related to the thicknesses, the MNPs are almost individually covered with a thin layer of cross-linked pAAc shell which offer a relatively high surface area which is perfectly suitable for adsorption of a relatively high concentration of TB.
- ✓ By electrochemical measurements, it was proved that this electrode presents electrocatalytic effect towards nitrite oxidation and can be used for nitrite detection.
- ✓ The electrocatalytic effect of MNPs-SiO$_2$-pAAc is good because the nitrite oxidation peak appears in this case at a potential closer to +100 mV *vs.* Ag/AgCl/KCl$_{sat}$
- ✓ The main analytical parameters are: sensitivity: 10.79 mA/M (R/N = 0.999/5); linear domain: 0.08–1 mM. The detection limit was calculated as 20 µM.

References

1. *G.M. Ispas, I. Crăciunescu, S. Porav, R. Turcu and D. Gligor, Sens. Actuators, A* ***276****, 43 (2018). doi:10.1016/j.sna.2018.03.032.*
2. *M.A. Cîmpean, I. Crăciunescu and D. Gligor, Mater. Chem. Phys.* ***200****, 233 (2017). doi:10.1016/j. matchemphys.2017.07.057.*

Cluj-Napoca 2021