

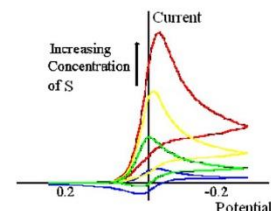
ВОЛТАМЕТРИСКИ СЕНЗОРИ ЗА ДЕТЕКЦИЈА НА ВОДОРОД ПЕРОКСИД

Rubin Gulaboski

Faculty of Medical Sciences

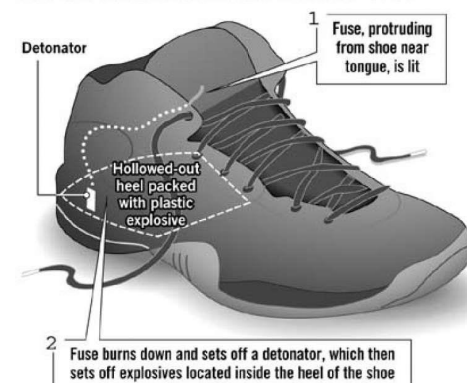
Goce Delcev University

EC' mechanism



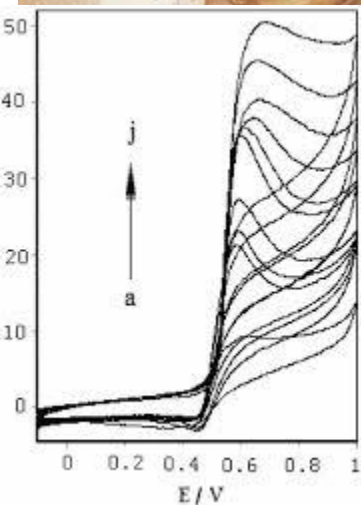
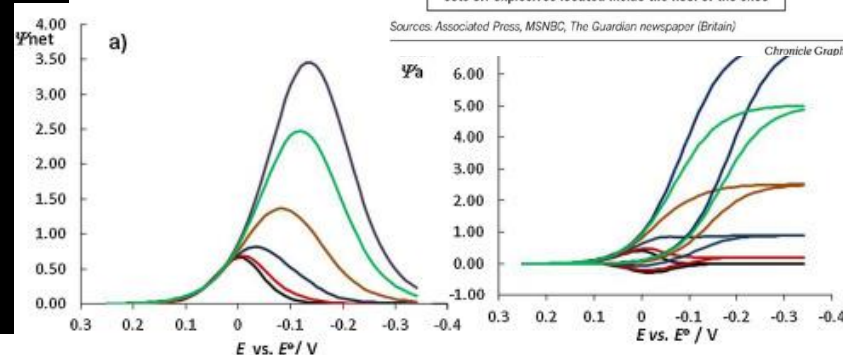
Sneakers loaded with explosives

Richard C. Reid was arrested last Saturday after flight attendants allegedly saw him try to touch a lit match to his black high-top basketball sneakers during a Paris-to-Miami flight. An FBI agent said tests showed that a highly volatile plastic explosive called TATP, or triacetone triperoxide, was in the sneakers. Here's how some officials think the device would have worked, according to news reports:



Sources: Associated Press, MSNBC, The Guardian newspaper (Britain)

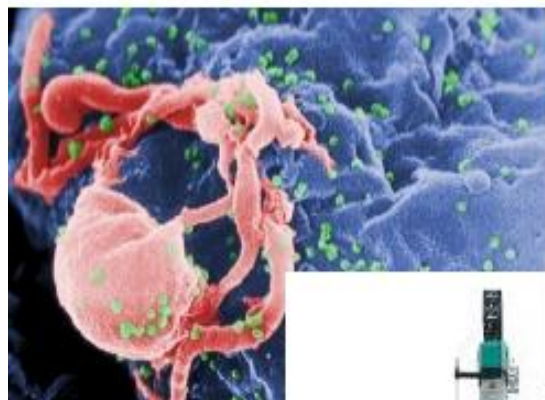
Chronicle Graph



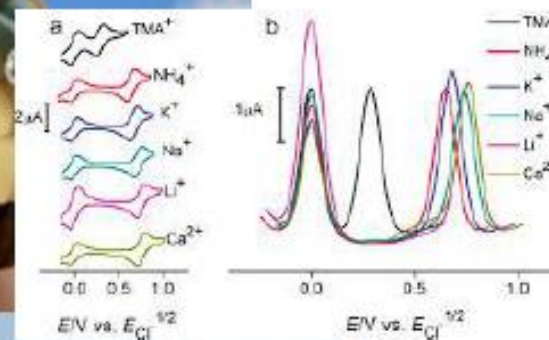
AIDS CURED!



...by Voltammetry!!!



Two Macedonian Scientists
Together with
D-r Kim Jong Un have
Explored Voltammetry to
Tackle AIDS and Ebola at once



That was to be expected...
Gulaboski, Mirceski and
Kim Jong Un have
Explored Voltammetry to
Build an Atomic Bomb



- First Atomic Bomb Used - Uranium
- Detonated over Hiroshima Aug. 6, 1945
- Weights 8,000 pounds

an 800-ton, 100-ft-long, 10-in.-dia. (2.5-m) cylindrical bomb

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2009 "UNDERPANTS BOMBER" PLOT

The Obama administration said on Monday that authorities in the Middle East recently seized an underwear bomb which had design features which were somewhat more sophisticated than a bomb used in two attempted attacks in 2009

Dec. 25, 2009

Northwest Airlines
Airbus
A330-300

Exit
G Galley
T Toilet

Economy
class

2
SEAT 20J
Passenger
notices
smoke and
dives across
to restrain
Abdulmutallab

Economy
class

Business
class



Seat 19A

1 Nigerian Umar Farouk Abdulmutallab tries to detonate a bomb which is stitched inside his underwear after covering himself with a blanket



3 The passenger and a flight attendant move to the front row where he is secured. Meanwhile a team of flight attendants extinguish the flames at his seat

PETN

- Also known as pentaerythritol
- Aug. 27, 2009 - a man with a bomb in his underwear tried to attack Prince Mohammed bin Nayef, a senior Saudi Arabian counter-terrorism official

Source: FBI

REUTERS





Paris Attack in 2015
-130 victims
Suicide bomber
wore **SHOES** filled with
Triacetone-Triperoxide
, or TATP

JIHADIS PLANNED AN EVEN BIGGER GAS CANISTER ATTACK

DEADLY ARSENAL: The canisters that would have been used in the attack

1 A house, above, in the small town of Alcanar is completely destroyed in an explosion on Wednesday. Police find the body of at least one suspected jihadi along with traces of the powerful explosive TATP – used in previous terror bombings and dubbed the ‘Mother of Satan’ – and gas canisters to be used in planned attacks.

2 Next day in Barcelona a van mows down pedestrians on Las Ramblas, killing 13 – but planned bomb attacks on La Sagrada Familia and the docks are abandoned

3 A car drives through pedestrians in Cambrils before five jihadi jump out and stab a woman to death. All five were shot dead by police.

Are there more bodies of jihadis in the rubble?

AT FIRST the authorities thought the blast that reduced an entire house to rubble was an accidental gas explosion.

In fact it was almost certainly caused by the deadly but unstable TATP homemade explosives favoured by suicide bombers. One jihadi was killed

In the blast and another injured and arrested. Police say there may still be a second body buried at the site.

Catalonia police tweeted on Friday: ‘We are working to determine if remains at Alcanar are a second corpse. ‘We are working to determine if biological traces from Alcanar are human.’

BARCELONA

CAMBRILS

ALCANAR

La Sagrada Familia

Placa Catalunya

BARCELONA

Liceu Theatre

Marina and docks

Mediterranean Sea

1,000 ft

A van ploughs into crowds in the Las Ramblas avenue on Thursday, killing at least 13 people



A stylized illustration of the Eiffel Tower in brown and tan colors, positioned on the right side of the page.

(U//FOUO) General information on TATP

(U//FOUO) TATP Hazards:

- (U//FOUO) Extremely sensitive to impact, friction, static/sparks, and heat.
- (U//FOUO) May react violently to illegal-drug field testing if large amounts are tested at once.

(U//FOUO) Key Identifiers:

- (U//FOUO) Crystals or powder
- (U//FOUO) Colorless or white
- (U//FOUO) Fruity smell; old TATP smells like bad vinegar.
- (U//FOUO) May be stored in refrigerator or freezer.

(U//FOUO) Chemical Components:

- (U) Acetone (nail polish remover, paint remover)
- (U) Acid (sulfuric, nitric, hydrochloric)
- (U) Hydrogen peroxide

(U//FOUO) Lab Equipment:

- (U) Glassware
- (U) Distillers
- (U) Mixers
- (U) Ice Bath
- (U) Filters



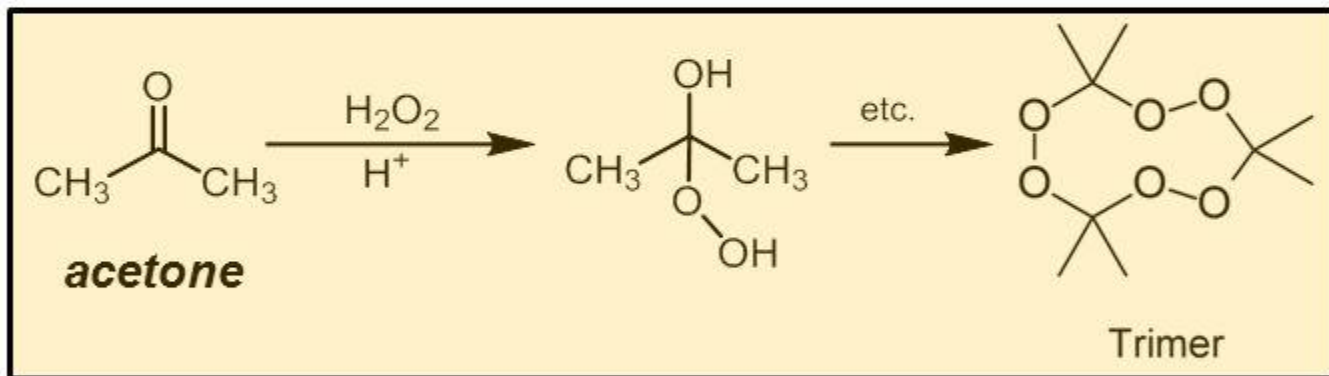
(U//FOUO) Photo of fine TATP.



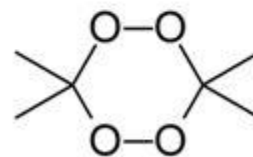
(U//FOUO) Photo of crude TATP.

TATP (*“triacetone triperoxide”*)

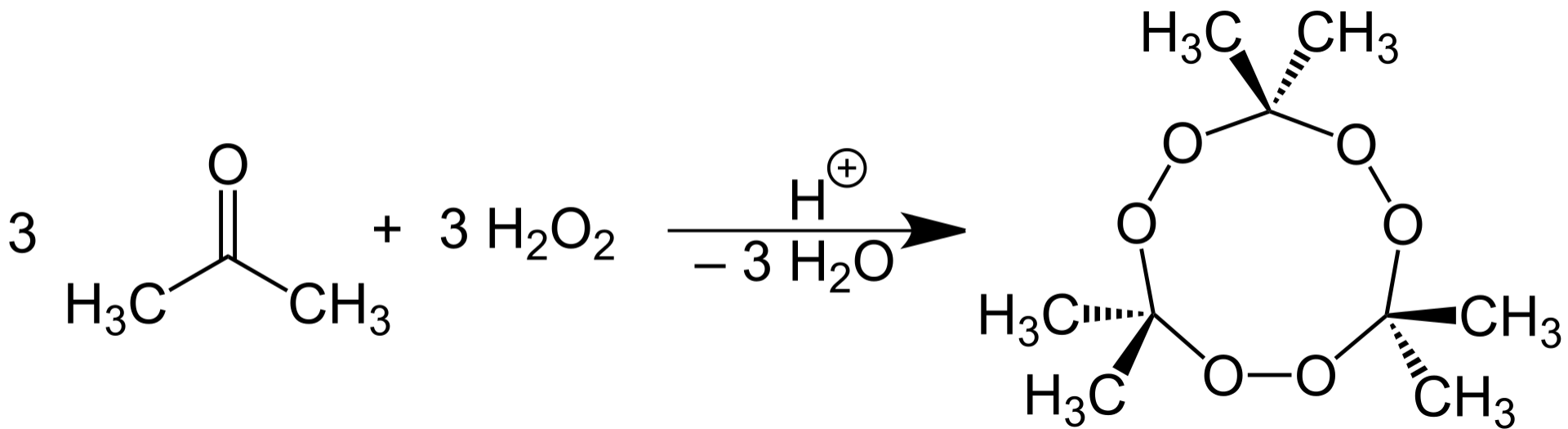
1. One of the most unstable of explosives
2. Readily made from acetone (ADDITION of hydrogen peroxide)
3. Commonly used by terrorists; difficult to detect
4. Explosive used in the London subway bombings (July 7, 2005)



*White crystalline
powder with bleach
odour*



Dimer



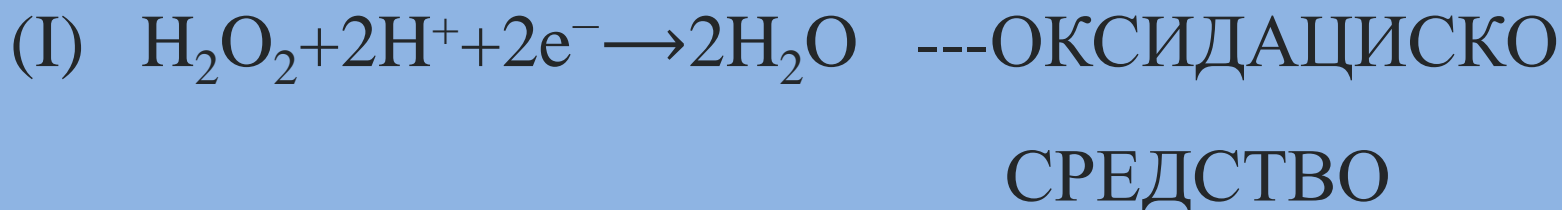
BUT.....Hydrogen peroxide (H₂O₂) is a synthetic precursor and degradation product of peroxide-based explosives, such as TATP.

The substrate: hydrogen peroxide

- Hydrogen peroxide is toxic to cells
 - Produced as a waste product during the reactions that occur in the body.
- Body needs way to remove it quickly so cells don't die
 - $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$. The products water and oxygen are not harmful.
 - Body can remove it quickly with enzyme called CATALASE. CATALASE changes H_2O_2 into water and oxygen.

H₂O₂ може да биде и ОКСИДАЦИСКО и РЕДУКЦИСКО СРЕДСТВО

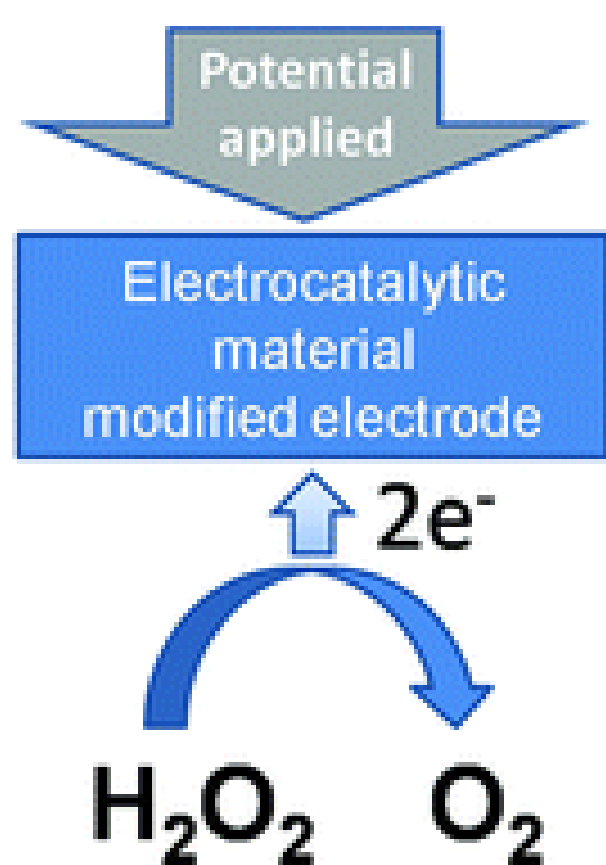
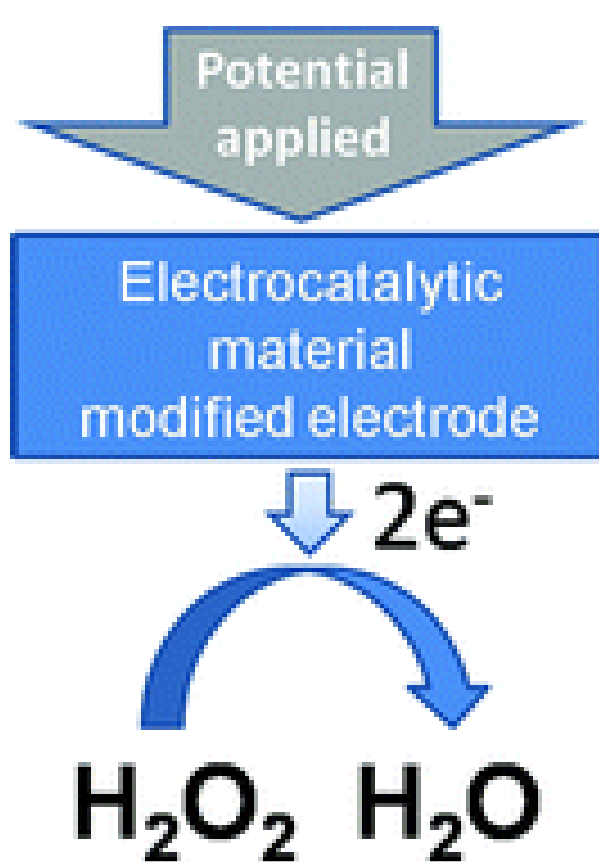
Две наједноставни сценарија за редукција и оксидација на H₂O₂



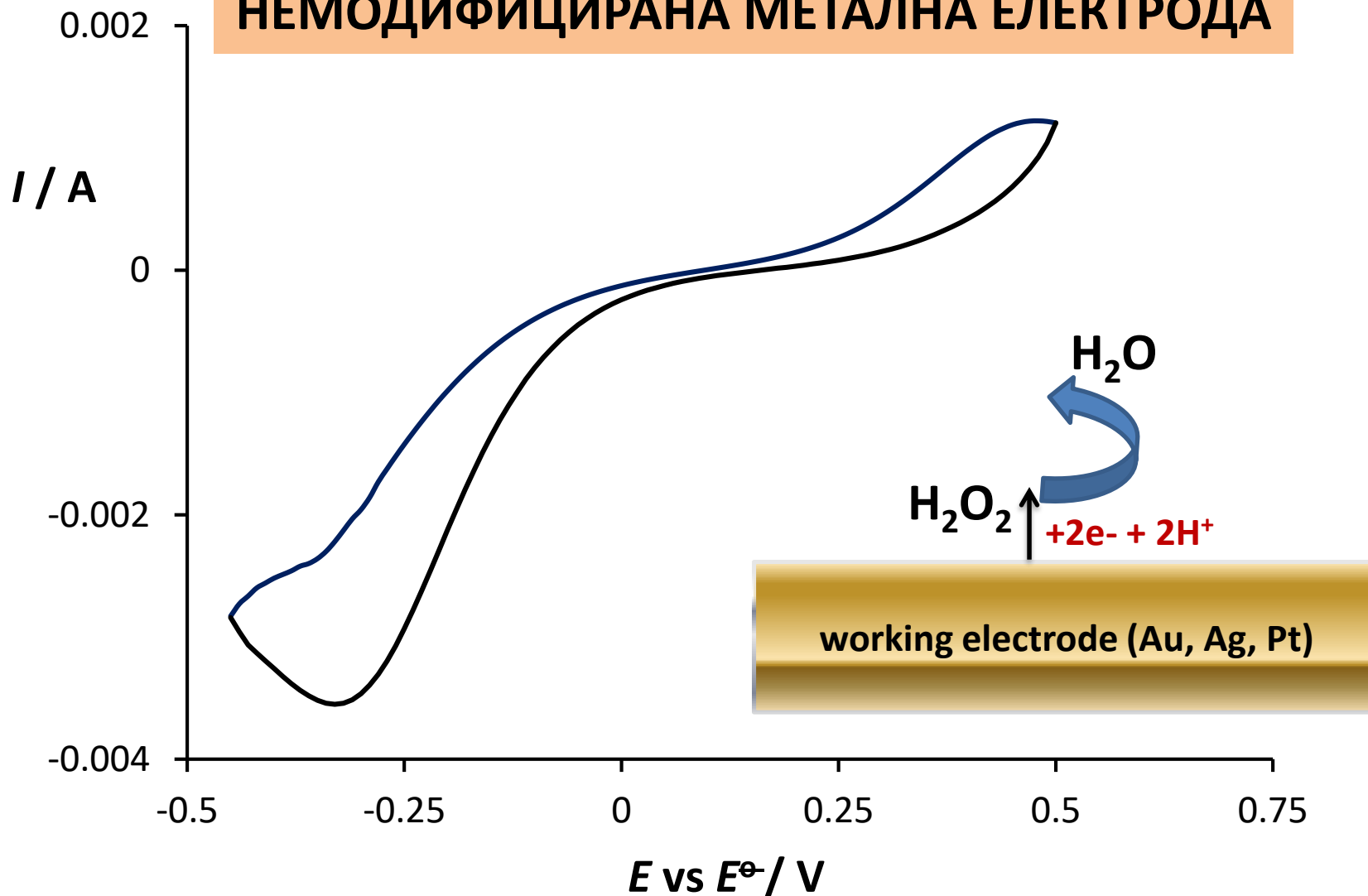
$$E^\circ = +1.534 \text{ V vs. SCE (at pH of 7.00)}$$



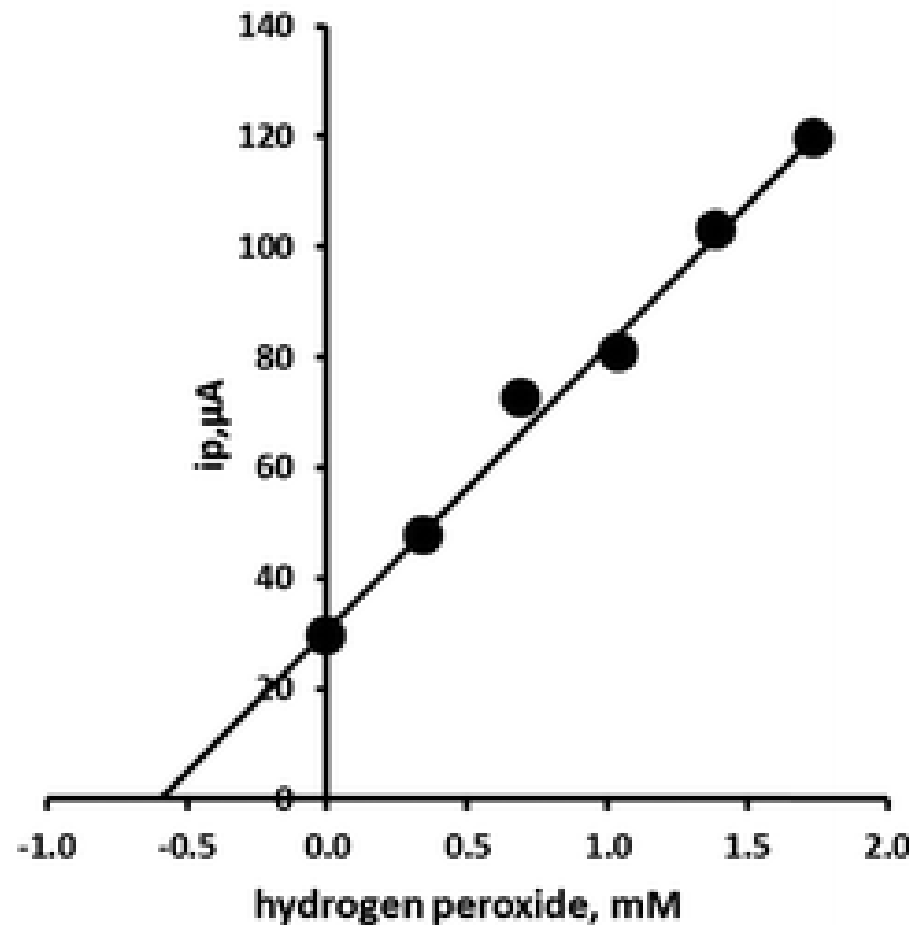
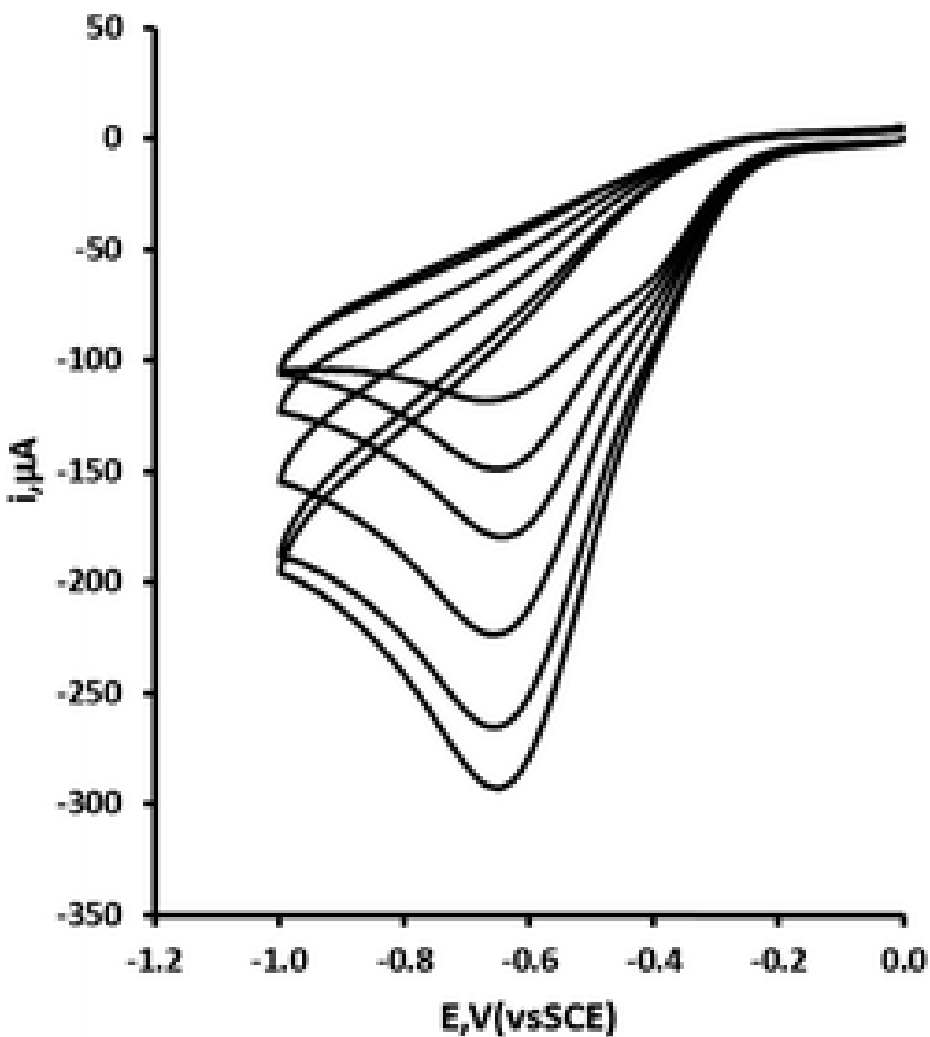
$$E^\circ = +0.440 \text{ V vs. SCE (at pH of 7.00)}$$



H₂O₂ сензори на НЕМОДИФИЦИРАНА МЕТАЛНА ЕЛЕКТРОДА



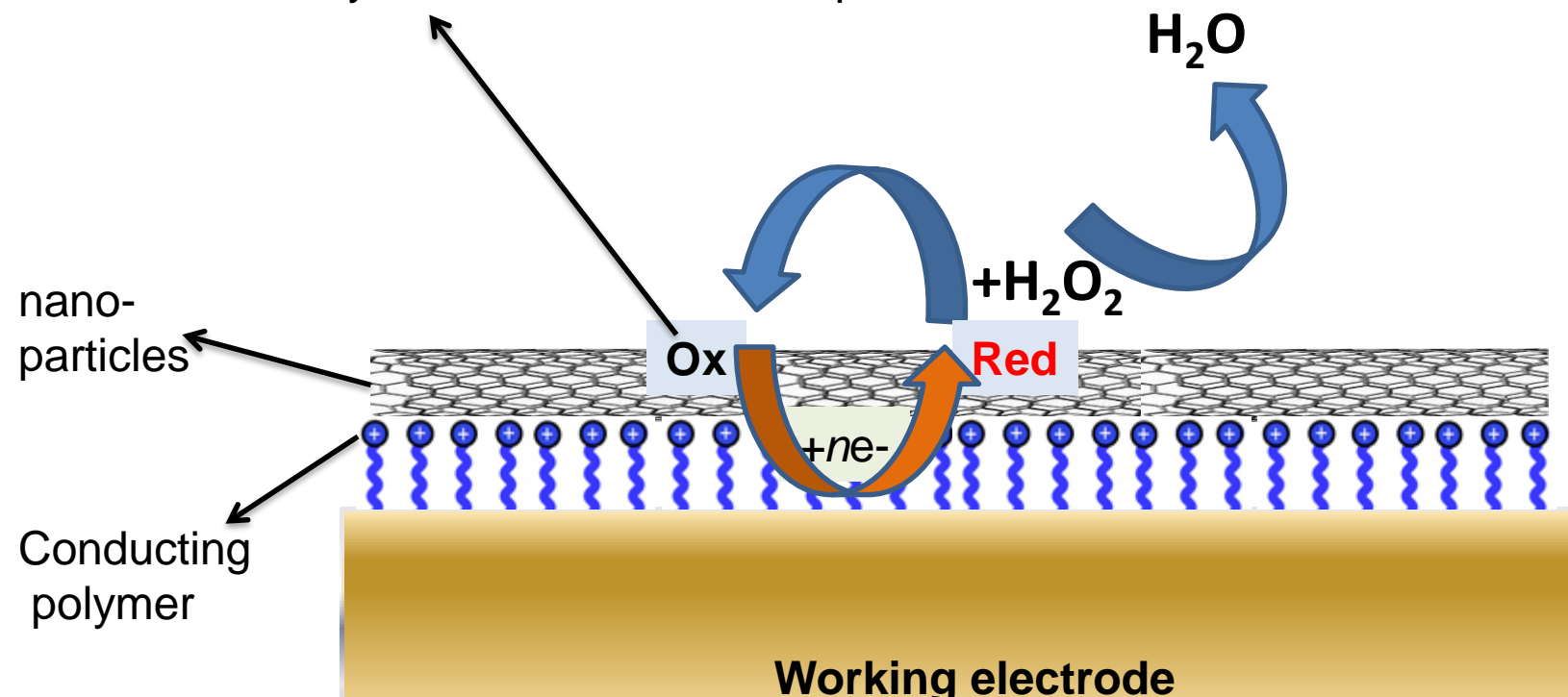
Features of the cyclic voltammogram showing the process of reduction of H₂O₂ at bare metallic electrodes



Директно определување на H_2O_2 на ПЛАТИНСКА ЕЛЕКТРОДА

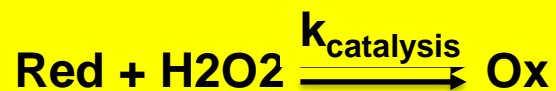
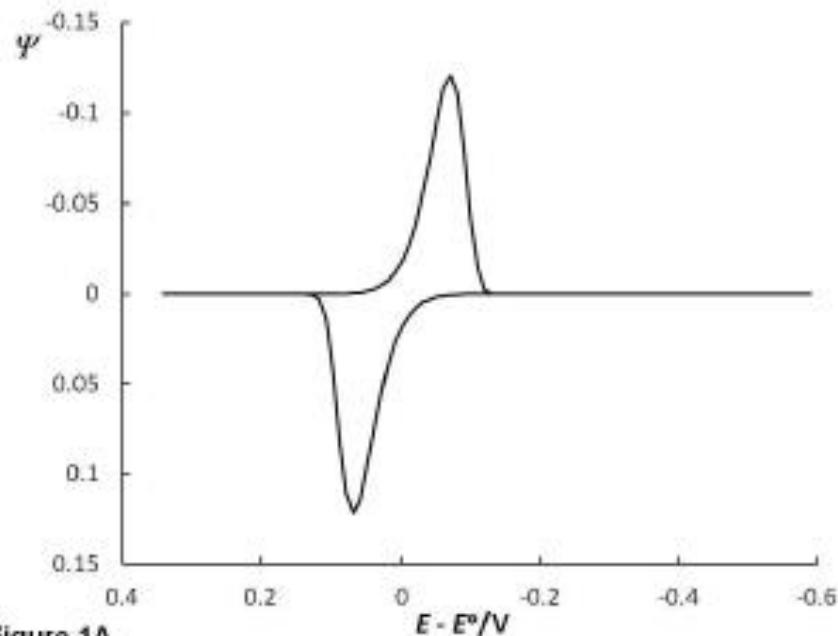
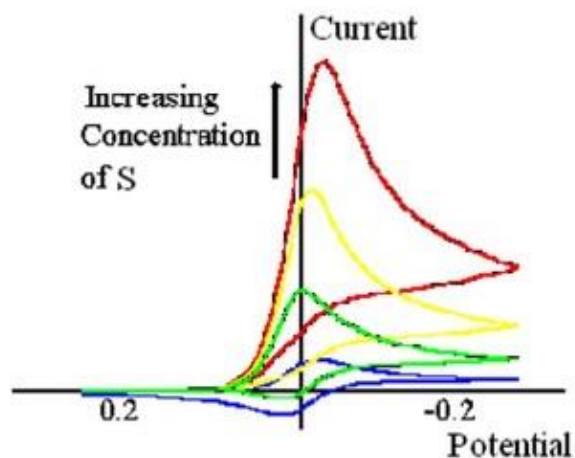
2. СЕНЗОРИ за H_2O_2 со модифицирана работна електрода и со РЕДОКС МЕДИЈАТОР кој е ШАТЛ за електрони помеѓу H_2O_2 и Модифицираната работна електрода

Ox is the oxidized form of redox active mediator that is initially adsorbed at the nano-particles

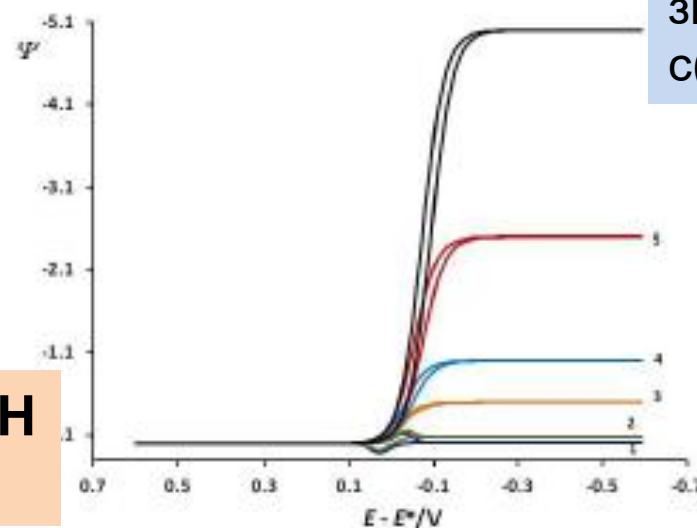


working electrode modified with conducting polymer and nano-particles, designed for hydrogen peroxide voltammetric detection. The Ox is the redox mediator adsorbed at the modified-electrode surface

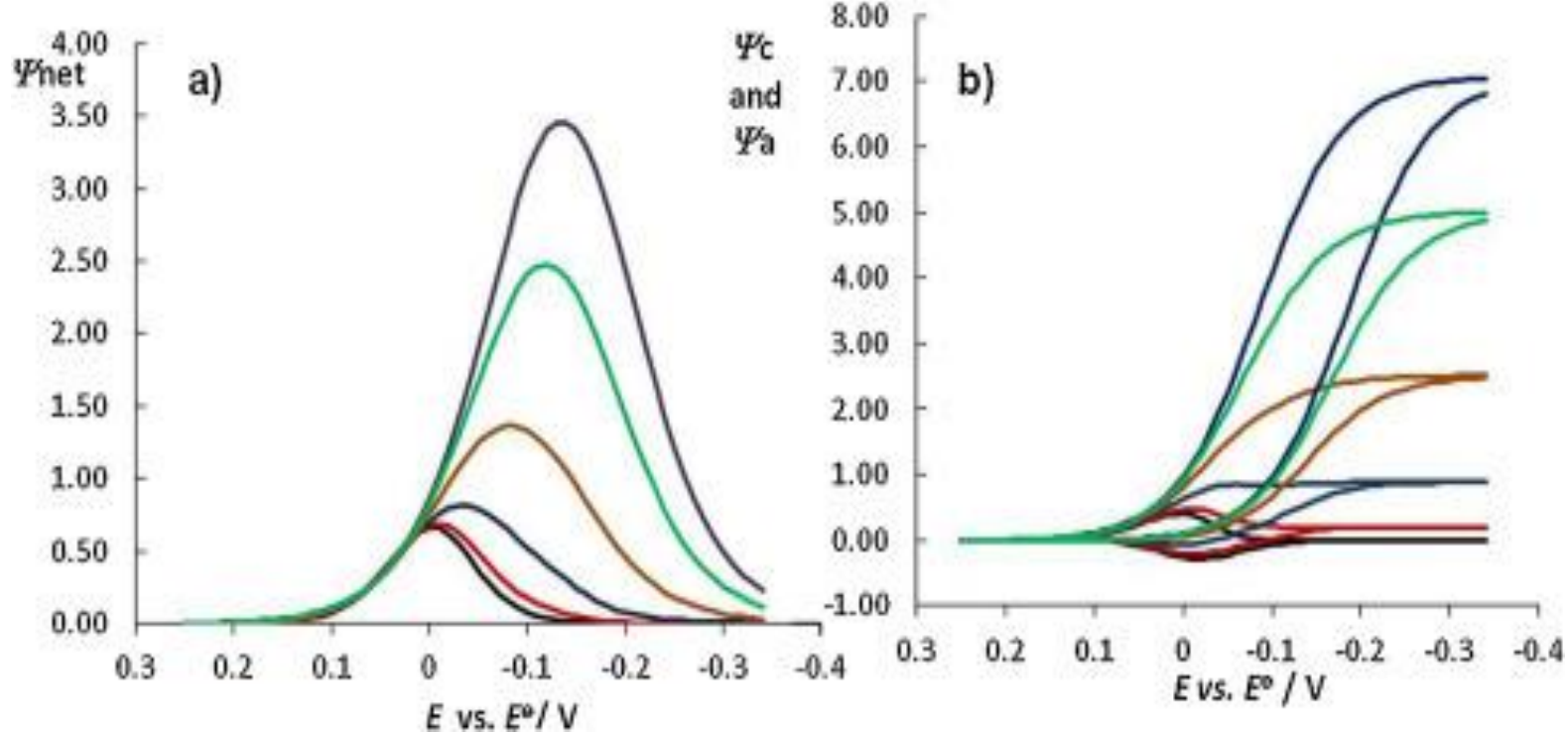
EC' mechanism



**ЕЛЕКТРОХЕМИСКИ-РЕГЕНЕРАТИВЕН
ЕЛЕКТРОДЕН МЕХАНИЗМ**

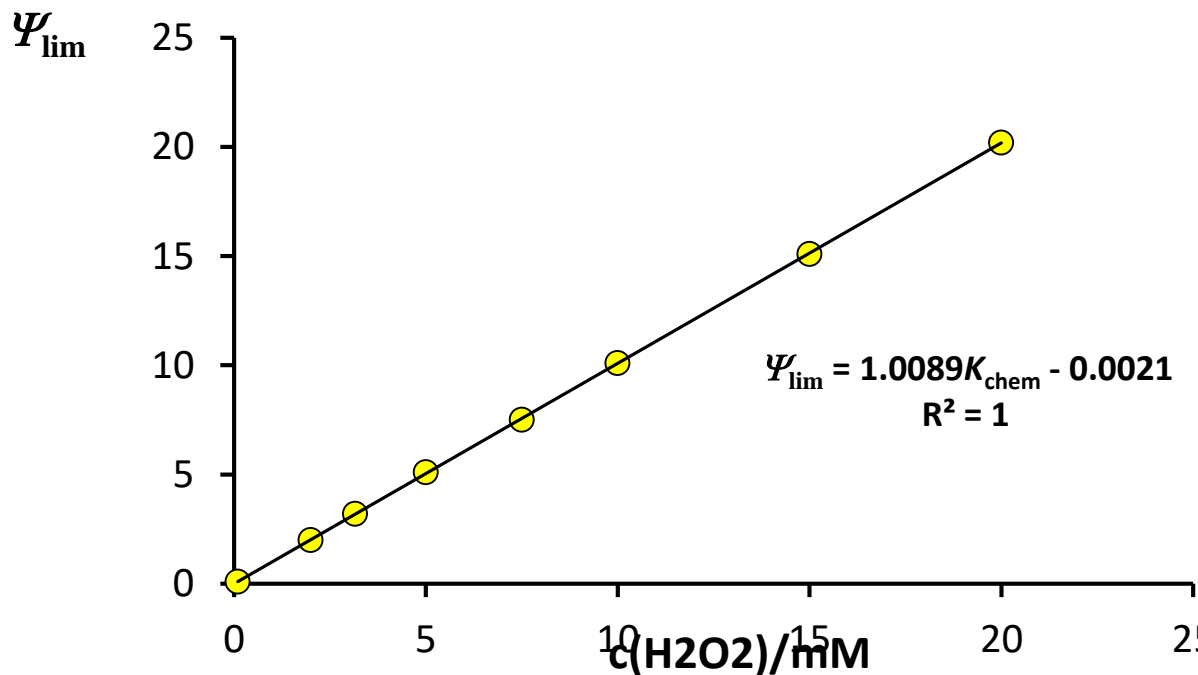


Ce
зголемява
с(H₂O₂)



Квадратно БРАНОВА ВОЛТАМЕТРИЈА

Електрохемиски РЕГЕНЕРАТИВЕН МЕХАНИЗАМ



**Графитна електрода
Модифицирана со
МЕКРАПТО-УНДЕКАНОИЧНА
Киселина и со
ЗЛАТНИ НАНОЧЕСТИЧКИ
-Сензор за H₂O₂ со
Редокс медијатор комплекс на
железо**

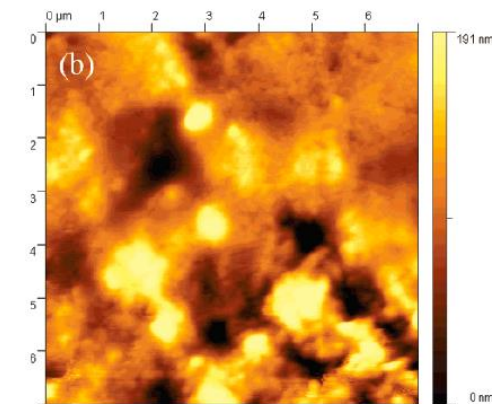


Figure 2. Topographic tapping mode AFM image of bare carbon electrode (a) and carbon electrode modified with Au-MUA NPs of 3.0 nm average diameter (b). Image sizes were $1.5 \times 1.5 \mu\text{m}$ (a) and $7 \times 7 \mu\text{m}$ (b), respectively.

Gulaboski et al

Graphite Electrodes Modified with Au-MUA NPs

J. Phys. Chem. C, Vol. 112, No. 7, 2008 2433

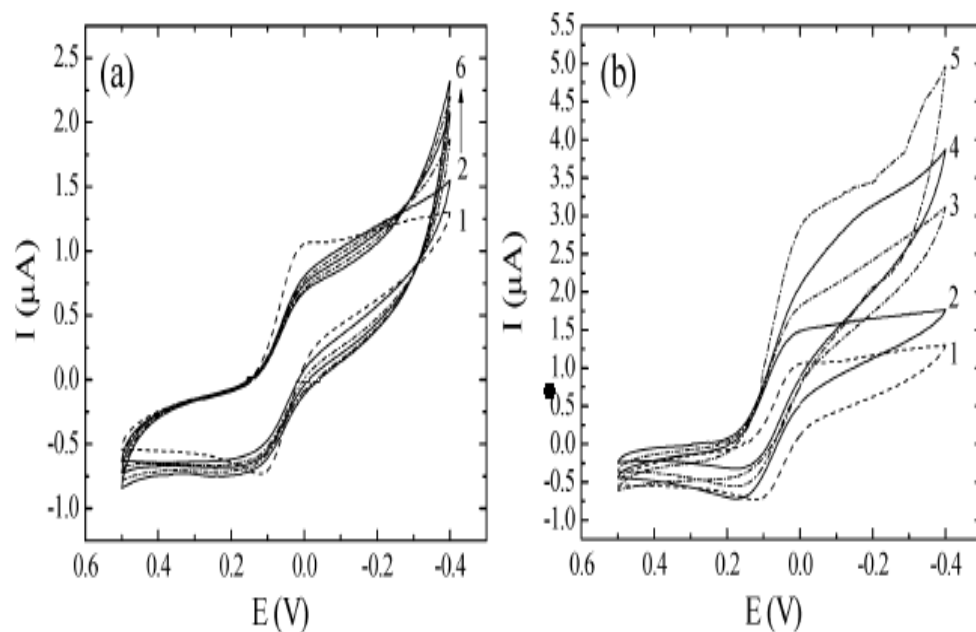


Figure 7. (a) Cyclic voltammograms showing the effect of hydrogen peroxide by the regeneration reaction of $\text{K}_3[\text{Fe}(\text{CN})_6]$ at the bare graphite electrode. $c([\text{Fe}(\text{CN})_6]^{3-}) = 0.25 \text{ mmol/L}$; $c(\text{H}_2\text{O}_2)/\text{mmol L}^{-1} = 0$ (1), 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), and 0.5 (6). (b) Cyclic voltammograms recorded at Au-MUA NP modified graphite electrode (adsorption time of 4 h): $c(\text{H}_2\text{O}_2)/\text{mmol L}^{-1} = 0$ (1), 0.1 (2), 0.2 (3), 0.3 (4), and 0.4 (5). The scan rate was 50 mV/s, while the supporting electrolyte was 0.1 mol/L acetate buffer (pH 4.70).

Волтаметриски сензор за квантификација на H₂O₂ со Атсорбиран Азобензен на живина електрода Мирчески, Гулабоски, ElectroANALYSIS 2001

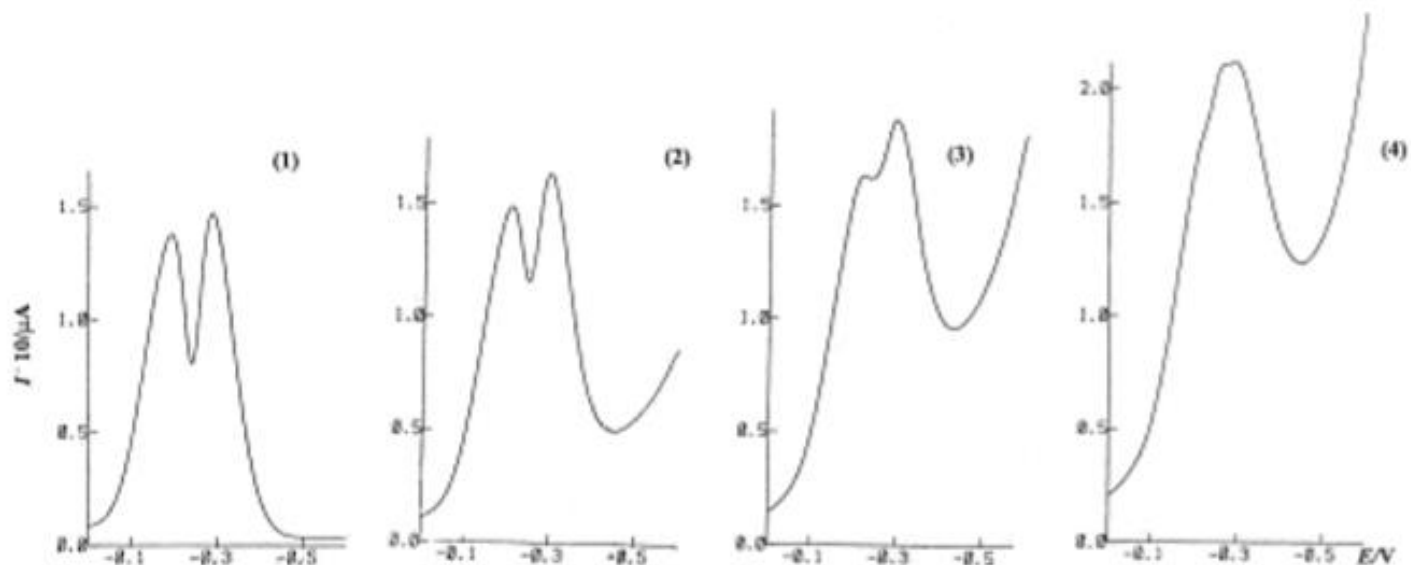
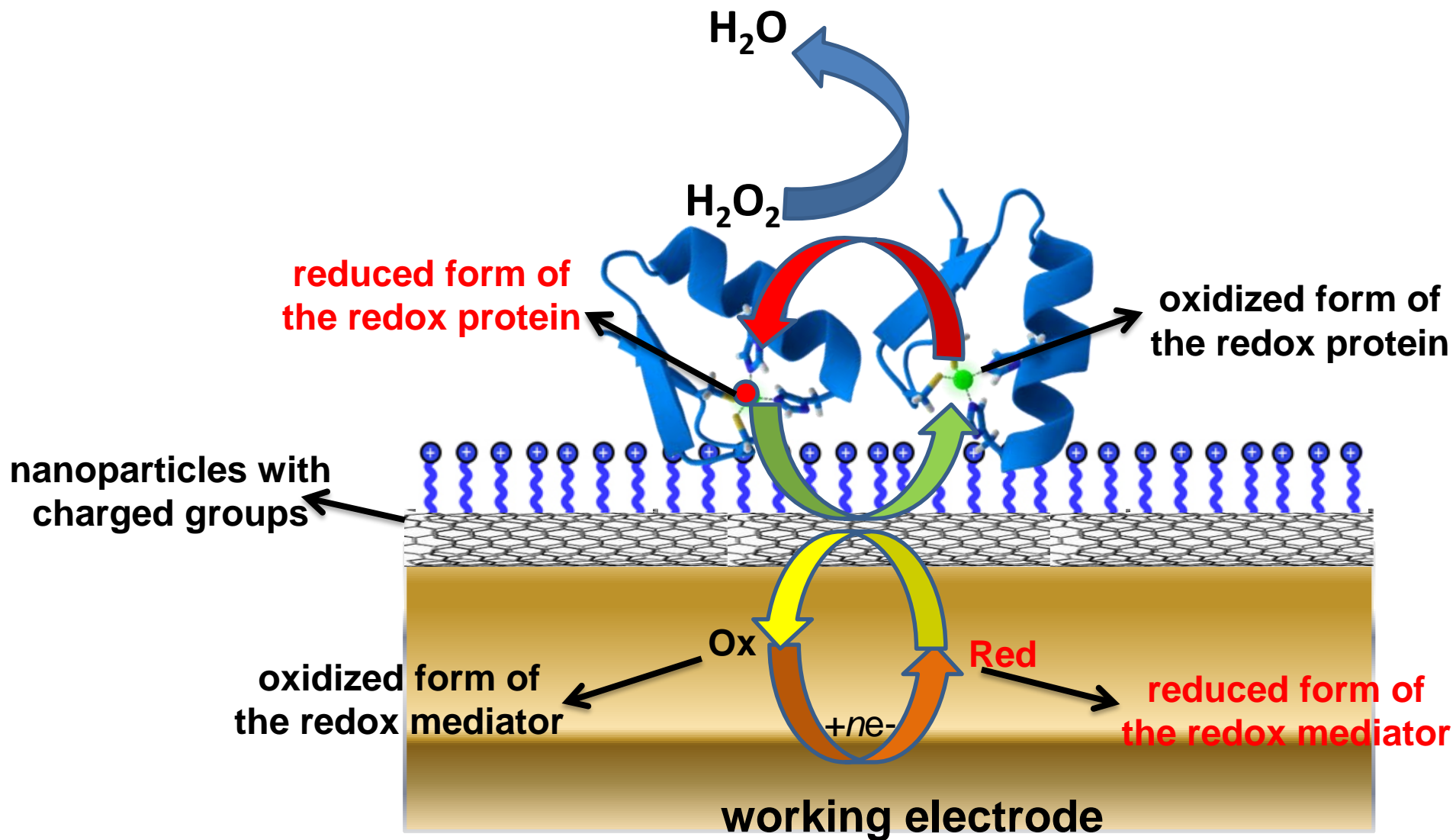


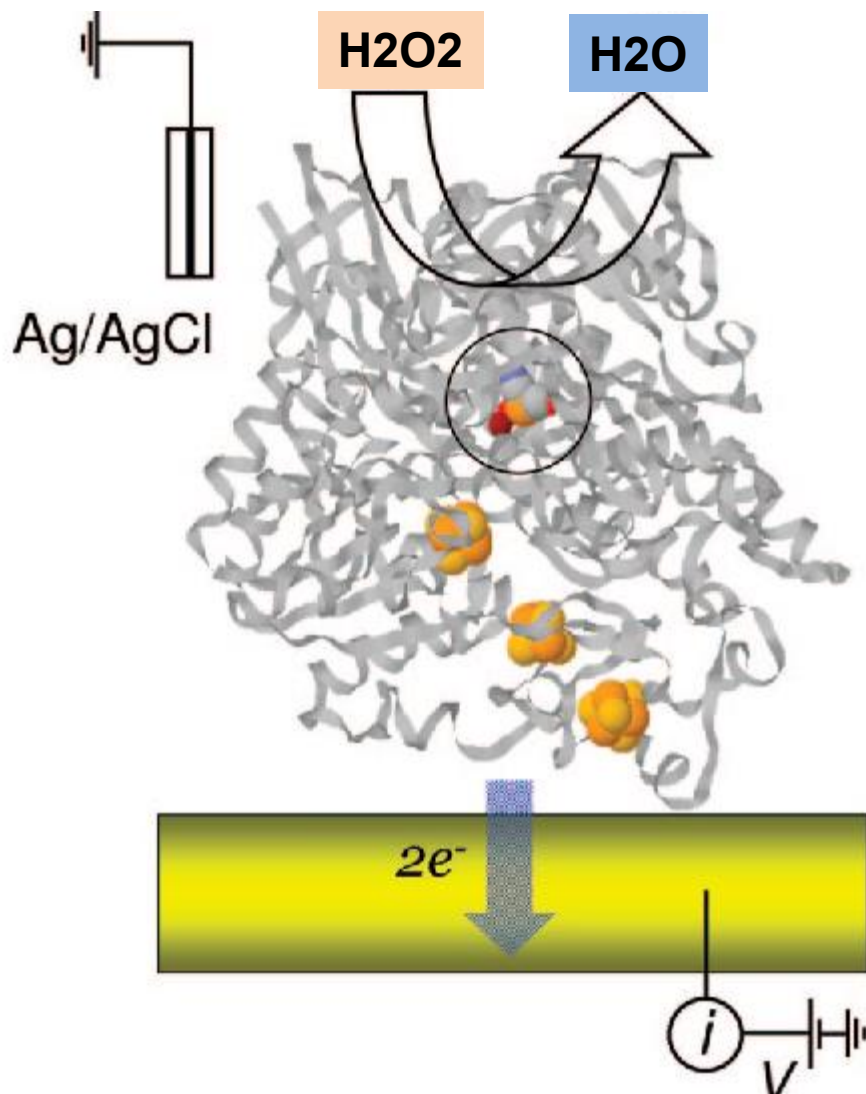
Fig. 12. Influence of hydrogen peroxide on the split SW response of azobenzene. The experimental conditions are: $c(\text{azo}) = 5 \times 10^{-5} \text{ mol/L}$, pH 4.2 (acetate buffer), $t_{\text{acc}} = 15 \text{ s}$, $E_{\text{acc}} = 0.0 \text{ V}$, $E_{\text{sw}} = 150 \text{ mV}$, $f = 40 \text{ Hz}$, $dE = 2 \text{ mV}$ and $c(\text{H}_2\text{O}_2)/\text{mol L}^{-1} = 0$ (1), 0.0116 (2), 0.0231 (3) and 0.0571 (4).

Electroanalysis 2001, 13, No. 16

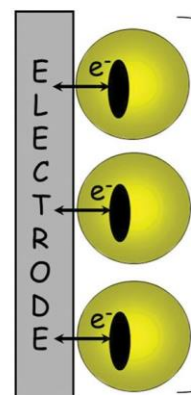
3. ЕНЗИМАТСКИ СЕНЗОРИ ЗА ДЕТЕКЦИЈА на H₂O₂



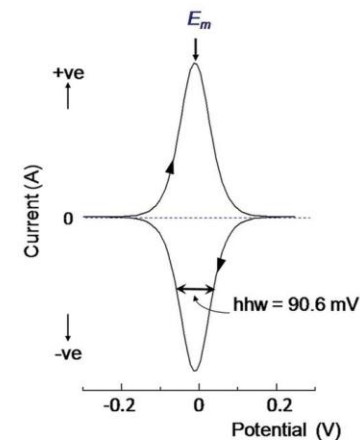
ДЕТЕКЦИЈА НА H₂O₂ со ПРОТЕИН-ФИЛМ ВОЛТАМЕТРИЈА



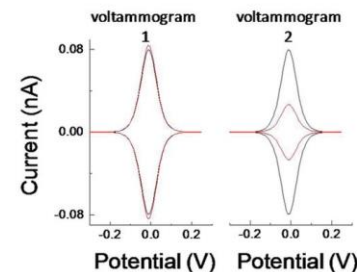
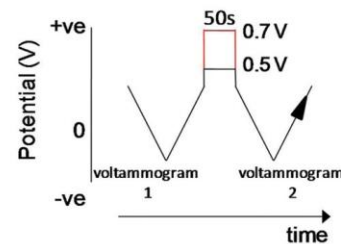
A



The adsorbed protein film can be placed in solutions of different composition, temperature etc.

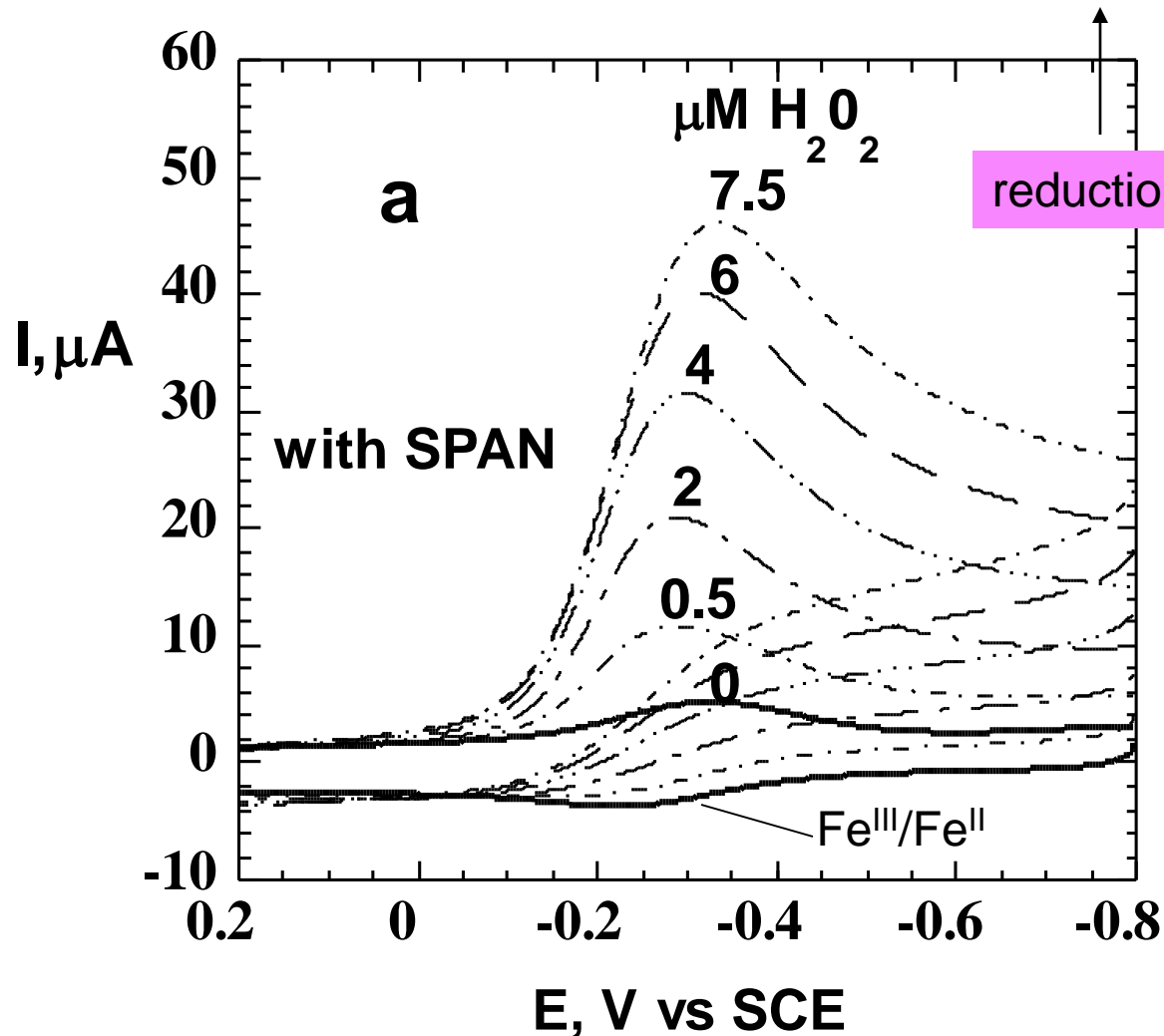


B



Catalytic reduction of H_2O_2 by peroxidase films

Catalytic cycles increase current



Nanocomplex formation



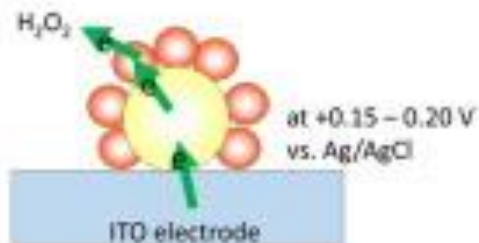
Малку различно

Сценарио....

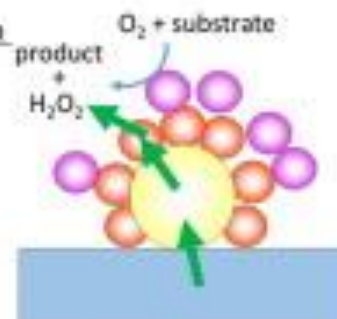
Аи-комплекс со пероксидаза

Ензим...

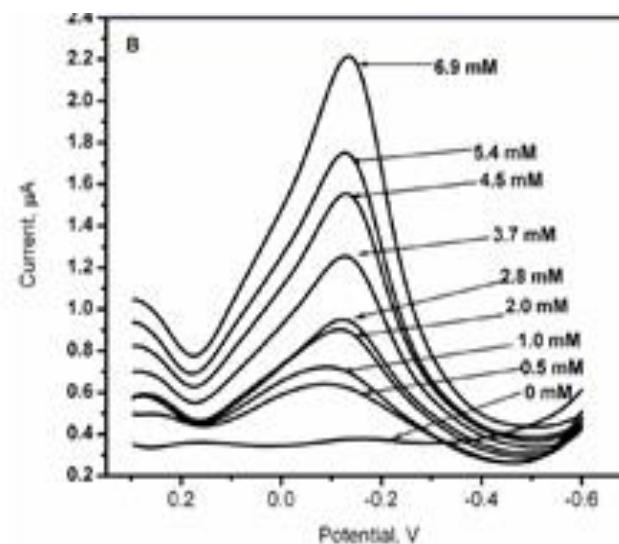
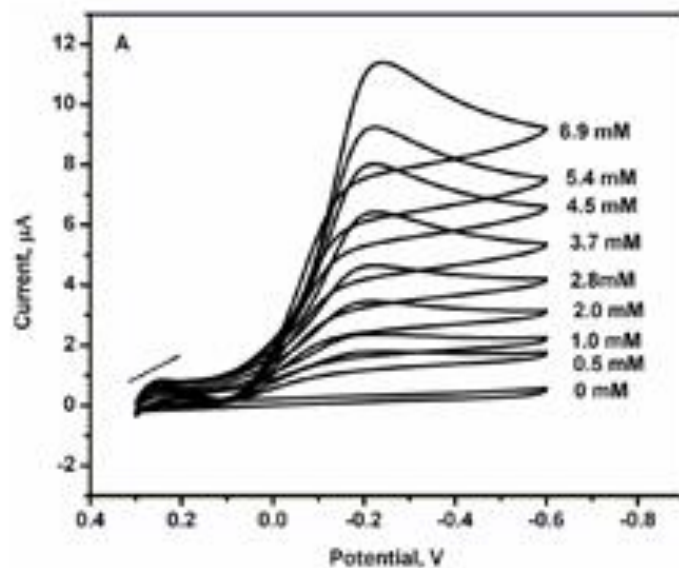
Direct electron transfer



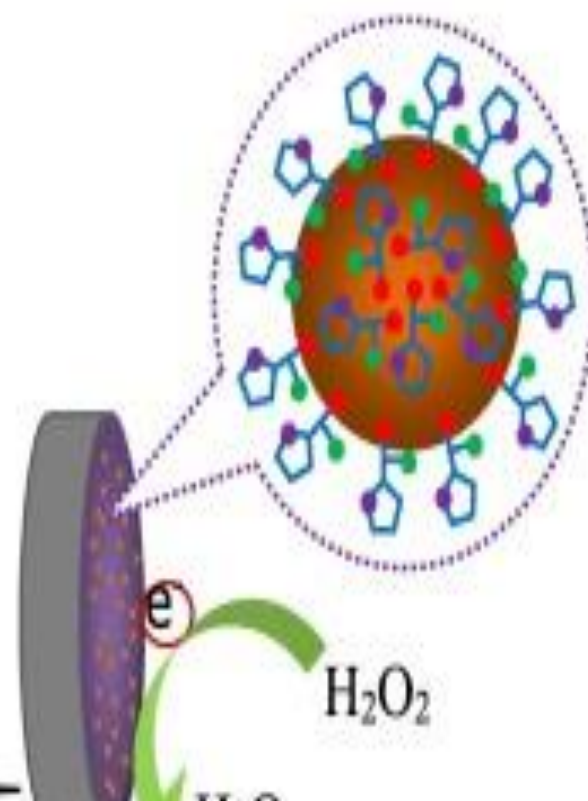
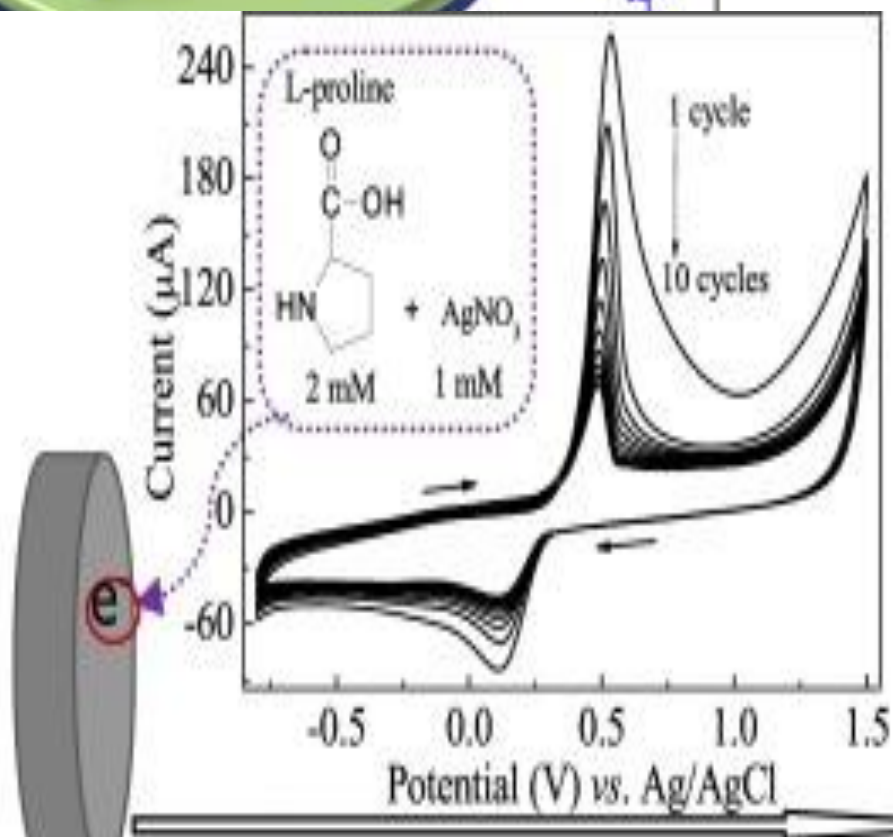
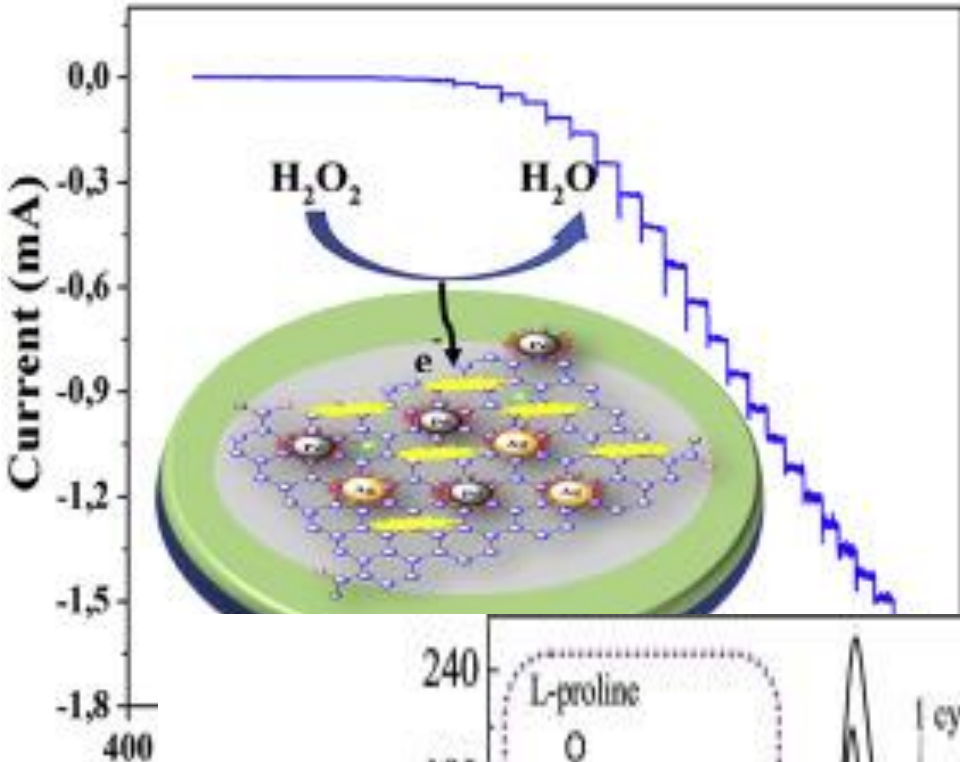
Combination with oxidases

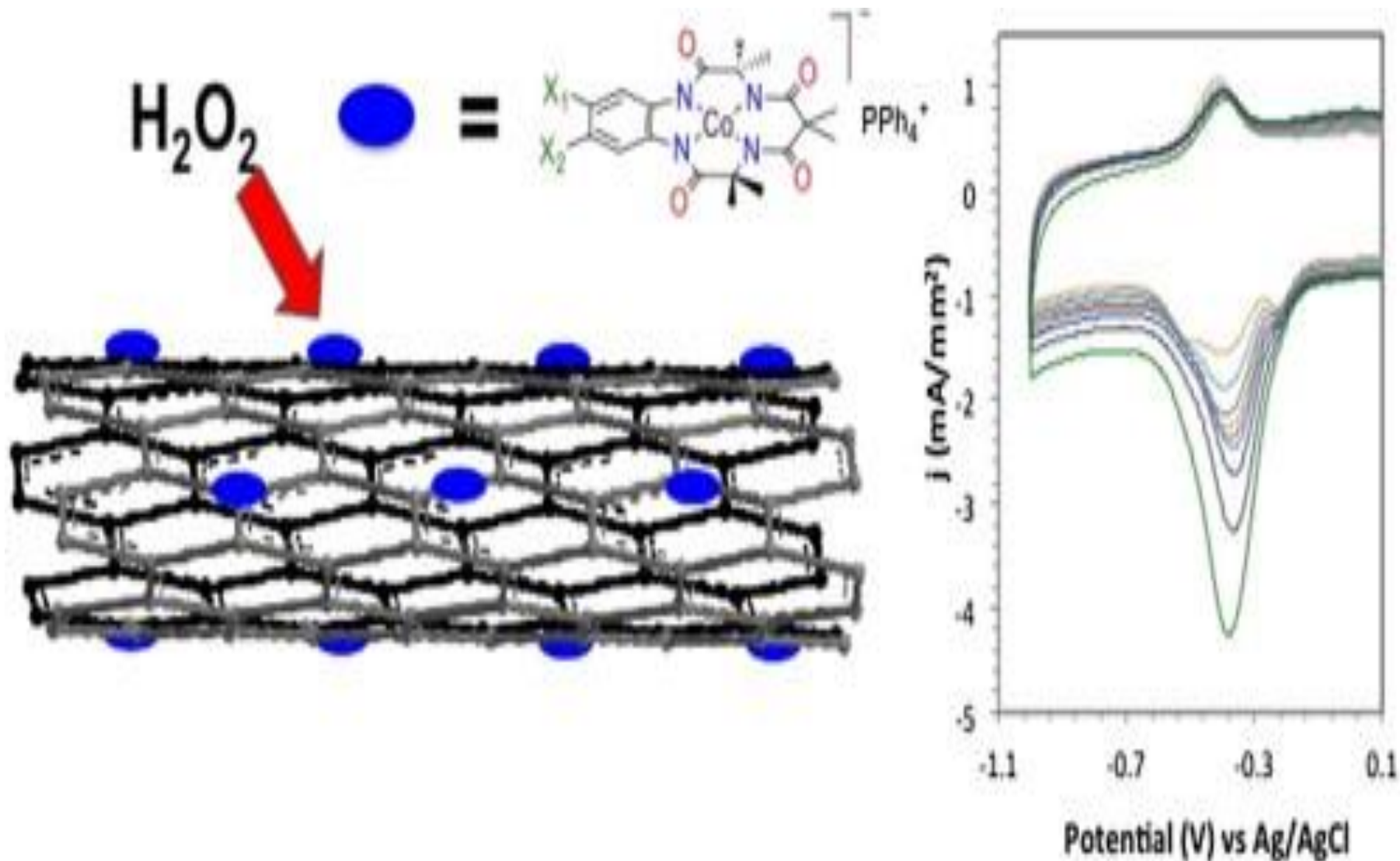


● : glucose oxidase or urate oxidase

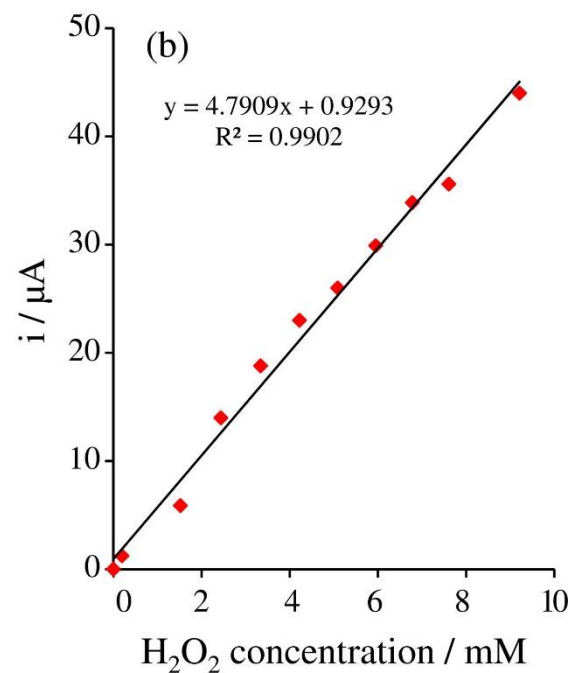
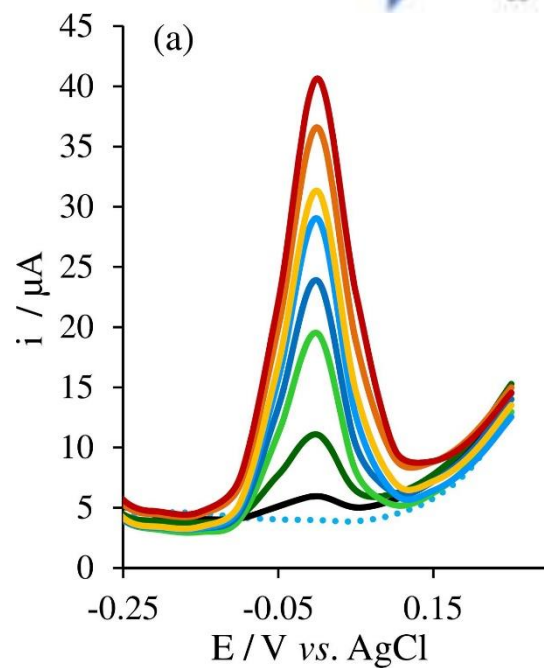
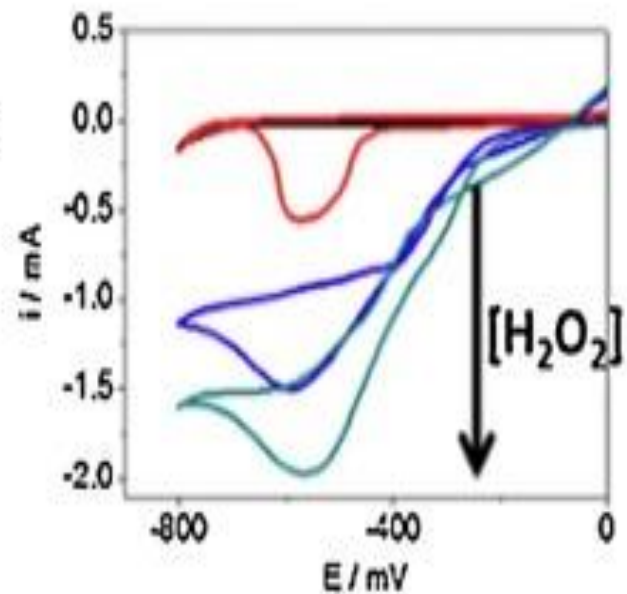
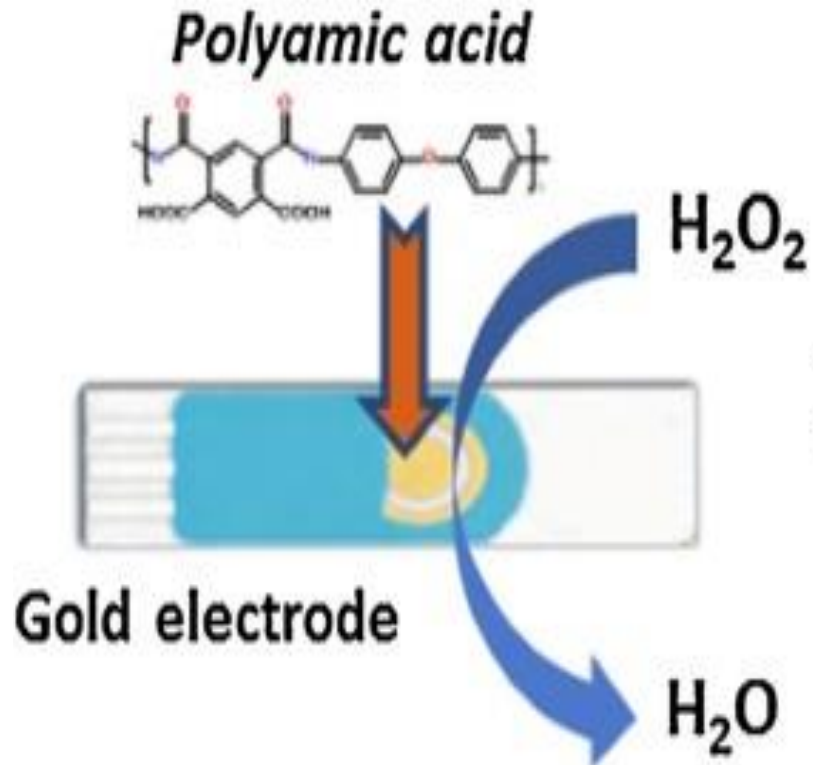


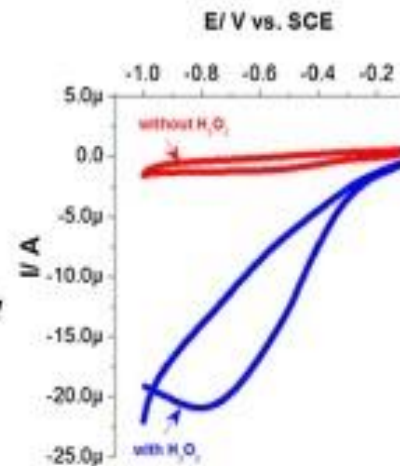
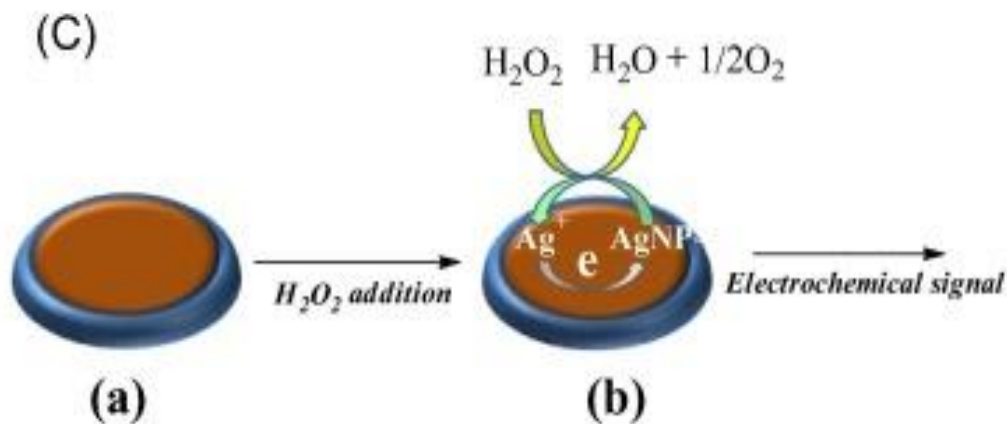
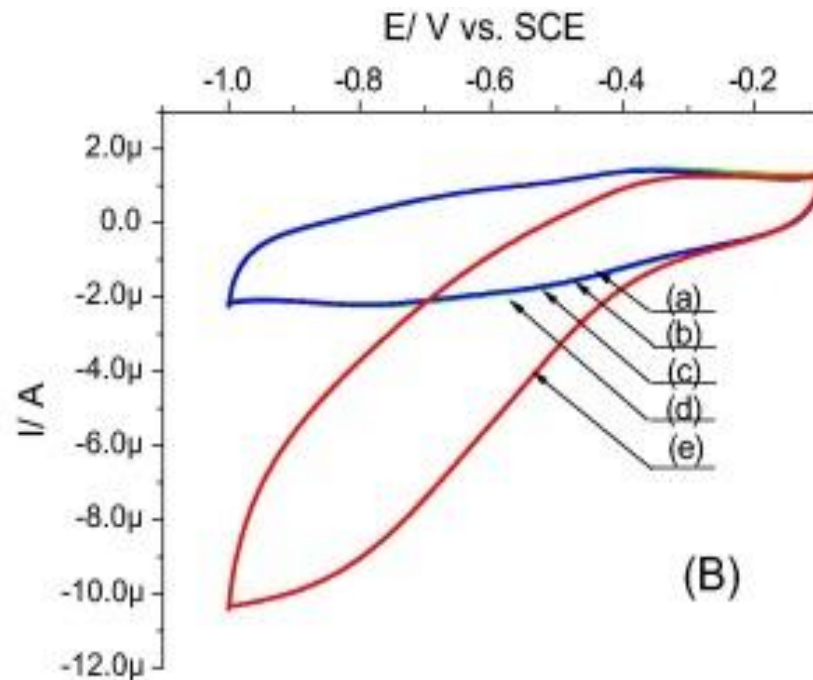
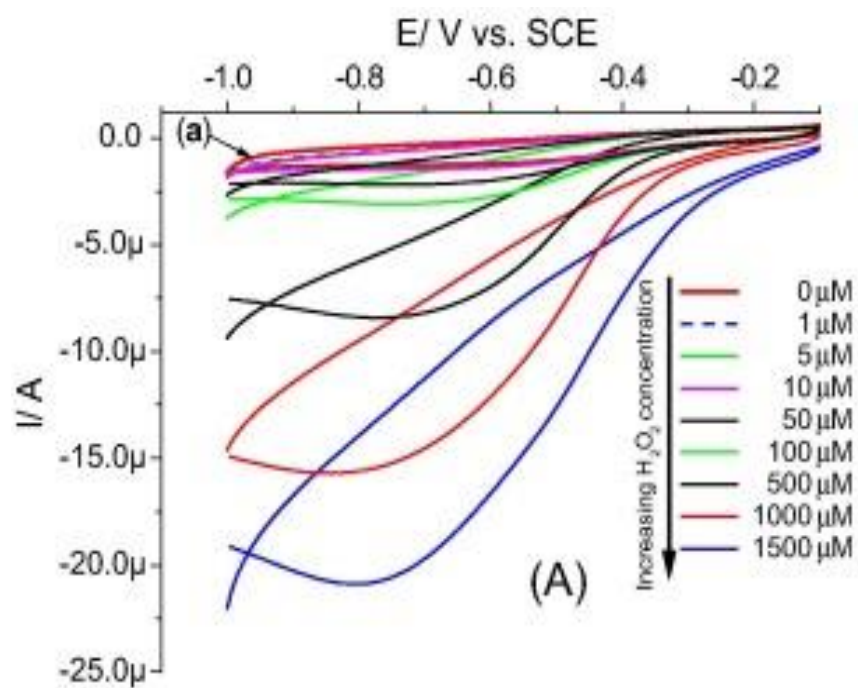
4. НЕ-ЕНЗИМСКИ СЕНЗОРИ За детекција на H₂O₂



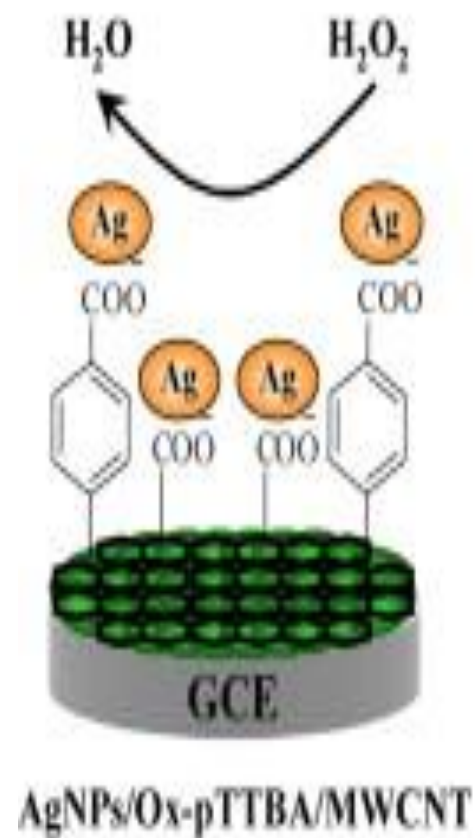


Hydrogen peroxide (H_2O_2) detection using a non-enzymatic cobalt(III) complex (2) of an amidomacrocyclic ligand

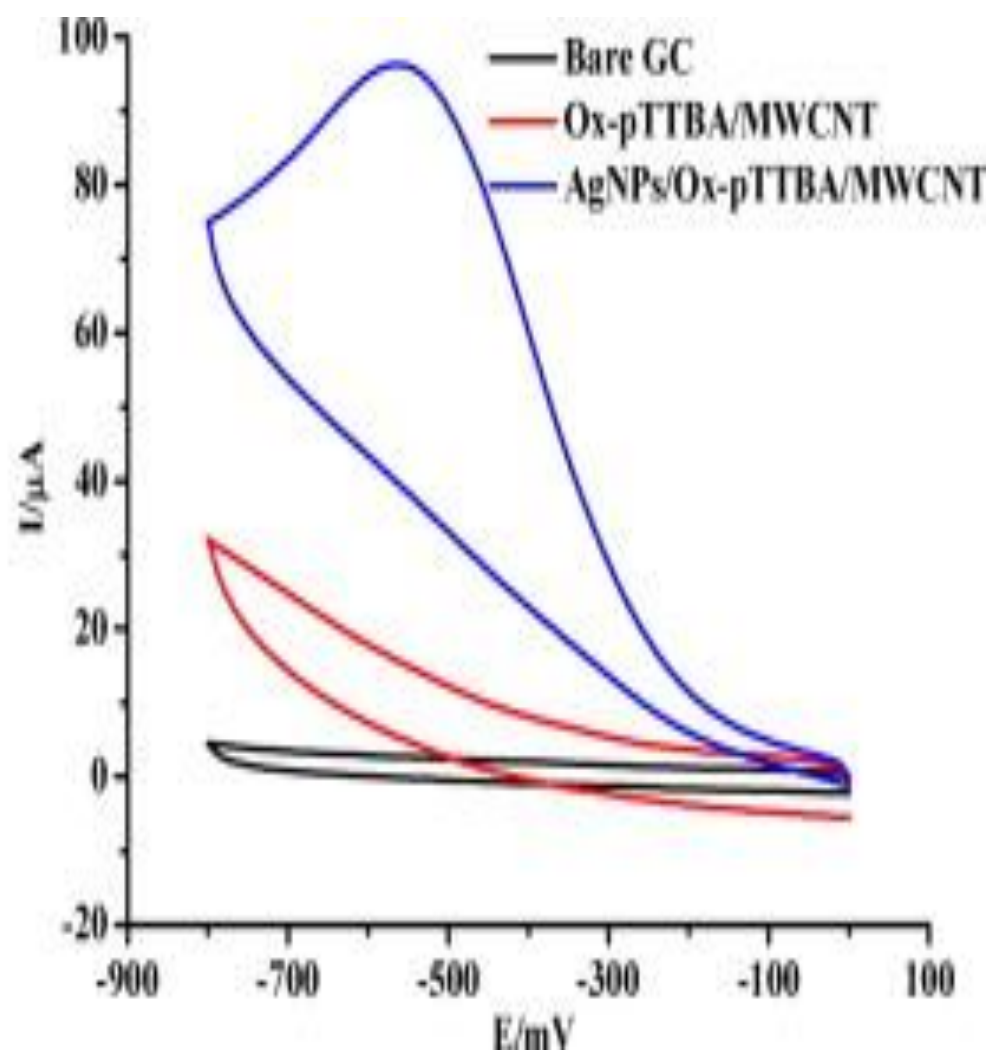


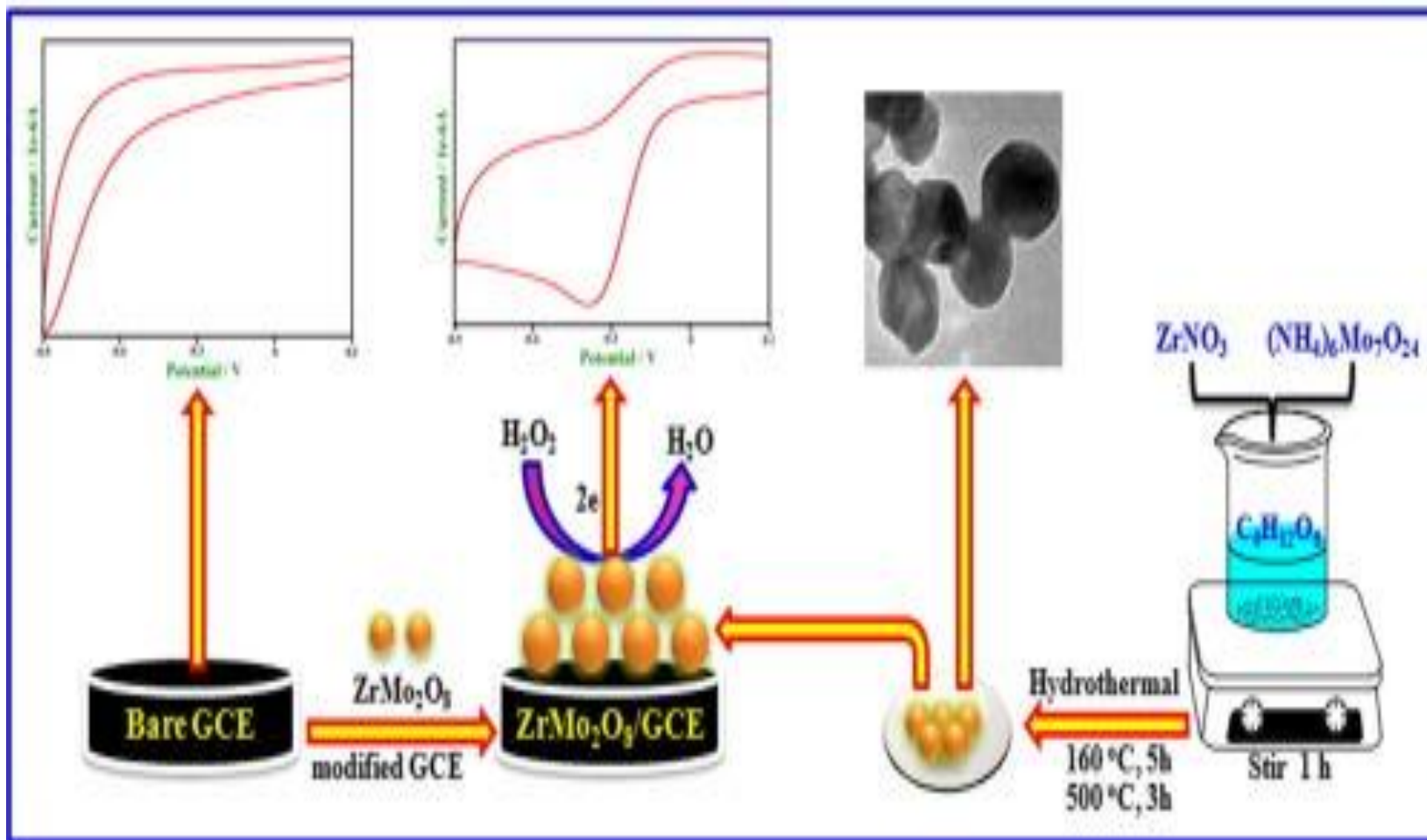


НЕ-ЕНЗИМСКИ СЕНЗОРИ за детекција и квантификација на H_2O_2 со Сребрени наночестички

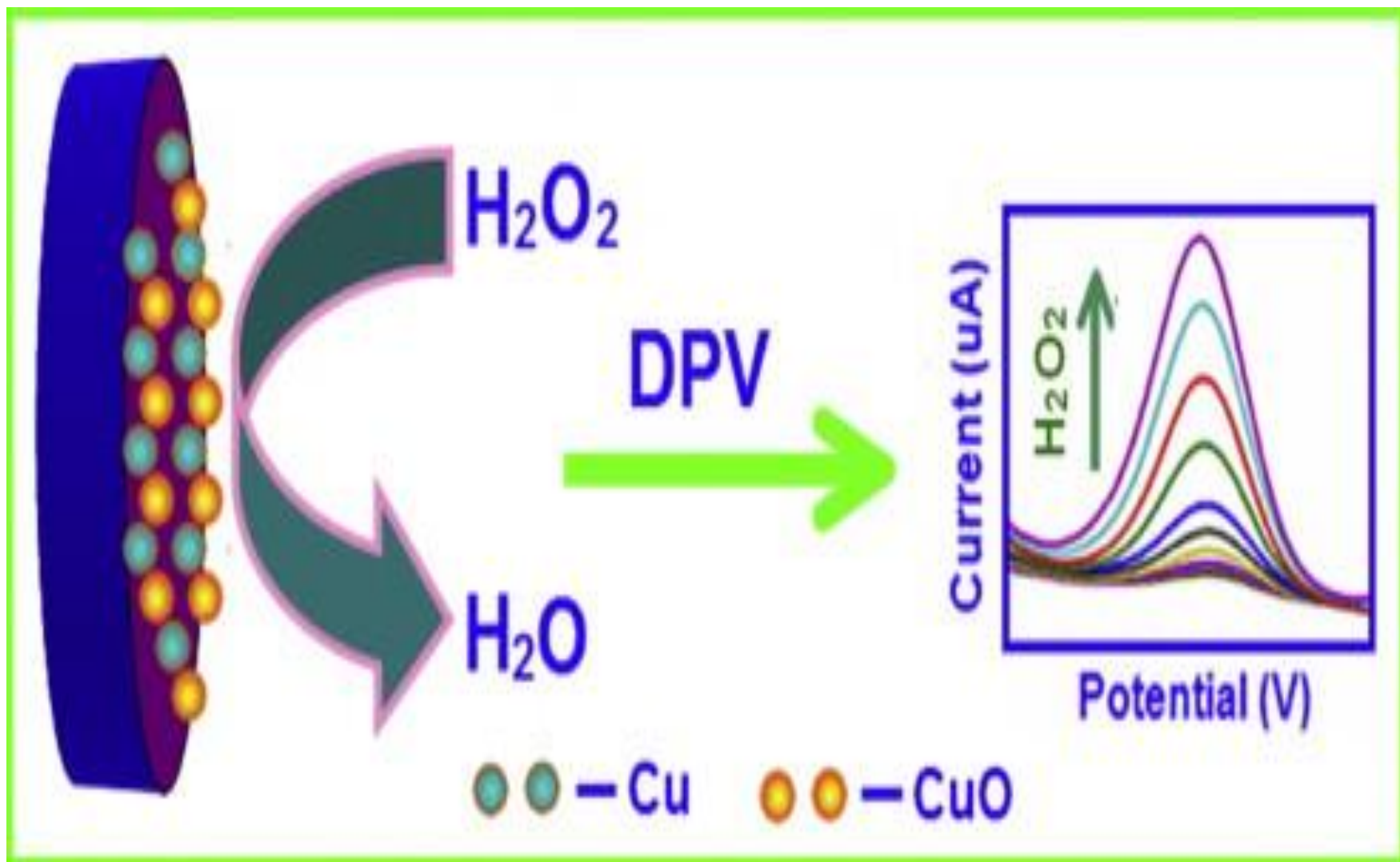


Detection
 H_2O_2





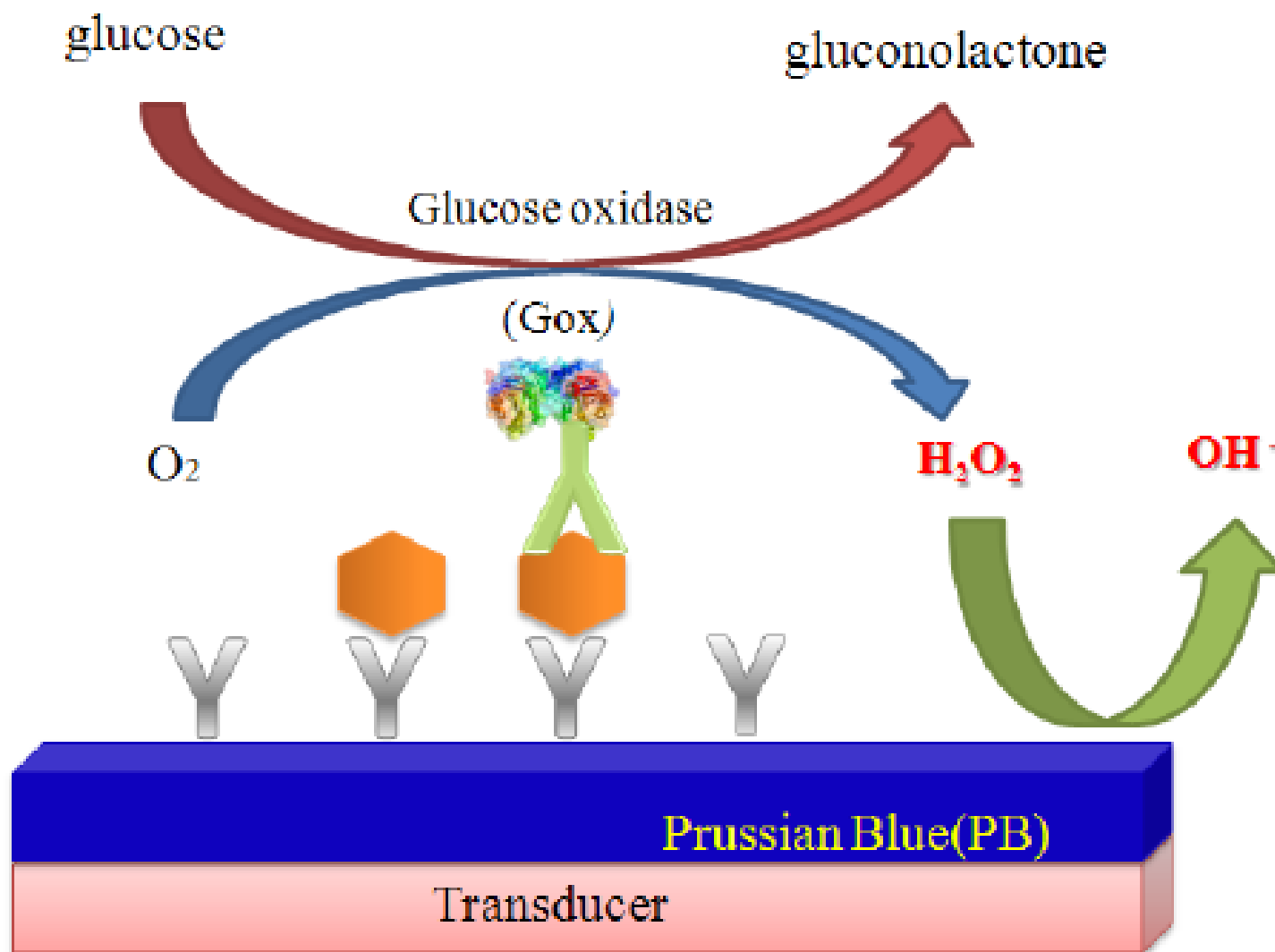
НЕ-ЕНЗИМСКИ СЕНЗОРИ за детекција и квантификација на H_2O_2 со мешани наночестички од циркониум и молибден

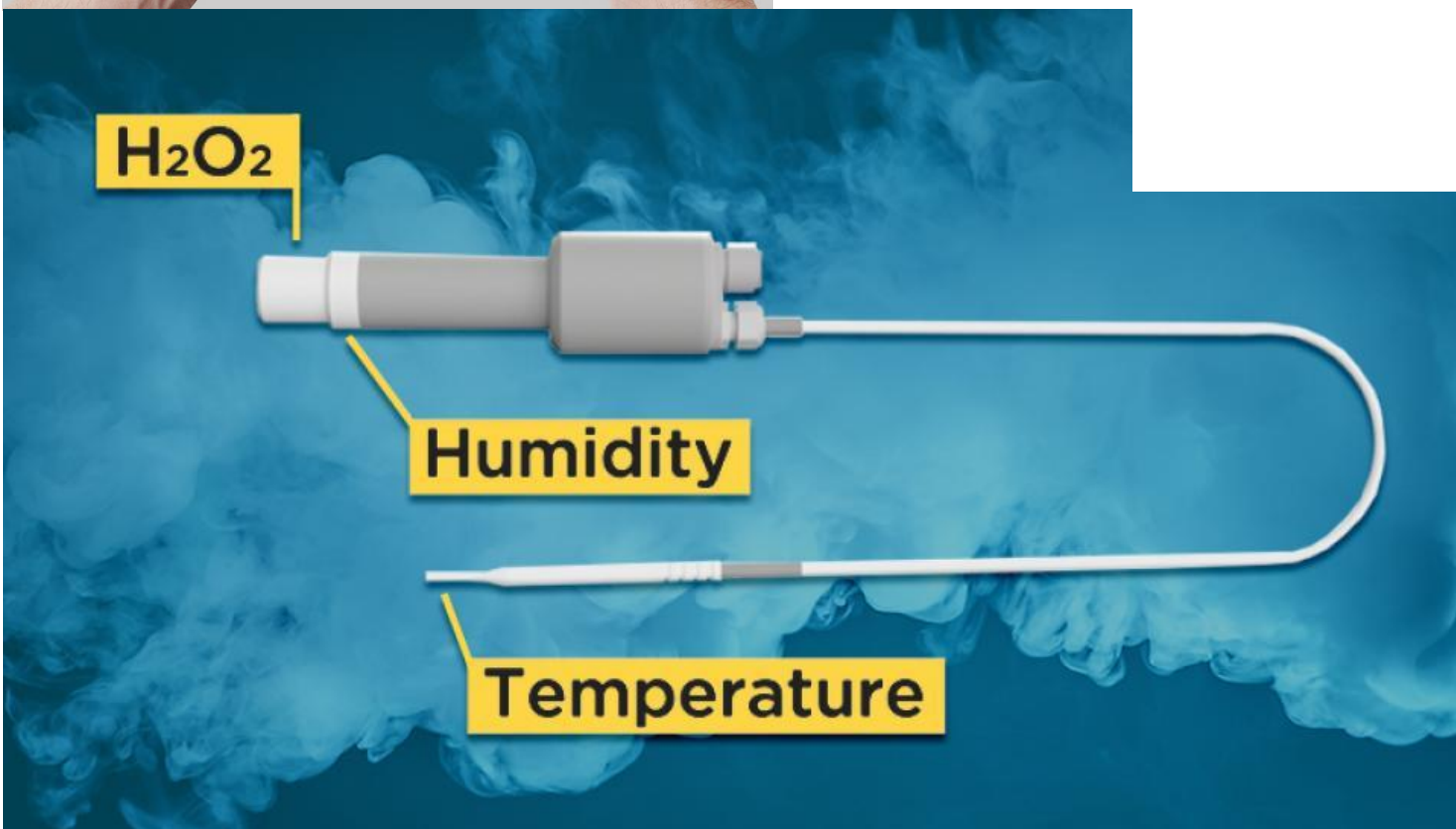


НЕ-ЕНЗИМСКИ СЕНЗОРИ за детекција и квантификација на H_2O_2 со
БАКАРНИ наночестички

ЕНЗИМАТСКИ СЕНЗОРИ ЗА КВАНТИФИКАЦИЈА НА H₂O₂

-----Индиректни методи-----



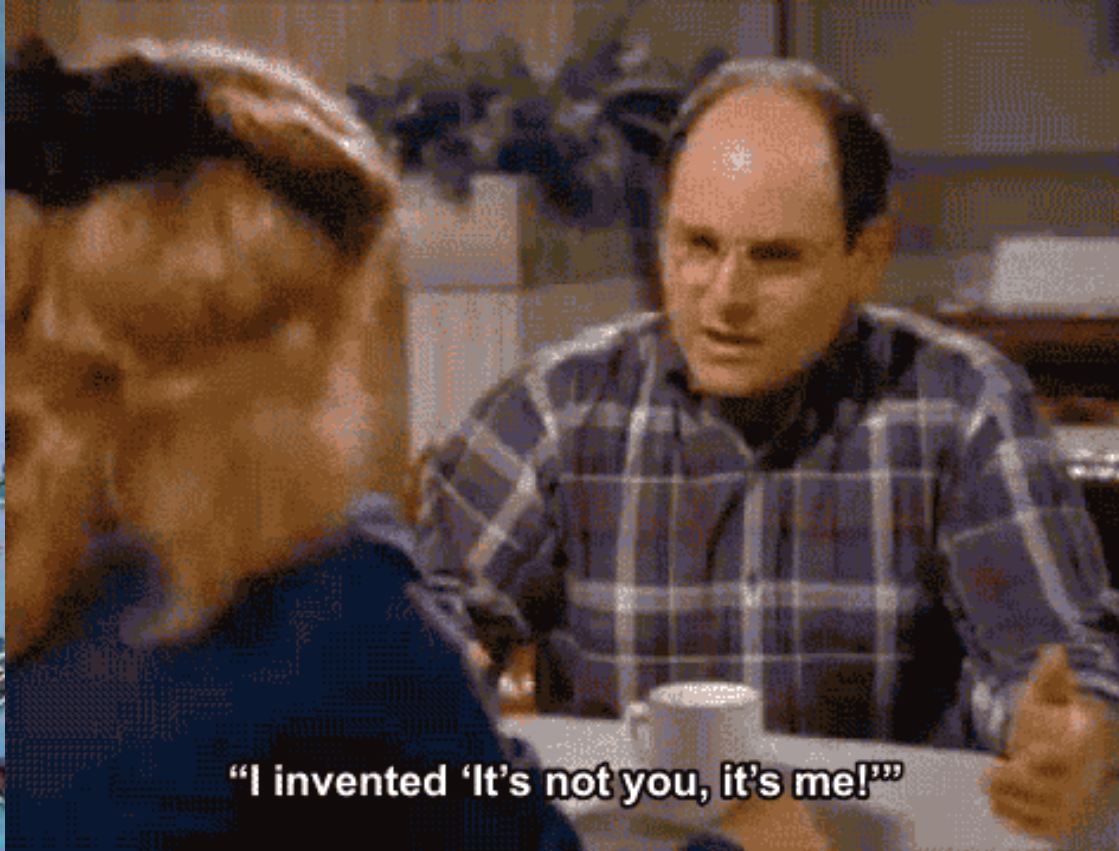
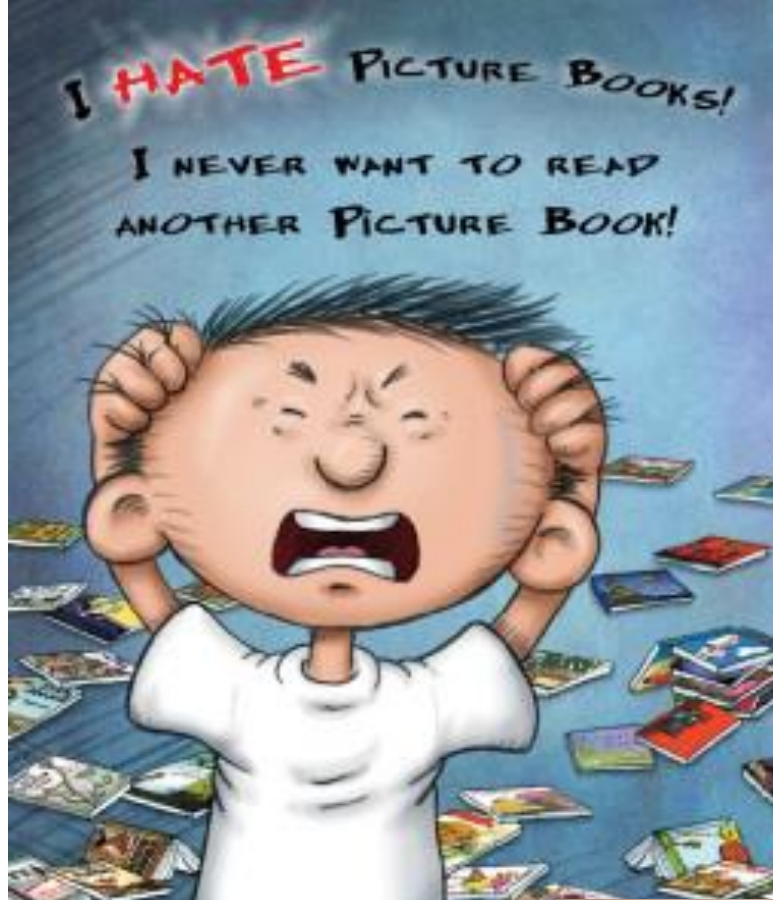


ДОБРИ И ЛОШИ СТРАНИ НА ВОЛТАМЕТРИСКИТЕ СЕНЗОРИ ЗА ДЕТЕКЦИЈА И КВАНТИФИКАЦИЈА НА H_2O_2

- евтини
- брзи
- дизајни достапни во разни варијанти и модификации
- во различни примероци може да се определува H_2O_2

НО....!!!

- сензорите со редокс медијатори-НАЈЧЕСТО СЕ - -----
-----НЕСЕЛЕКТИВНИ СЕНЗОРИ
- осетливи во високо микро и милимоларно подрачје на H_2O_2
- во единечни клетки може да се врши детекција и квантификација на H_2O_2 со т.н. Скенинг електрохемиска Микроскопија---топографија на клетка





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1. R. Gulaboski, S. Petkovska, A Time-Independent Approach to Evaluate the Kinetics of Enzyme-Substrate Reactions in Cyclic Staircase Voltammetry, *ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY* 10 (5), 566-575
2. R. Gulaboski, I. Bogeski, P. Kokoskarova, H. H. Haeri, S. Mitrev, M. Stefova, Marina, J. Stanoeva-Petreska, V. Markovski, V. Mirceski, M. Hoth, and R. Kappl, New insights into the chemistry of Coenzyme Q-0: A voltammetric and spectroscopic study. *Bioelectrochem.* 111 (2016) 100-108.
4. R. Gulaboski, V. Markovski, and Z. Jihe, Redox chemistry of coenzyme Q—a short overview of the voltammetric features, *J. Solid State Electrochem.*, 20 (2016) 3229-3238.
5. V. Mirceski, D. Guziewski and R. Gulaboski, Electrode kinetics from a single square-wave voltammograms, *Maced. J. Chem. Chem. Eng.* 34 (2015) 1-12.
6. V. Mirceski, D. Guziewski and R. Gulaboski, Electrode kinetics from a single square-wave voltammograms, *Maced. J. Chem. Chem. Eng.* 34 (2015) 1-12. 7. Gulaboski and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, *Electrochim. Acta*, 167 (2015) 219-225.
8. V. Mirceski, Valentin and R. Gulaboski, Recent achievements in square-wave voltammetry (a review). *Maced. J. Chem. Chem. Eng.* 33 (2014). 1-12.
9. V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl and M. Hoth, Square-Wave Voltammetry: A Review on the Recent Progress, *Electroanal.* 25 (2013) 2411–2422.
10. R. Gulaboski, I. Bogeski, V. Mirčeski, S. Saul, B. Pasieka, H. H. Haeri, M. Stefova, J. Petreska Stanoeva, S. Mitrev, M. Hoth and R. Kappl, "Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers *Sci. Reports*, 3 (2013) 1-8.
11. Rubin Gulaboski, Valentin Mirčeski and Fritz Scholz, ["Determination of the standard Gibbs energies of transfer of cations and anions of amino acids and small peptides across the water nitrobenzene interface."](#), *Amino Acids*, 24 (2003) 149-154

11. V. Mirčeski and R. Gulaboski, "Surface Catalytic Mechanism in Square-Wave Voltammetry", *Electroanal.* 13 (2001) 1326-1334.
12. V. Mirčeski, R. Gulaboski and I. Kuzmanovski, "Mathcad-a Tool for Numerical Calculation of Square-Wave Voltammograms", *Bull. Chem. Technol. Macedonia*, 18 (1999) 57-64.
13. Scholz, F.; Schroeder U.; Gulaboski R. *Electrochemistry of Immobilized Particles and Droplets* Springer Verlag, New York, pp. 1-269, 2005.
14. Gulaboski R. in *Electrochemical Dictionary*, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2nd Edition in 2012.
15. I. Bogeski, R. Kappl, C. Kumerow, R. Gulaboski, M. Hoth and B. A. Niemeyer "Redox regulation of calcium ion channels: Chemical and physiological aspects, *Cell Calcium* 50 (2011) 407-423.
16. R. Compton, *Understanding Voltammetry*, 2012.
17. V. Mirceski, S. Komorsky Lovric, M. Lovric, *Square-wave voltammetry, Theory and Application*, Springer 2008 (F. Scholz, Ed.)
18. Rubin Gulaboski, Theoretical Contribution Towards Understanding Specific Behaviour of "Simple" Protein-film Reactions in Square-wave Voltammetry, *Electroanalysis* 2018, <https://doi.org/10.1002/elan.201800739>
19. R. Gulaboski, P. Kokoskarova, S. Petkovska, Time-Independent Methodology to Access Michaelis-Menten Constant by Exploring Electrochemical-Catalytic Mechanism in Protein-Film Cyclic Staircase Voltammetry, *Croatica Chemica Acta* 91 (2018) <https://doi.org/10.5562/cca3383>
20. R. Gulaboski, V. Mirčeski, M. Lovrić and I. Bogeski, "Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry." *Electrochem. Commun.* 7 (2005) 515-522.
22. R. Gulaboski, V. Mirčeski, C. M. Pereira, M. N. D. S. Cordeiro, A. F Silva, F. Quentel, M. L'Her and M. Lovrić, "A comparative study of the anion transfer kinetics across a water/nitrobenzene interface by means of electrochemical impedance spectroscopy and square-wave voltammetry at thin organic film-modified electrodes." *Langmuir* 22 (2006) 3404-3412.
23. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, I. Bogeski, E. Ferreira, D. Ribeiro, M. Chirea and A. F. Silva, "Electrochemical study of ion transfer of acetylcholine across the interface of water and a lipid-modified 1,2-dichloroethane." *J. Phys. Chem. B* 109 (2005) 12549-12559.
24. F. Scholz and R. Gulaboski "Determining the Gibbs energy of ion transfer across water-organic liquid interfaces with three-phase electrodes." *Chem. Phys. Chem.*, 6 (2005) 1-13.
25. R. Gulaboski, V. Mirčeski, Š. Komorsky-Lovrić and M. Lovrić, "Square-Wave Voltammetry of Cathodic Stipping Reactions. Diagnostic Criteria, Redox Kinetic Measurements, and Analytical Applications", *Electroanal.* 16 (2004) 832-842.
26. V. Mirčeski and R. Gulaboski, "A Theoretical and Experimental Study of Two-Step Quasireversible Surface Reaction by Square-Wave Voltammetry" *Croat. Chem. Acta* 76 (2003) 37-48.
27. V. Mirčeski and R. Gulaboski, "The surface catalytic mechanism: a comparative study with square-wave and staircase cyclic voltammetry", *J. Solid State Electrochem.* 7 (2003) 157-165.