Graphene Oxide-Copper Plasmonic Interfaces for SPR Biosensing

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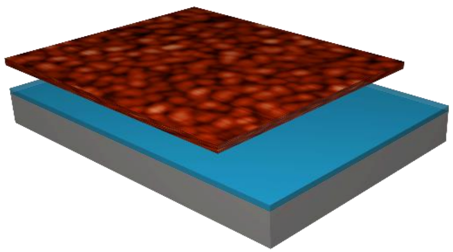
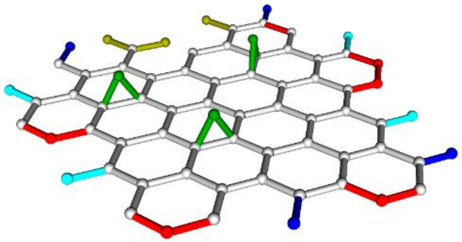
Copper and graphene oxide for plasmonic biosensing

Copper



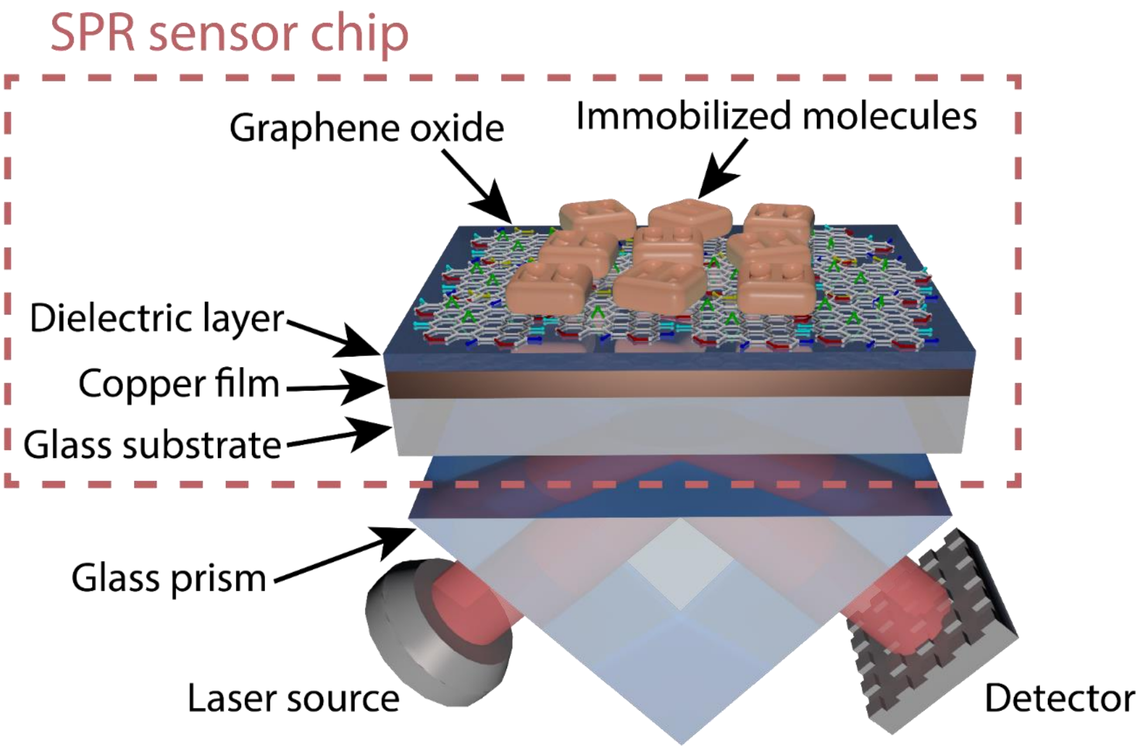
- Good optical properties in visible range
- Variety of structures for plasmonic biosensors (films, WG, resonators)
- Low cost
- Compatible with CMOS
- Ideal material for mass-production

Graphene oxide



- Deposition on various substrates
- 2D material – high surface area
- Pi-stacking immobilization
- Easy manufacturing process
- Low optical absorption
- Oxygen-containing functional groups: COOH, OH, C=O, C-O-C

Copper-based SPR biosensing

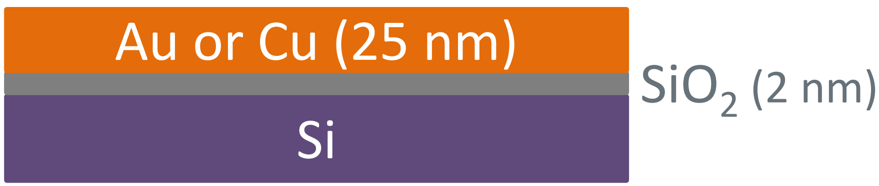


- Biosensors format: instrument and sensor chips
- Simple theoretical description
- Thin film structures (no lithography and etching)
- Wide range of developed protocols

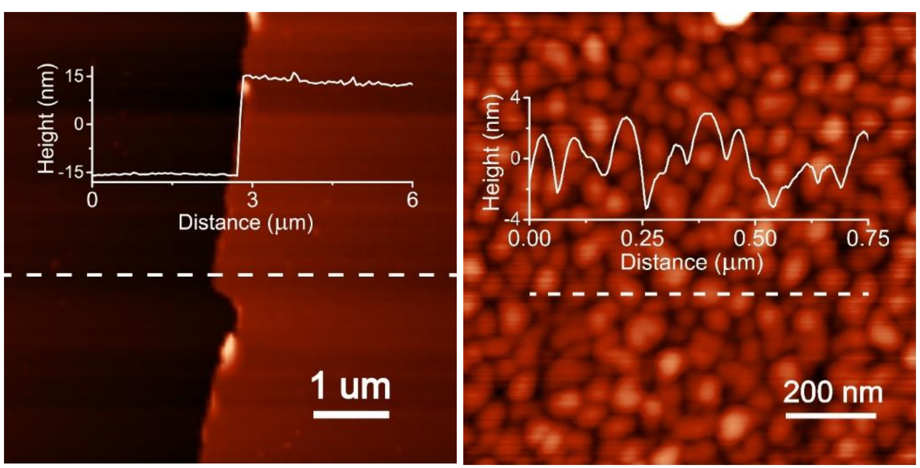
Stebunov et al., Langmuir 34 (15), 2018

Optical properties of thin copper films

Structures for ellipsometry measurements



AFM images of copper films



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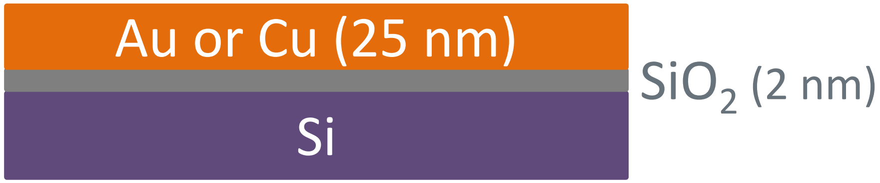
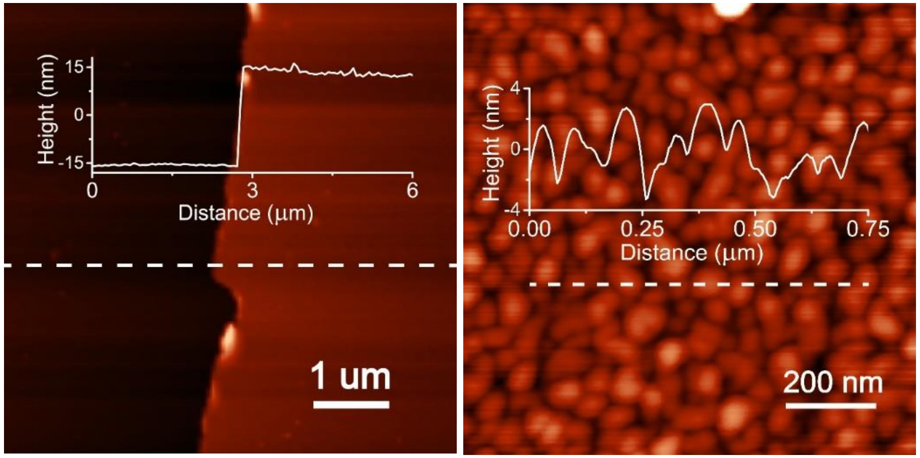
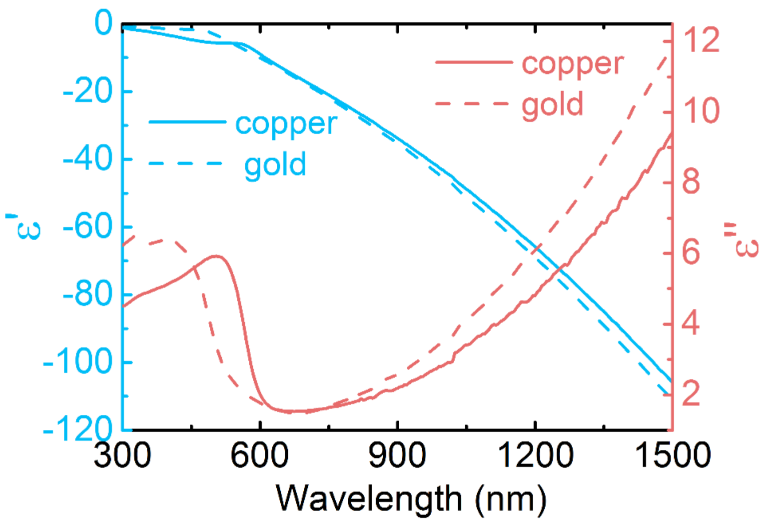


AFM images of copper films



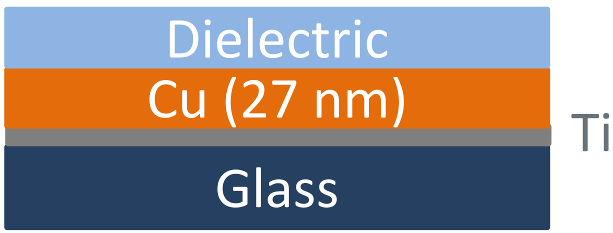
Dielectric constants



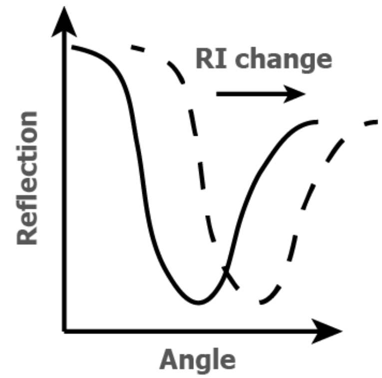
Drude model: $\varepsilon = \varepsilon_\infty - \dfrac{\omega_p^2}{\omega^2 + i\Gamma\omega}$,

	ε_∞	ω_p [10^{16}/s]	Γ [10^{13}/s]
Cu	4.68	1.32	10.5
Au	5.08	1.35	12.8

Simulation of SPR excitation



Copper-based SPR chips



SPR angle changes

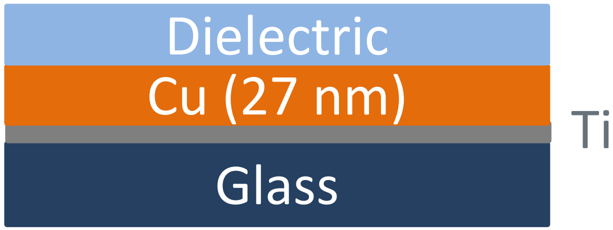
Sensitivity to RI changes

$$S_{\mathrm{RI}} = \frac{\Delta P}{\Delta n}$$

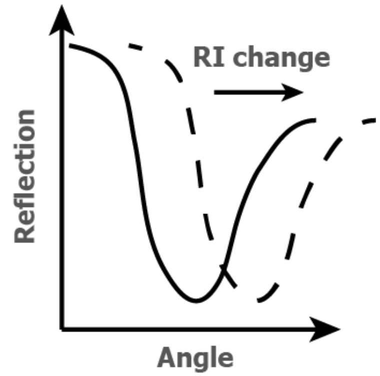
Δn – RI change

ΔP – resonant angle change

Simulation of SPR excitation



Copper-based SPR chips



SPR angle changes

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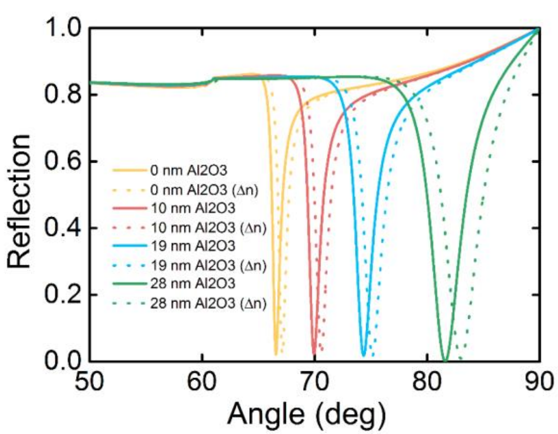
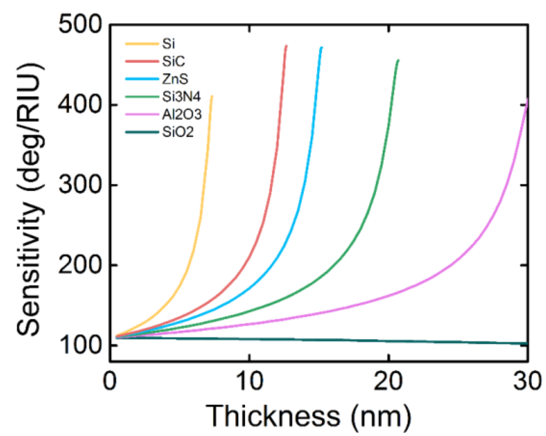
Angular reflection (Al_2O_3 coatings)



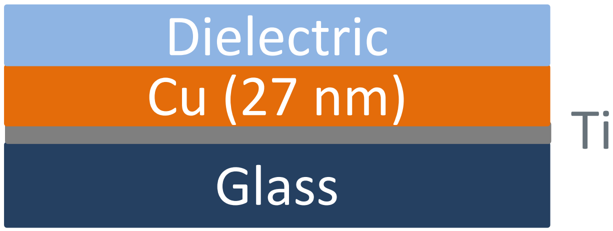
Sensitivity



3-4 times improvement in sensitivity

Yakubovsky et al., Optics Express 25(21), 2017

SPR measurements – salt testing



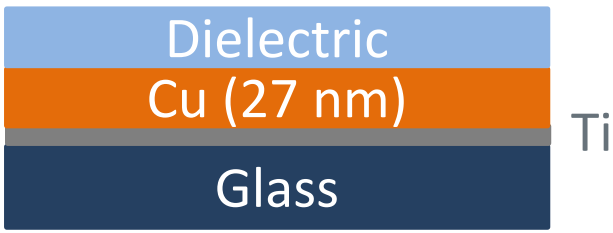
Copper-based SPR chips

+

BiOptix Accolade 104SA

- Phase measurements
- 0.5% NaCl injections

SPR measurements – salt testing



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- Phase measurements
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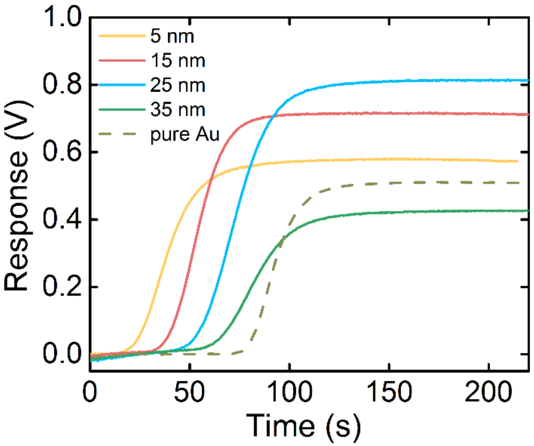
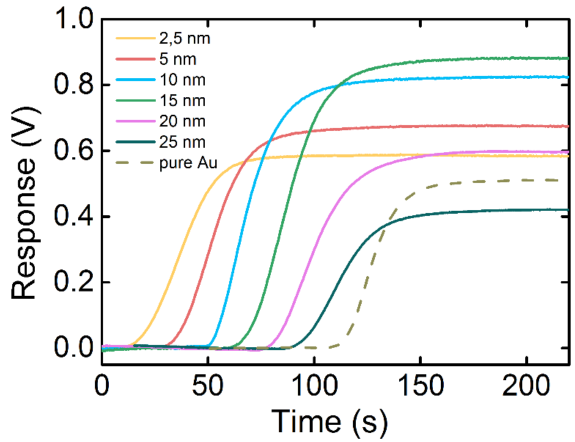
Copper-based SPR chips

BiOptix Accolade 104SA

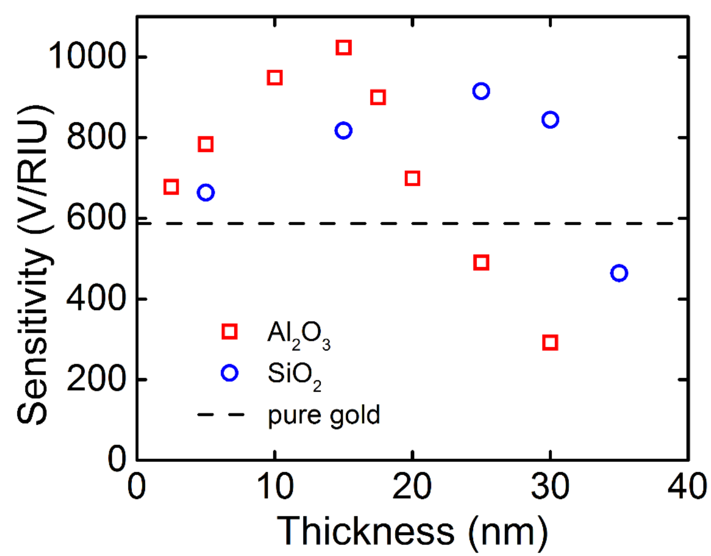
SiO_2



Al_2O_3



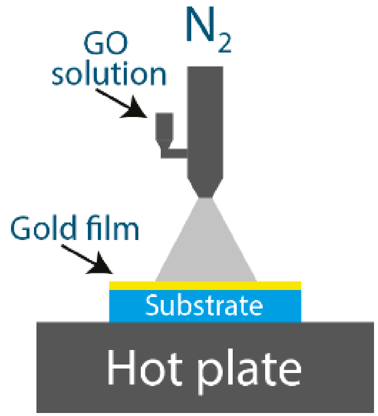
Sensitivity to RI changes



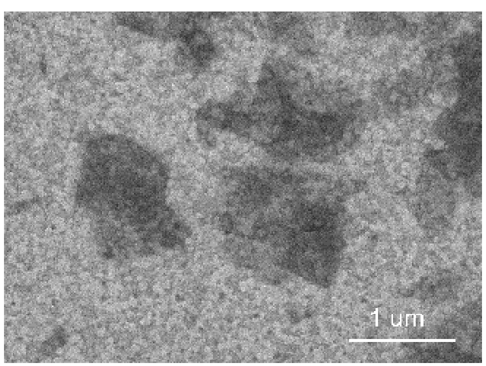
Graphene oxide linking layers for SPR analysis

Deposition of GO films

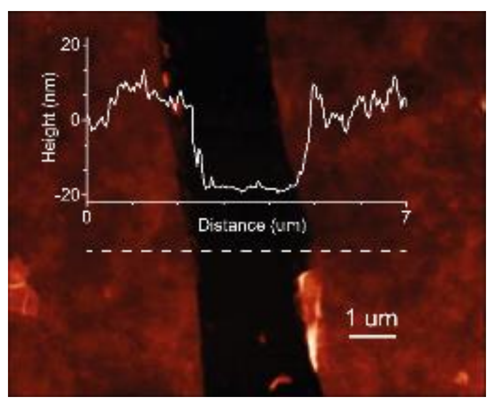
- Electrodeposition
- Spin-coating
- **Spray-coating**



80% of one-atomic-layer flakes (0.3-0.7 um)



Uniform GO film



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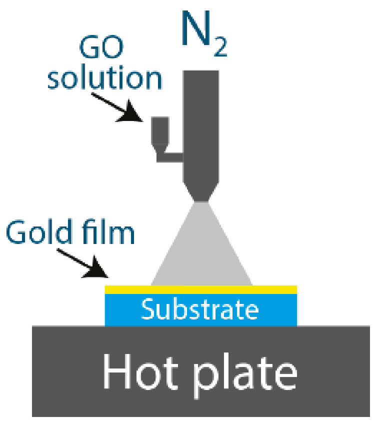
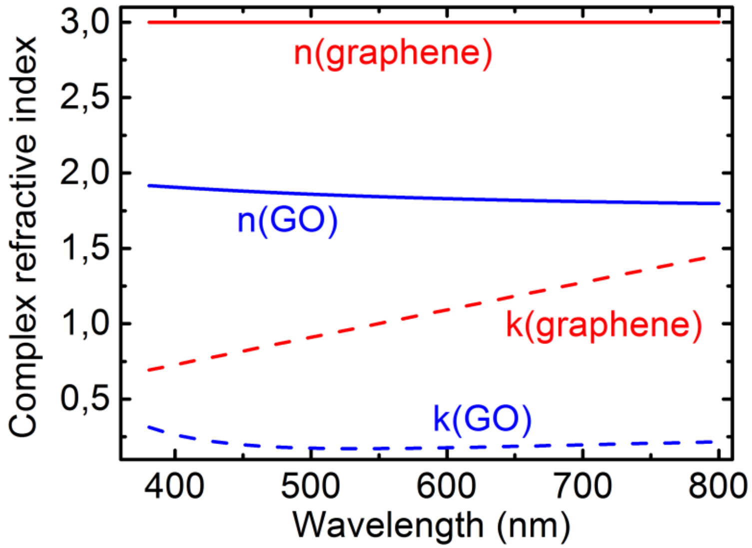


Ellipsometry of GO film



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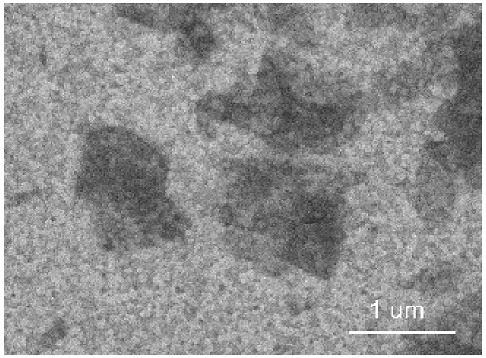
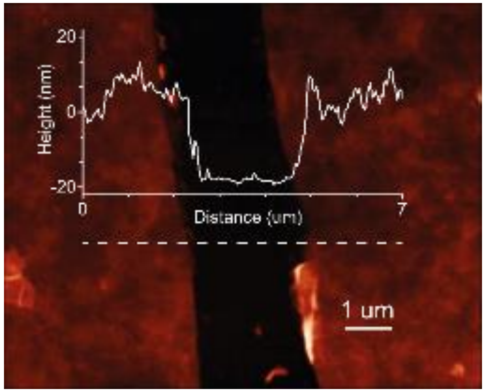


Uniform GO film

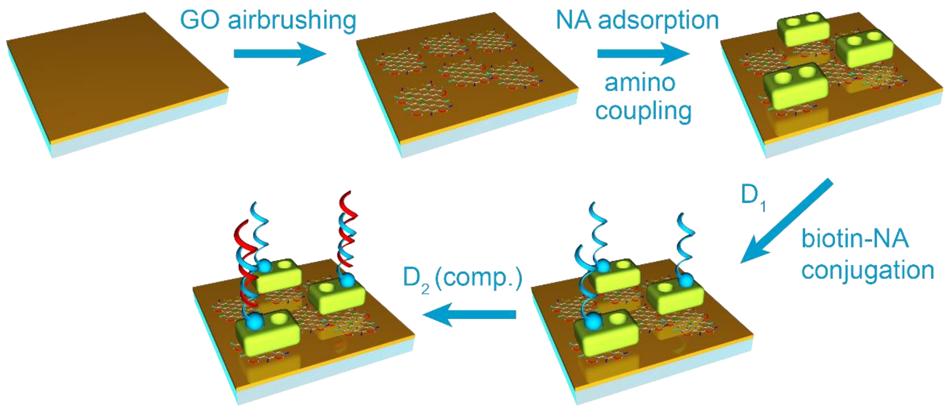


Refractive index at 635 nm

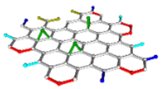
Graphene: $n_{gr} = 3, \quad k_{gr} = 1.16$

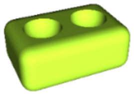
GO: $n_{GO} = 1.82, \quad k_{GO} = 0.184$

Neutravidin-biotin interaction



Neutravidin-coated surface is used for immobilization of biotinylated ligands such as proteins, peptides, nucleic acids, etc

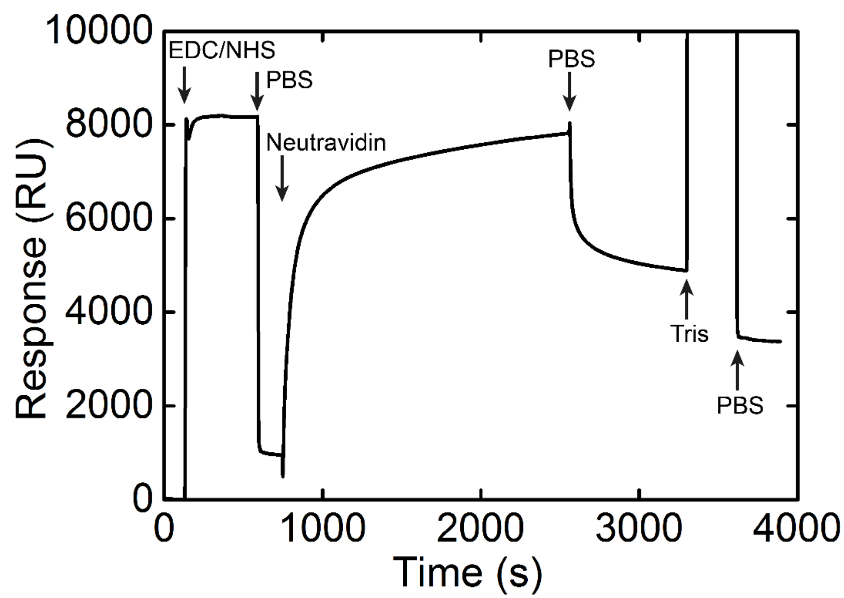
 – GO film with the thickness of 5 nm

 – neutravidin selectively binding the molecules with biotin residue

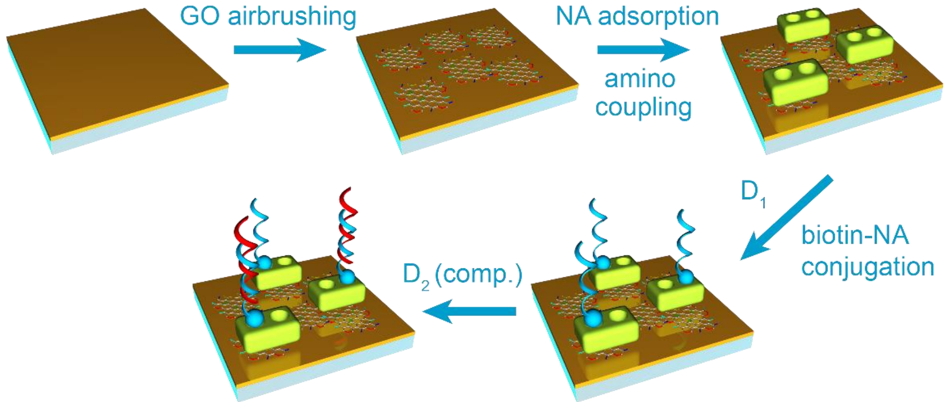
 – D1, biotinylated 56bp oligonucleotide sequence

 – D2, 50bp oligonucleotide sequence complementary to D1

Neutravidin immobilization



Neutravidin-biotin interaction



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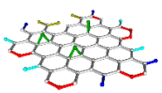
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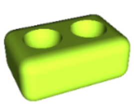
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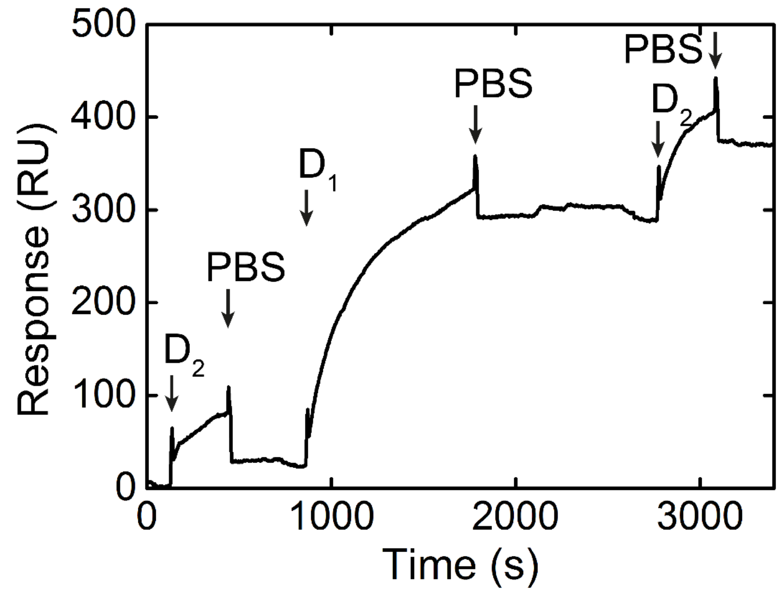
Oligonucleotide interactions



Summary

- Copper can substitute gold in plasmonic biosensors
- Dielectric coatings protect copper from oxidation and increase biosensing sensitivity
- Biomolecule immobilization using graphene oxide linking layers
- Copper and GO-based interfaces will open the way towards the integration of biosensors into consumer electronics

Stebunov et al., Langmuir 34, 4681 (2018)

Thank you for your attention!

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