WO_3 Nanoparticles Probes for Direct Electron Transfer of Proteins

L. Santos[1,*], C. Silveira[2,3], R. Martins[1], S. Todorovic[3], M. G. Almeida[2,4], E. Fortunato[1,*]

[1]CENIMAT/I3N, Dep. de Ciência dos Materiais, FCT-UNL and CEMOP-UNINOVA, 2829-516 Caparica, Portugal
[2]REQUIMTE, Departamento de Química, CQFB, FCT-UNL, 2829-516 Caparica, Portugal
[3]ITQB, Universidade Nova de Lisboa (UNL), Av. da República, 2780-157 Oeiras, Portugal
[4]Instituto Superior de Ciências da Saúde Egas Moniz, Monte da Caparica, 2829-511 Caparica, Portugal
*corresponding authors: ls.santos@campus.fct.unl.pt, emf@fct.unl.pt

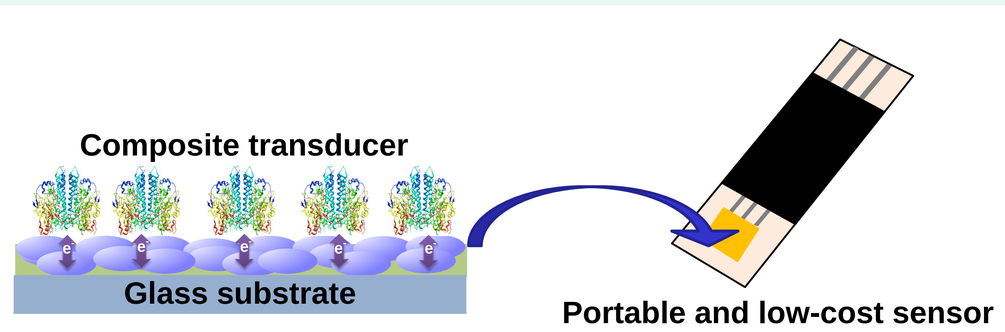
Introduction

Nitrites are constantly monitored for clinical diagnosis in physiological fluids and for environmental toxicity control in soil, water and air.

Electrochemical enzyme based biosensors are of particular interest due to their:
- operational simplicity,
- low cost fabrication,
- portability,
- real-time monitoring ability.

The ideal approach (3rd generation biosensors) allows direct electron transfer (DET) between the oxidoreductase and the electrode, thereby:
- increasing selectivity,
- simplifying the manufacturing process,
- requiring fewer reagents.

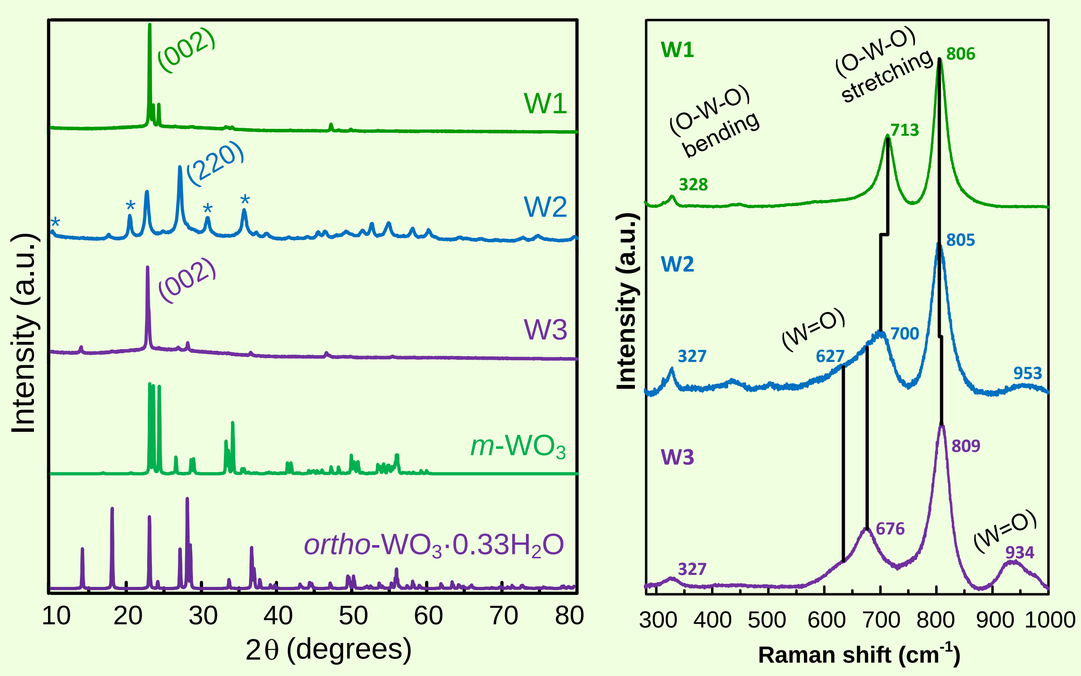
Propose of this work: Study of the electron transfer ability of WO_3 nanoprobes for the development of electrochemical nitrite biosensors and future implementation in a portable and low-cost sensing platform.



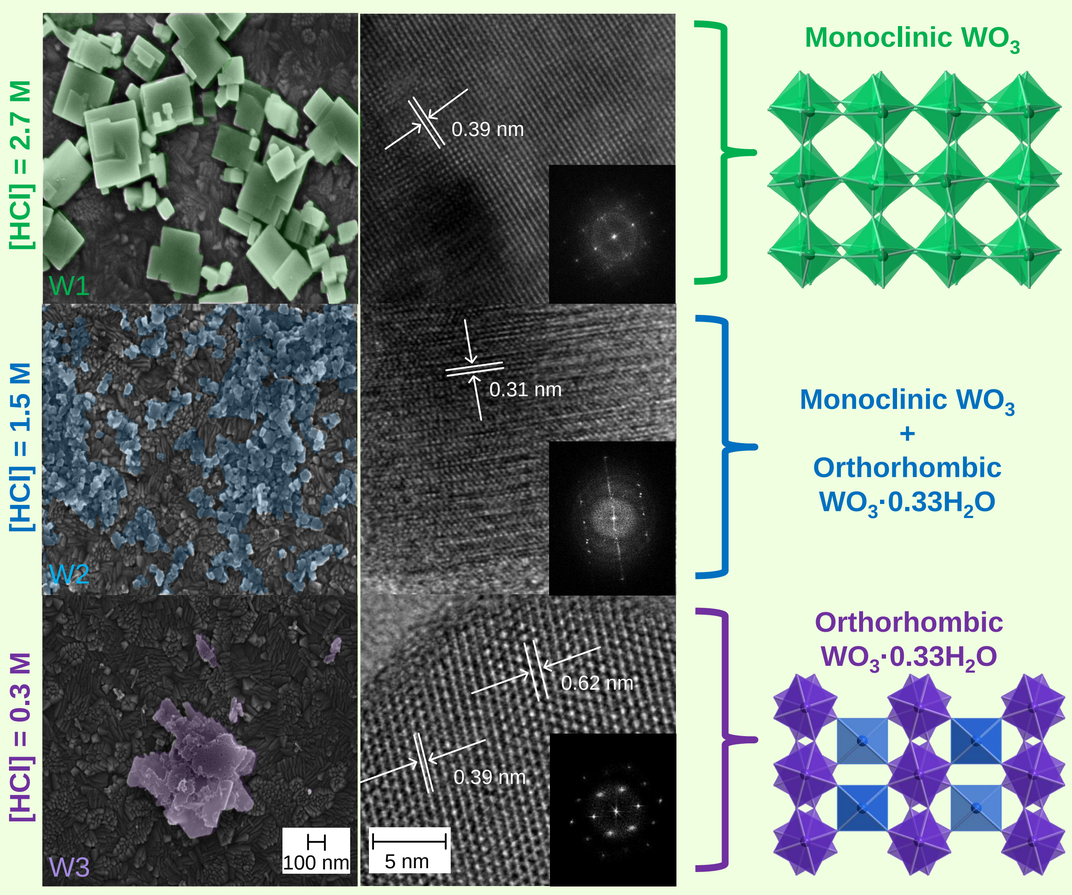
Experimental section

1. Hydrothermal synthesis of WO_3 nanoparticles

2. XRD and Raman characterization



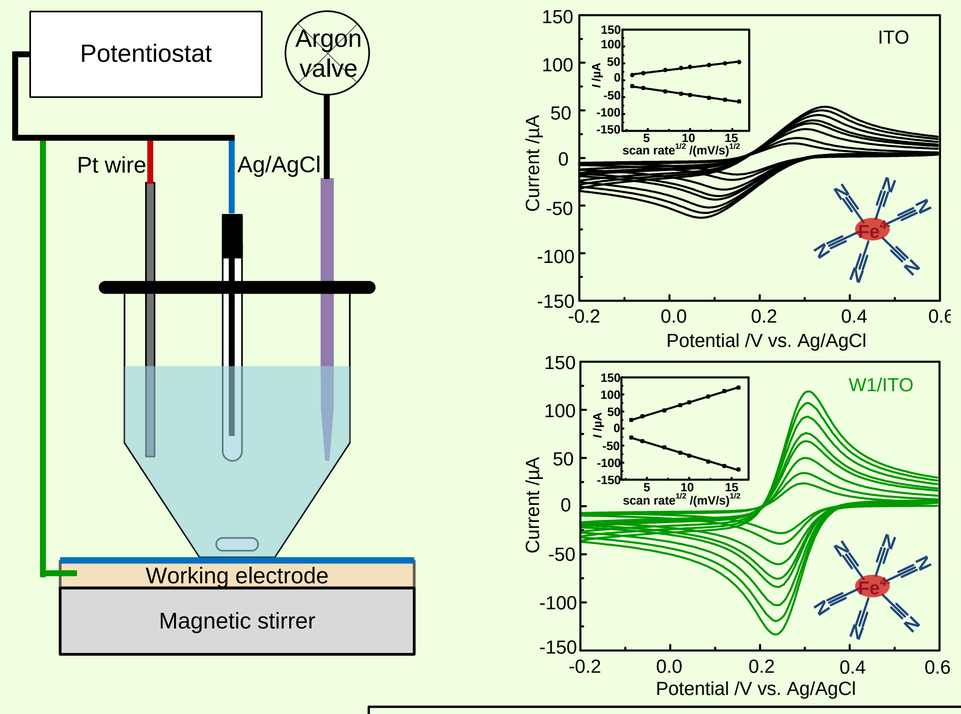
3. SEM and TEM characterization



4. Electrochemical characterization

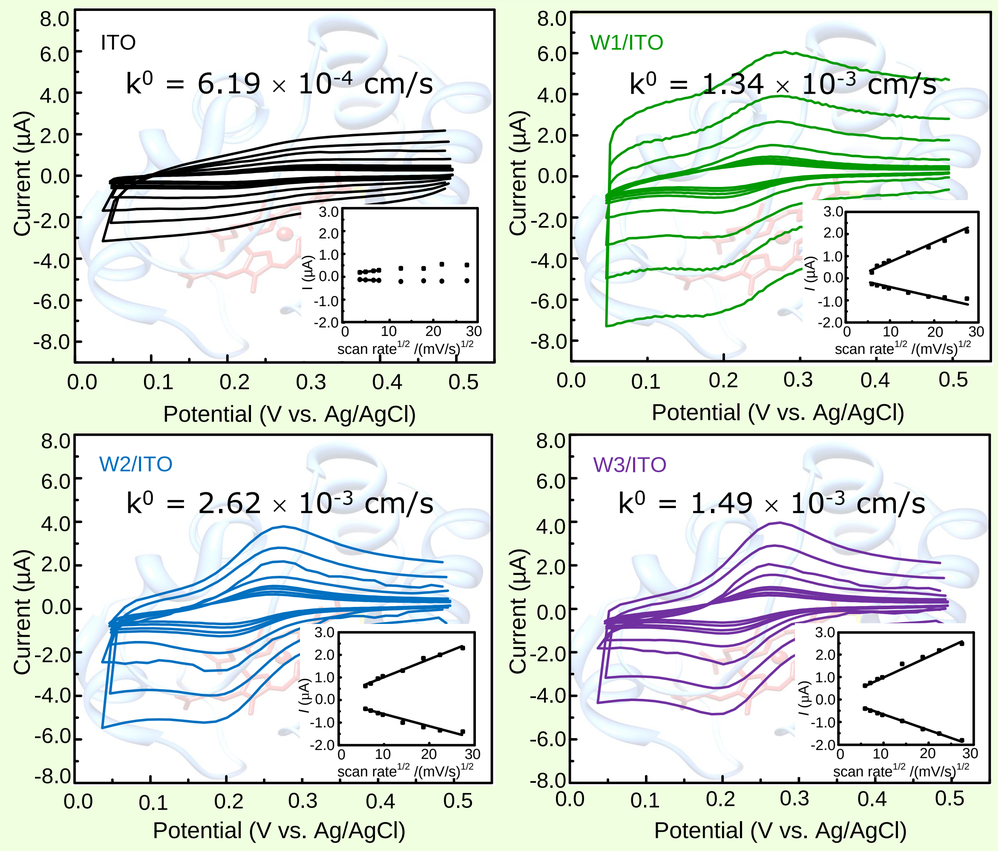
Ferrocyanide: $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$

Nernst equation: $I_p = 2.69 \times 10^5\, n^{3/2}\, A\, C\, D^{1/2}\, \upsilon^{1/2}$

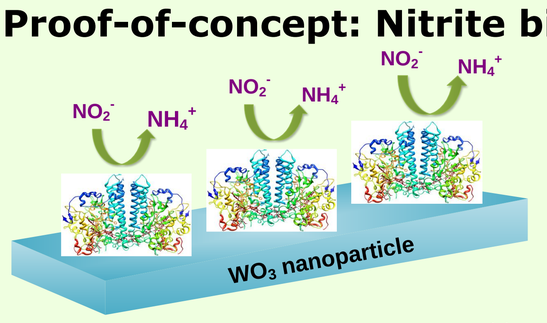


Cytochrome *c* (cyt *c*)

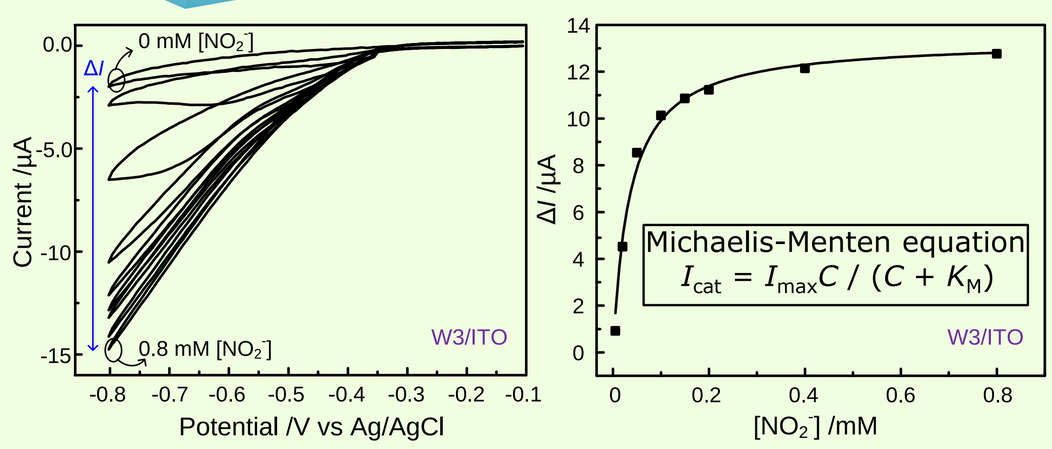
Kochi method
$k^0 = 2.18\, (\alpha \upsilon n F D_0 / RT)^{0.5} \exp(-\alpha 2 n F \Delta E_p / RT)$



5. Proof-of-concept: Nitrite biosensor



- Drop casted immobilized enzyme (ccNiR)
- Sensitivity between 1421 and 2143 mA/M cm²



Conclusions

- The interfacial electron transfer properties of the three WO_3 nanostructures were compared.
- The electroactive areas of the WO_3/ITO electrodes were calculated using ferrocyanide electron transfer probe and showed a significant increase due to the surface area of the nanostructured films.
- The higher conductivity of the $WO_3 \cdot 0.33H_2O$ nanostructures contributed for faster and reversible redox reactions with cyt *c*.
- ccNiR modified electrodes showed good electroactivity towards the reduction of nitrite. The lowest response was attained with the W2 electrodes as a result of the high capacitive current and impedance of this electrode.
- ccNiR/WO_3/ITO is a promising alternative for ccNiR based electrochemical biosensor as the sensitivities are similar to those obtained for single-walled carbon nanotubes.
- WO_3/ITO electrodes represent novel, biocompatible and efficient platforms for the development of protein electron transfer reactions.

FCT Fundação para a Ciência e a Tecnologia
This work is funded by FEDER funds through the COMPETE 2020 Programme and National Funds throught FCT-MEC under the project EXCL/CTM-NAN/0201/2012.