



# **Utilizarea SPR, a EIS si a combinarii unitare a acestor metode pentru relevarea adsorbtiilor specifice, respectiv nespecifice la analiza aceluiasi biosenzor afin**

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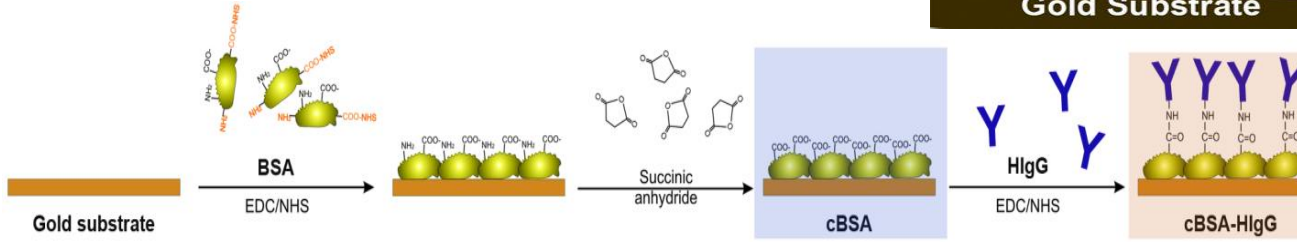
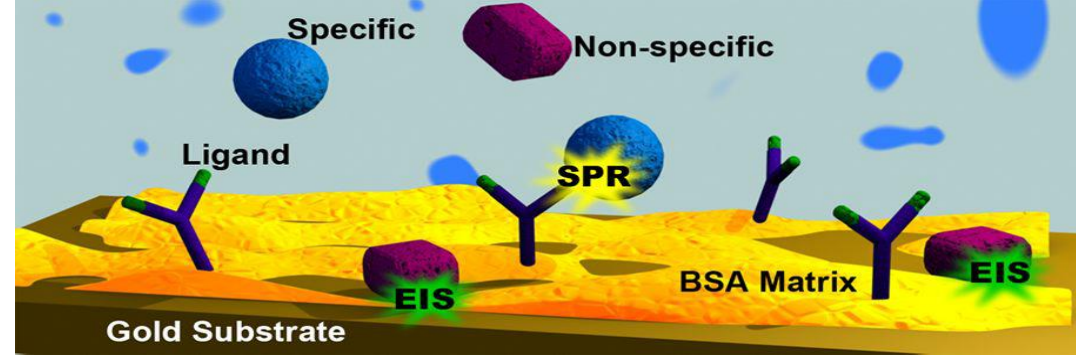
**Centrul International de Biodinamica**

# Structura Prezenterii

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1. Conceptul analitic & Set-up experimental
2. Ce este Plasmonic-EIS, care sunt avantajele combinarii EIS cu SPR si relatia cu raspunsul EIS & SPR
3. Efectul adsorbției specifice/nespecifice relevata de analize EIS & SPR
4. Explicatia sensibilitatii EIS la adsorbția nespecifica (in cazul analizei unui senzor functionalizat cu un strat dielectric)- efectul nanoporilor
5. Relevanta studiului

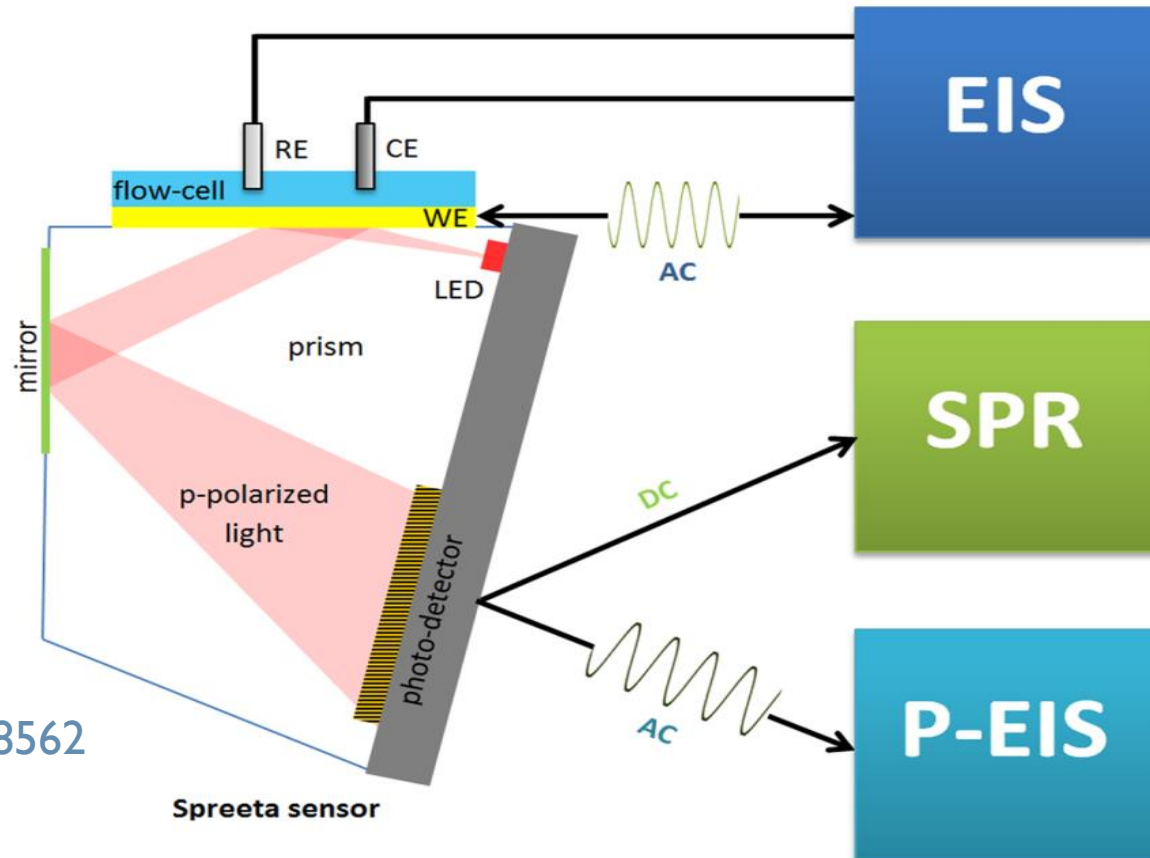
# Conceptual analitic



## Structura Senzorului

*Talanta*, 80, 5, 2157-2164 (2010)

## Set-up experimental



*Analytical Chemistry* (2014), 86 (17), 8553–8562



# Ce este Plasmonic-EIS, care sunt avantajele combinarii EIS cu SPR si relatia cu analizele EIS & SPR

## I. Ce este Plasmonic-EIS?

$$\delta(\epsilon_s \epsilon_0 \frac{\partial V_s(\omega, x, y, z \rightarrow 0)}{\partial z} - \epsilon_m \epsilon_0 \frac{\partial V_m(\omega, x, y, z \rightarrow 0)}{\partial z}) = \delta\sigma(\omega, x, y);$$

$$\delta\sigma(\omega, x, y) = \alpha \cdot \delta\theta_{SPR}(\omega, x, y)$$

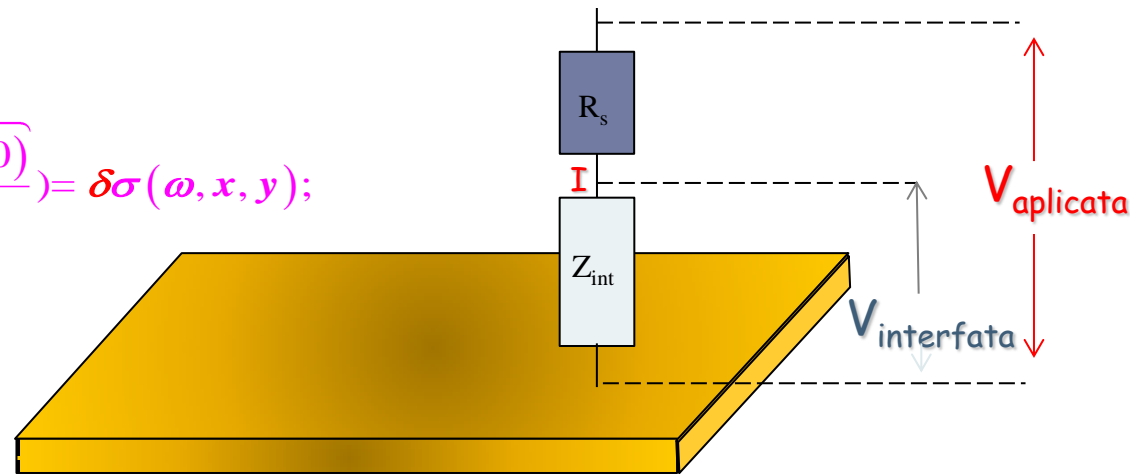
Modelul Drude:

$$\epsilon_{metal}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i \frac{\Gamma \omega_p^2}{\omega(\omega^2 + \Gamma^2)} = \epsilon'_{metal} + i \cdot \epsilon''_{metal};$$

$$\Gamma = \frac{1}{\tau} \approx 10^{14}; \omega_p^2 = \frac{n_e e^2}{m_e \cdot \epsilon_0} \Rightarrow \omega_p \approx 1.37 \cdot 10^{16}$$

$$\delta\sigma = -e \cdot d_m \cdot \delta n_e \Rightarrow \delta n_e = -\frac{\delta\sigma}{e \cdot d_m}$$

$$\delta\epsilon'_{metal} = -\frac{\delta n_e (1 - \epsilon'_{metal})}{n_e} \Leftrightarrow \delta\epsilon'_{metal} = -\delta\sigma \frac{(1 - \epsilon'_{metal})}{n_e \cdot e \cdot d_m}$$



$$k_{x-plasmon} = \frac{\omega}{c} \sqrt{\frac{\epsilon'_{metal} \cdot \epsilon_{medium}}{\epsilon'_{metal} + \epsilon_{medium}}} \quad - \text{plasmoni}$$

$$k_{x-light} = \frac{\omega}{c} \sqrt{\epsilon_{prism}} \sin \theta \quad - \text{lumina polarizata p}$$

$$k_{x-light} = k_{x-plasmon} \quad \text{la rezonanta, i.e. } \theta = \theta_{SPR}$$

$$\sin \theta_{SPR} = \sqrt{\frac{\epsilon'_{metal} \cdot \epsilon_{medium}}{(\epsilon'_{metal} + \epsilon_{medium}) \epsilon_{prism}}} \quad \alpha \stackrel{Def}{=} \frac{\delta\sigma}{\delta\theta_{SPR}} = \frac{\delta\sigma}{\delta\epsilon'_{metal}} \frac{\delta\epsilon'_{metal}}{\delta \sin \theta_{SPR}} \cos \theta_{SPR}$$

$$\alpha = -\sin 2\theta_{SPR} \frac{e \cdot d_m n_e \epsilon_{prism} (\epsilon'_{metal} + \epsilon_{medium})^2}{\epsilon_{medium}^2 (\epsilon'_{metal} - 1)}$$

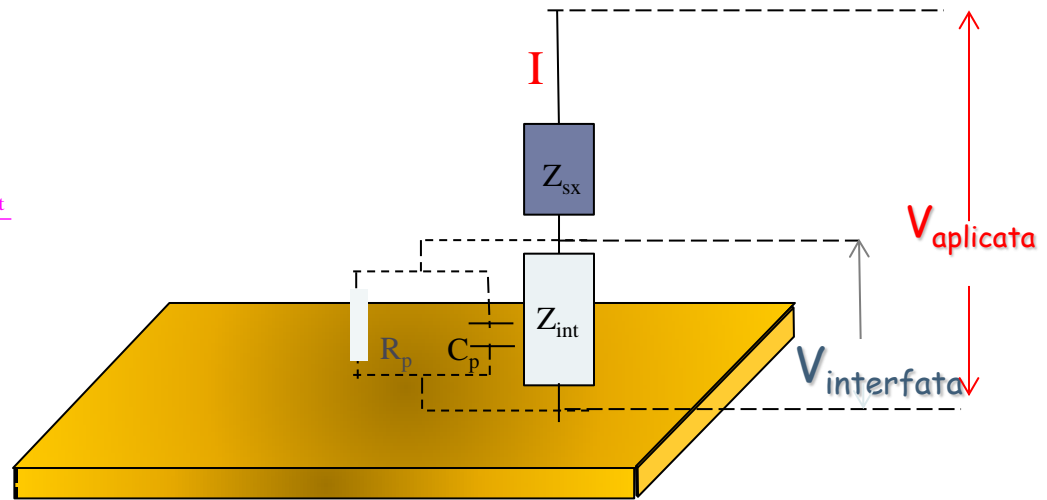


## II. Legatura dintre impedanta probei si unghiul SPR la aplicarea unui camp AC

$$\delta\sigma(\omega, x, y) = \alpha \cdot \delta\theta_{SPR}(\omega, x, y)$$

$$\delta\sigma(\omega, x, y) = \frac{\delta Q(\omega, x, y)}{A} = \frac{C_p(\omega, x, y) \cdot \delta V_{int}}{A}$$

$$C_p(\omega, x, y) = \frac{1}{\omega} \text{Im} \left[ \left( Z_{int}(\omega, x, y) \right)^{-1} \right]$$



$$\delta\sigma(\omega, x, y) = \frac{\delta V_{int}}{A \cdot \omega} \text{Im} \left[ \left( Z_{int}(\omega, x, y) \right)^{-1} \right] = \alpha \cdot \delta\theta_{SPR}(\omega, x, y)$$

$$\frac{1}{j\omega \cdot C_p} = X_{cint} \ll R_p \Rightarrow \delta\theta_{SPR}(\omega, x, y) = \frac{-j}{\alpha \cdot A \cdot \omega} \frac{\delta V_{int}}{Z_{int}(\omega, x, y)} \Rightarrow \delta\theta_{SPR}(\omega, x, y) = \frac{-j}{\alpha \cdot A \cdot \omega} \cdot \delta I(\omega, x, y)$$

$$\delta\theta_{SPR}(\omega, x, y) = -j \frac{\delta V_{appl}}{\alpha \cdot \omega} \cdot \frac{Y_t(\omega, x, y)}{A}$$

$$\frac{Y_t(\omega, x, y)}{A} = j \frac{\alpha \cdot \omega \cdot \delta\theta_{SPR}(\omega, x, y)}{\delta V_{appl}}$$

$$Z_t(\omega, x, y) = -j \frac{1}{\alpha \cdot A \cdot \omega} \cdot \frac{\delta V_{appl}}{\delta\theta_{SPR}(\omega, x, y)}$$

# Avantajele combinarii EIS cu SPR

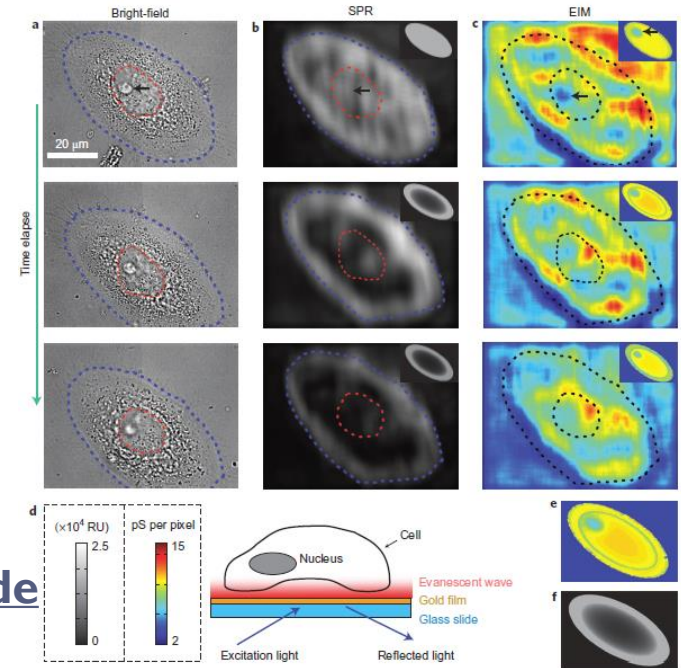
$$\delta\theta_{SPR}(\omega, x, y) = \frac{-j}{\alpha \cdot A \cdot \omega} \cdot \delta I(\omega, x, y)$$

$$Z_t(\omega, x, y) = -j \frac{1}{\alpha \cdot A \cdot \omega} \cdot \frac{\delta V_{appl}}{\delta\theta_{SPR}(\omega, x, y)}$$

Masuratori de impedanta, fara contacte individuale, cu inalta rezolutie spatiala !! (limitata de propagarea laterala a plasmonilor).



Exemplu utilizare: Imagini cu rezolutie inalta a proprietatilor electrice a celulelor, proprietati inaccesibile prin alte metode



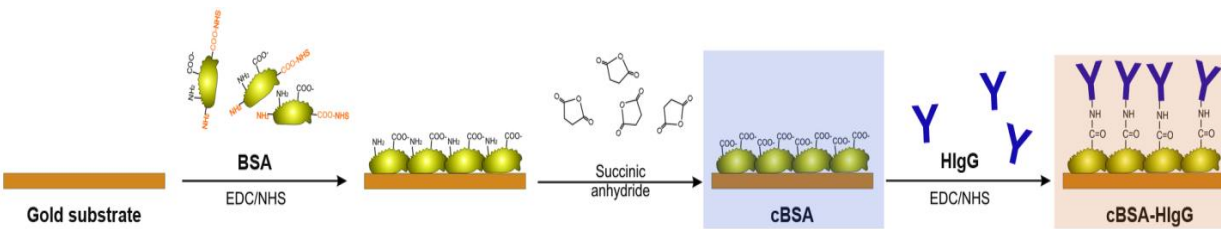
Reprodus din: Wang, W., Foley, K., Shan, X., Wang, S., Eaton, S., Nagaraj, V.J., Wiktor, P., Patel, U., Tao, N., 2011. Nature Chemistry 3, 251–257.

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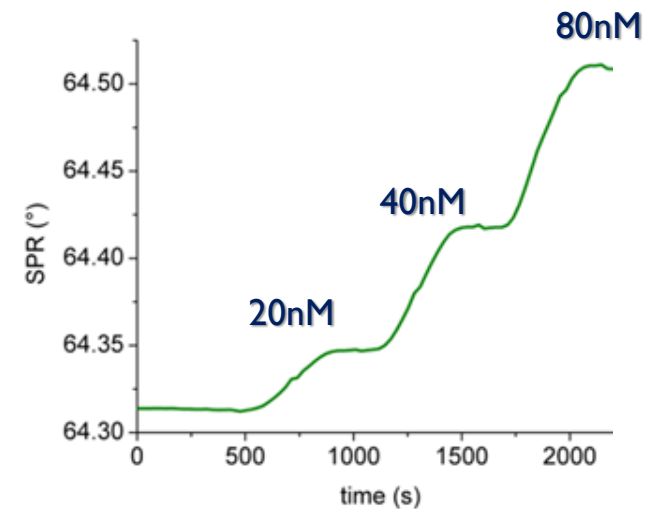
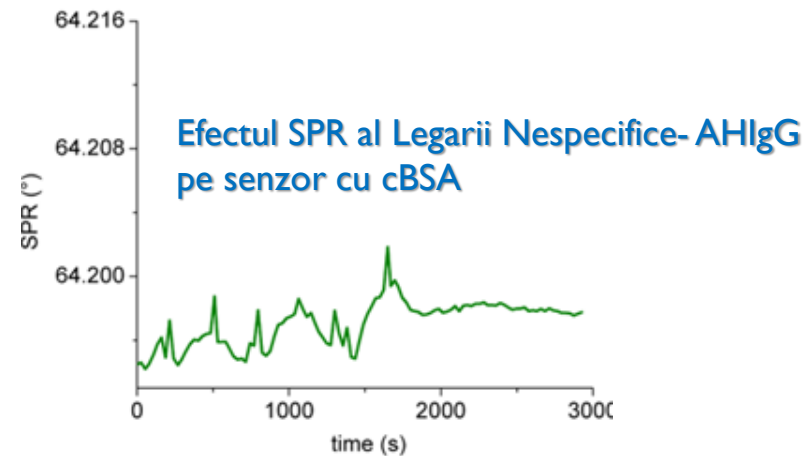
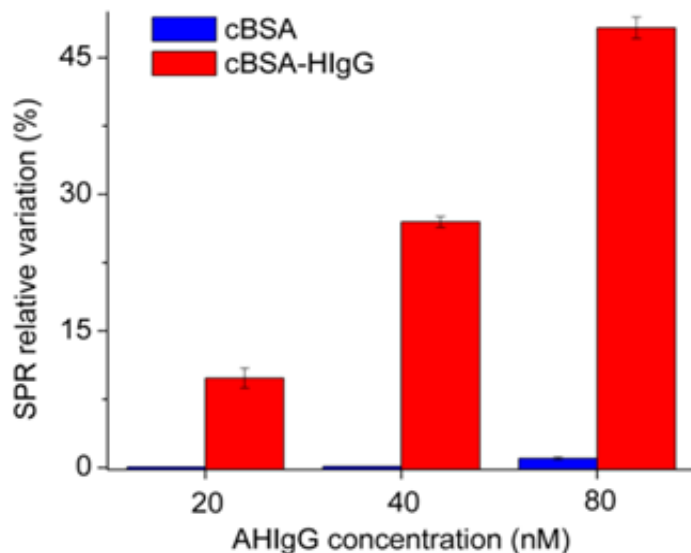
- dependenta de parametri de iluminare (lungimea de unda a iluminarii)
- dependenta de structura particulara a cipului (configuratia multistrat)



# Efectul adsorbției nespecifice & specifice relevat de analize SPR

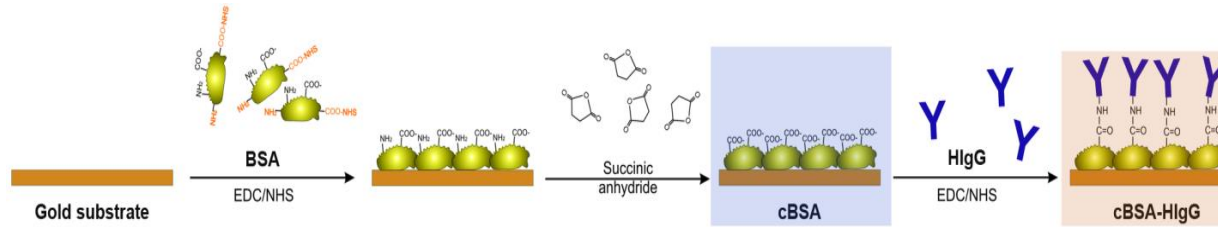


Răspunsul SPR la injecții succesive de soluții test cu concentrații crescătoare de AHlgG (20nM, 40nM & 80nM) pe senzor cu cBSA, respectiv pe senzor cu cBSA-AHlgG



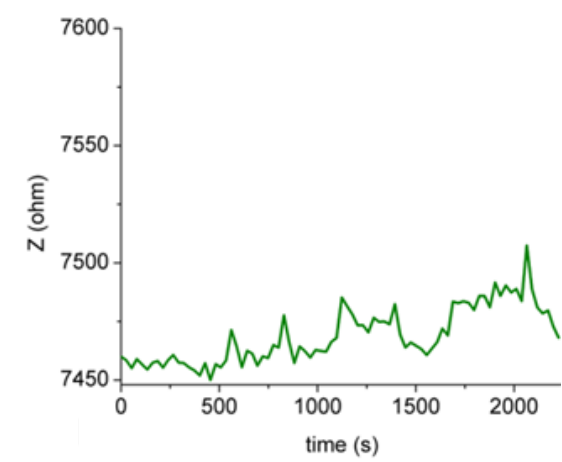
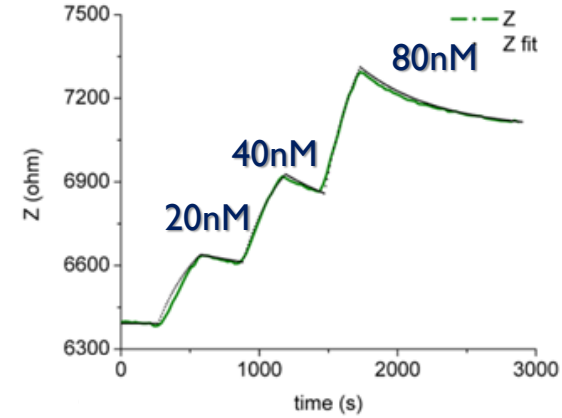
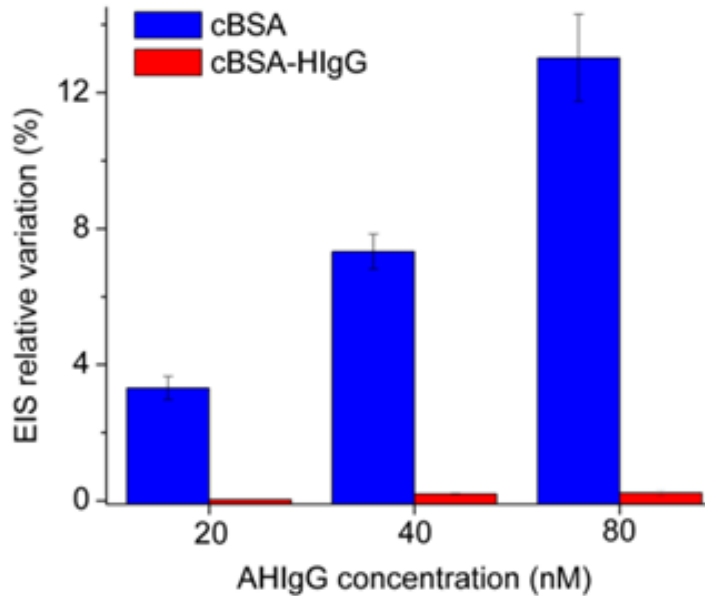
Efectul SPR al Legării Specifice-AHlgG pe senzor cu cBSA-AHlgG

# Efectul adsorbției nespecifice & specifice relevat de analize EIS



Efectul EIS al Legării Nespecifice- AHlgG pe senzor cu cBSA

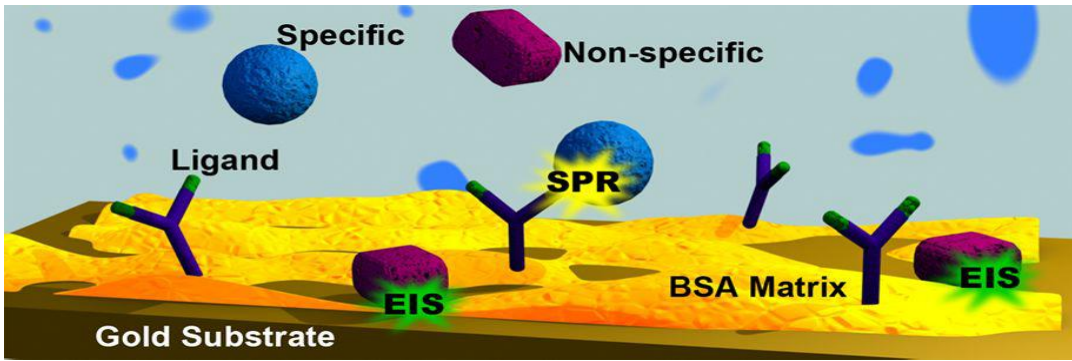
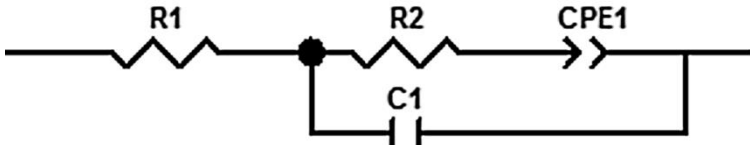
Răspunsul EIS ( $|Z|$  la 3.5 Hz) la injecții succesive de soluții test cu concentrații crescătoare de AHlgG (20nM, 40nM & 80nM) pe senzor cu cBSA, respectiv pe senzor cu cBSA-HlgG



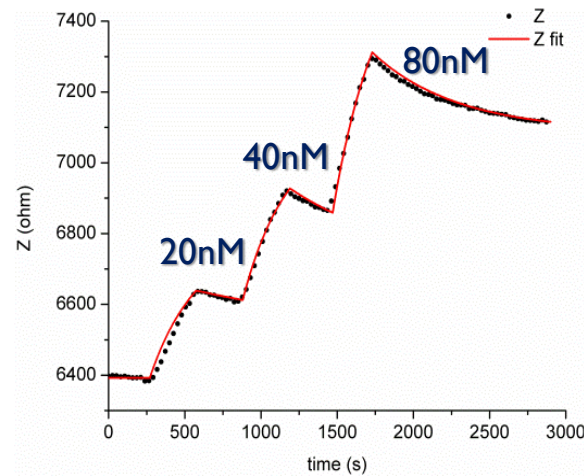
Efectul EIS al Legării Specifice- AHlgG pe senzor cu cBSA-HlgG



# Explicatia sensibilitatii EIS la adsorbția nespecifică (în cazul analizei unui senzor funcționalizat cu un strat dielectric) - efectul nanoporilor din structura senzorului



$$Z_{echi}[t, \omega] = R_s + \frac{1}{\frac{N_0}{X_C[\omega]} + \frac{N_1 - n[t]}{Z_{CPE_p}[\omega]} + \frac{n[t]}{Z_{CPE_n}[\omega]}}$$



Curba simulată & cea experimentală a impedanței, |Z| la 3.5 Hz

## Relevanta

- 1) Este primul studiu care releva complementaritatea raspunsului SPR/EIS cu privire la adsorbția specifica/nescifica
- 2) La analiza unor probe care contin amestecuri dintre analitul tinta si compusi cu masa moleculara mica sau a unor medii complexe cu diferite dilutii, atat SPR cat si EIS indica variatii de semnal semnificative, dar aceste semnale au origini complementare aferente continutului de analit specific, respectiv de “impuritati”
- 3) Masuratorile cuplate Plasmonic-EIS i.e. de impedanta, realizate unitar prin analiza efectului plasmonic al aplicarii asupra probei a unui camp AC (similar ca la EIS) permit obtinerea simultana a raspunsului SPR ( $\theta_{SPR}$ ) si EIS (via  $\delta\theta_{SPR}$ )

## Mulumiri

Cercetarile au fost sustinute prin proiectul Bioscope (No. I I/2012, ID: PN II-ID-PCCE-2011-2-0075) care dezvolta o platforma de microscopie Plasmonic –EIS de inalta rezolutie

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Multumesc pentru Atentie!

