Graphene/Metal Nanoparticle/Biomolecule Plasmonic Multifunctional Hybrid Platform

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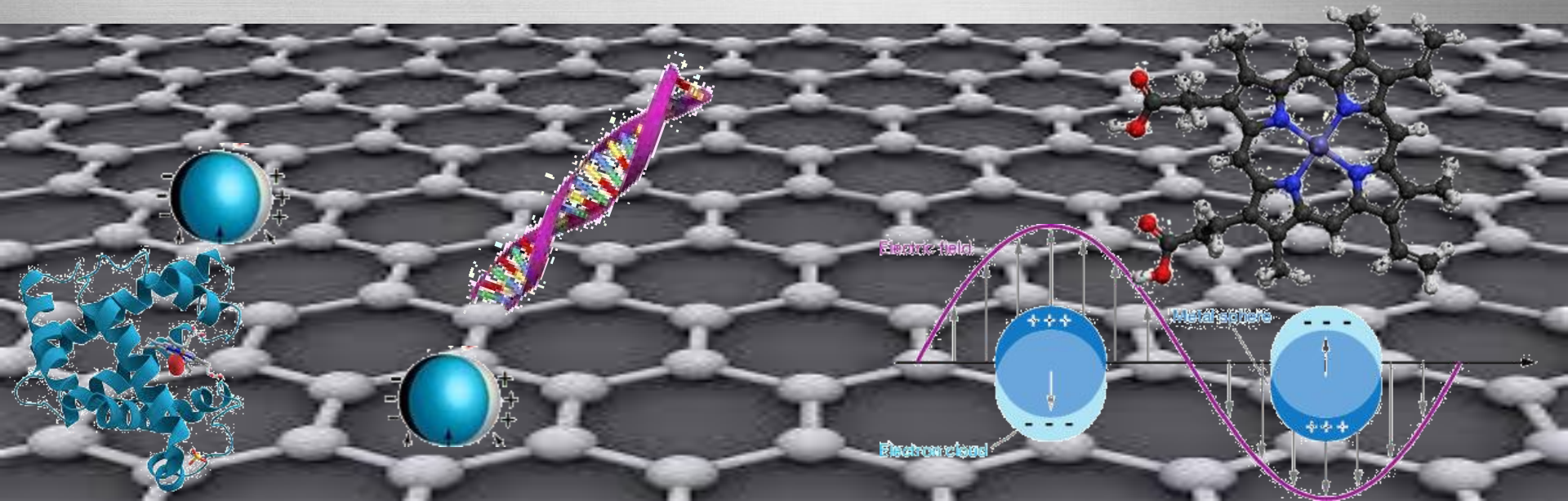
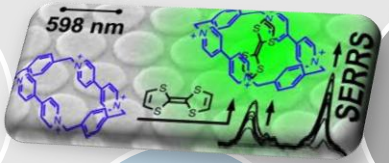
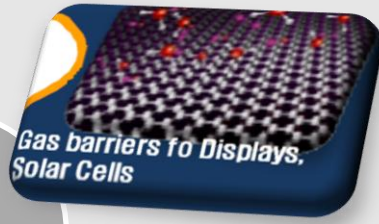


Motivation_Enabling Technologies

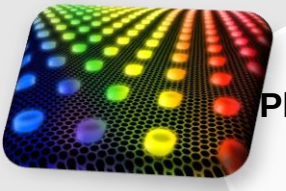
Composites



Printable Inks

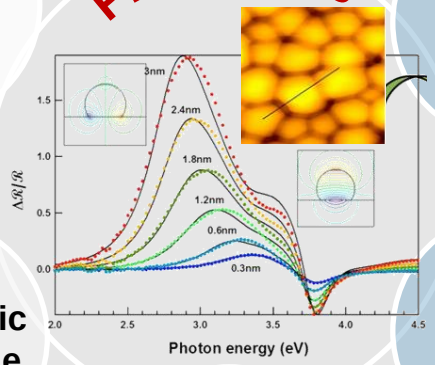


Gas Barrier



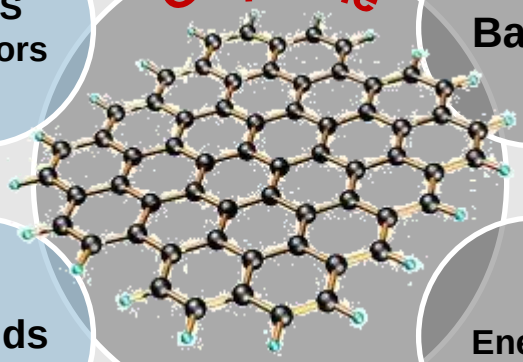
Plasmonic LEDS

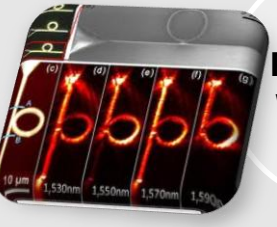
Plasmonics



SERS Sensors

Graphene



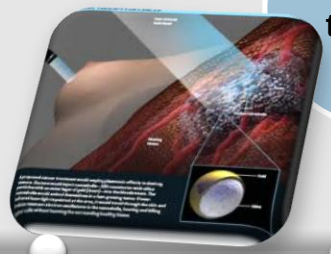


Plasmonic Wavguide

Hybrids

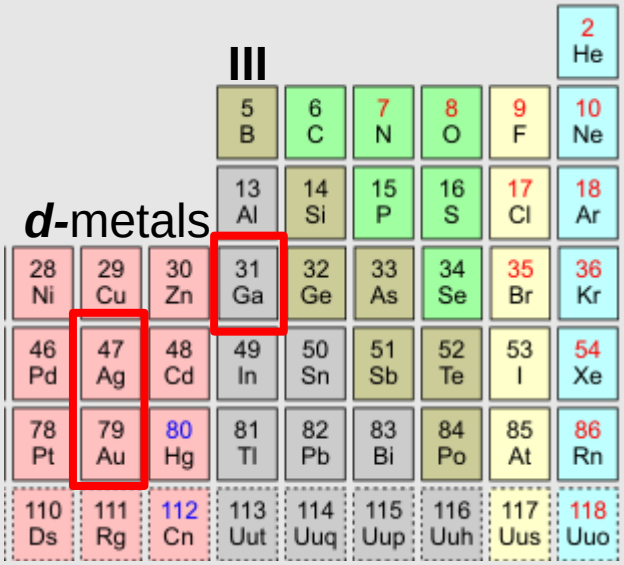
Energy

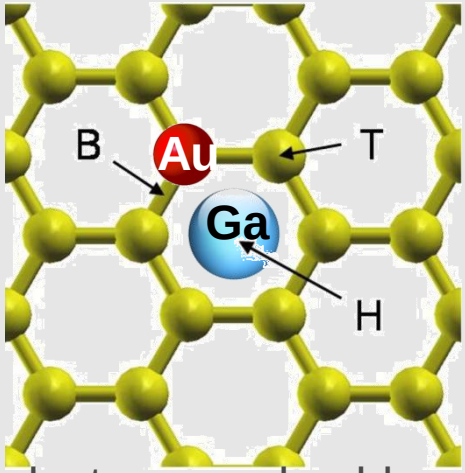
Cancer therapy



Transparent Electrodes

What differentiates plasmonic Ga, Ag and Au coupled to graphene?





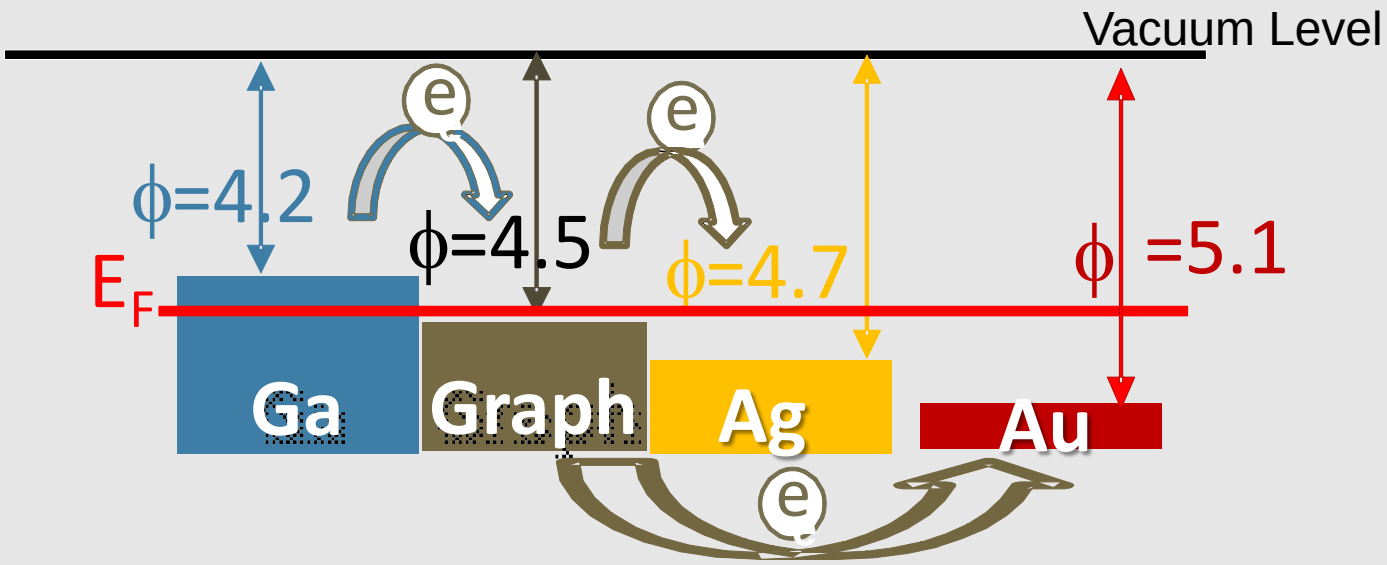
[K. T. Chan et al. PHYSICAL REVIEW B 77, 235430 (2008)]

Atom	Site	ΔE (eV)	d_{GC} (10^{-1} Å)
Ga	*H*	0.858	0.0
	B	0.762	0.0
	T	0.749	0.1
Au	*H*	0.085	0.0
	B	0.089	0.4
	T	0.096	1.4

Adsorption Energy **Graphene Distorsion**

- Metal atoms with d-valence electrons and noble metals exhibit covalent bonding on the T-site with strong hybridization of adatom and garphene electronic states, with strong distorsion changing some of the graphene sp2-like C to a more covalent reactive sp3-like C
- Elements from groups I-III (i.e. Ga) adsorbe on H-site and do not distort the graphene sheet. Thus the C-C bonds near the adatom retain their sp2 character
- Ga does **not** react with C to form carbide

Charge Transfer between Graphene and Metal Nanoparticles

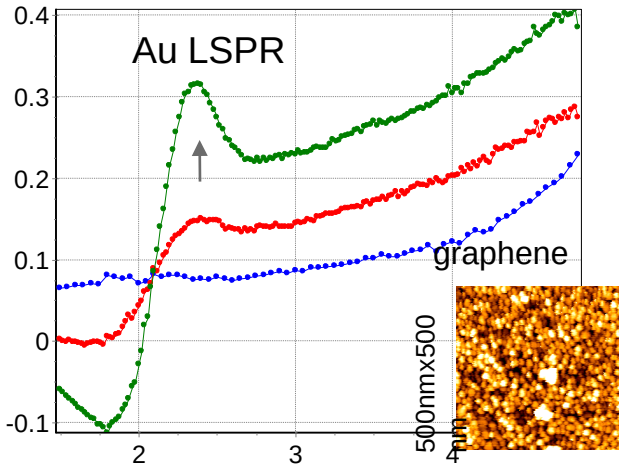


» As soon as the systems can communicate, equilibration of the Fermi energies takes place by the transfer of electrons from the low to the high work-function system

» Charge transfer in opposite directions can be exploited to activate biomolecules, sensing and drug delivery

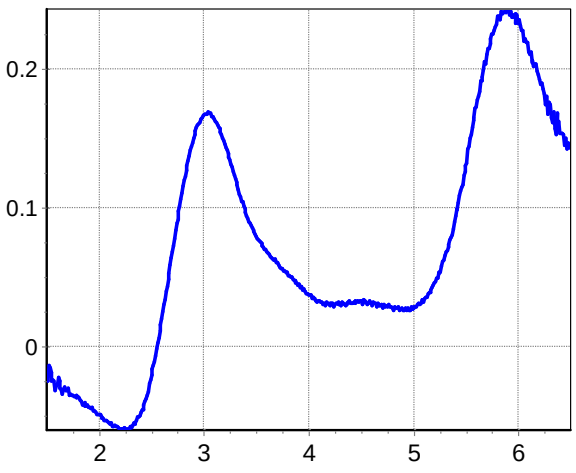
Tunability of the Localized Surface Plasmon resonance

Au NPs-Graphene-Glass



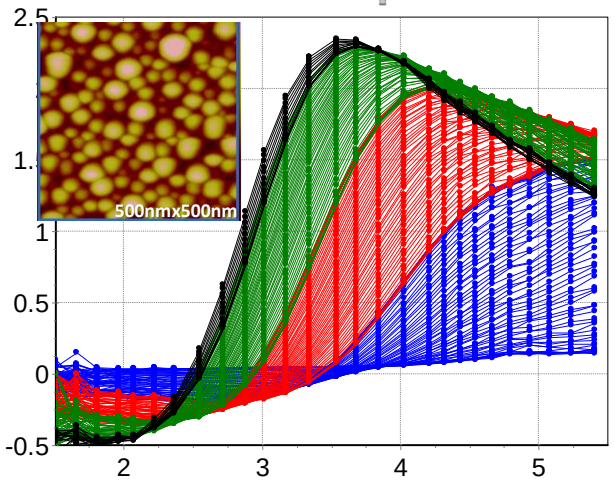
LSPR <2.3 eV

Ag NPs-Graphene



LSPR >3.4 eV

Ga NPs-Graphene



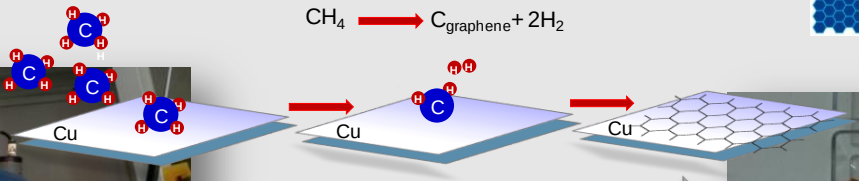
LSPR from UV to NIR

• Ga NP-based platforms are effective for creating localized surface plasmon resonances (LSPR) tunable over the UV to the near IR spectral range and we have demonstrated SERS activated by Ga NPs in both the visible and UV

[P. Wu, M. Losurdo et al. JACS 131, 12032 (2009)]
[M. Losurdo et al. Small 8, 2721 (2012)]

Approach - Process

CVD

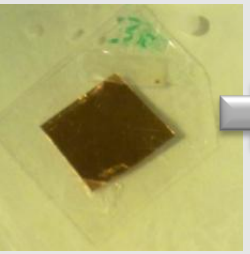


- CH_4:H_2
- 1000°C
- 0.5Torr

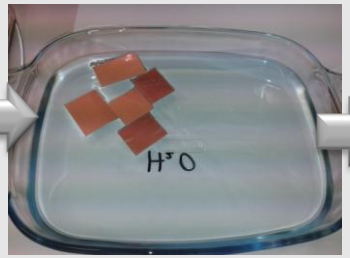
(max size = 20cm* 25cm)

Thermal Tape Transfer

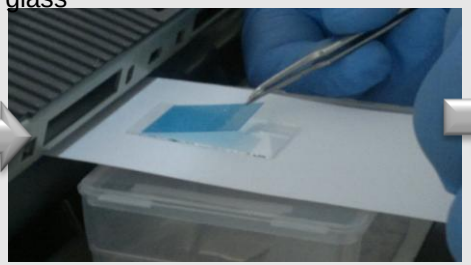
Tape on G/Cu



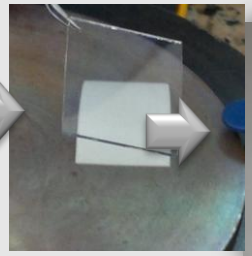
Cu dissolution



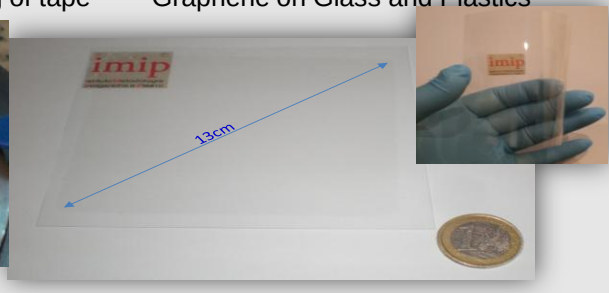
Lamination of Thermal Tape /G on glass



Thermal detaching of tape



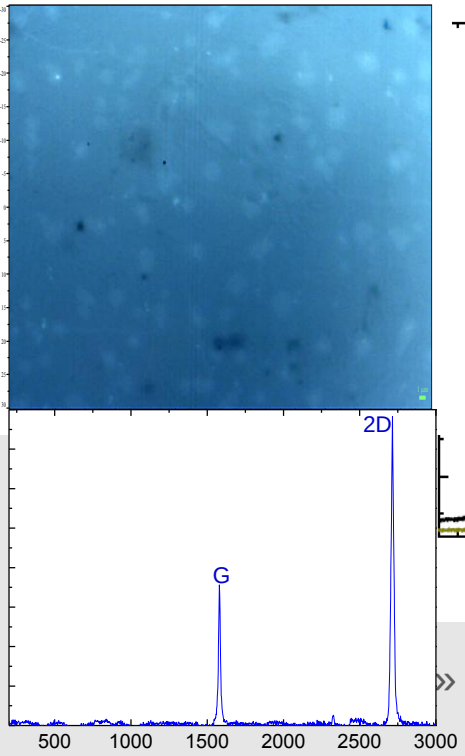
Graphene on Glass and Plastics



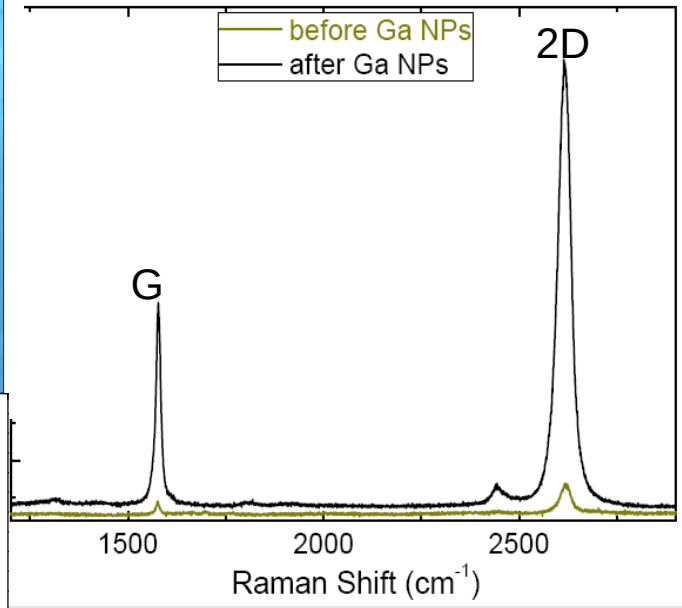
Evaporation of Metal Nanoparticles and Functionalization by Biomolecuels dipping in solution

Raman Enhancement by Ga NPs and Suppression by Au NPs

Graphene

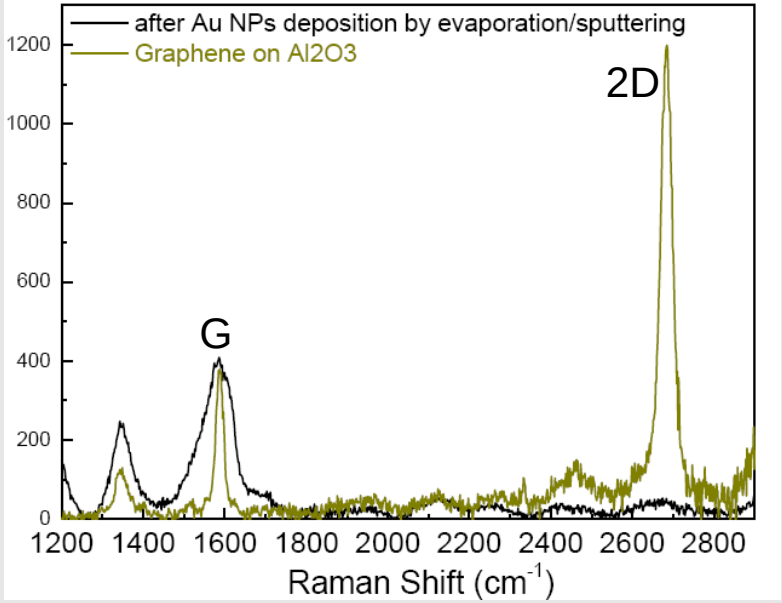


Ga NPs-Graphene



» Raman spectrum of graphene after Ga NPs indicates absence of creation of defects by Ga deposition and a Raman enhancement

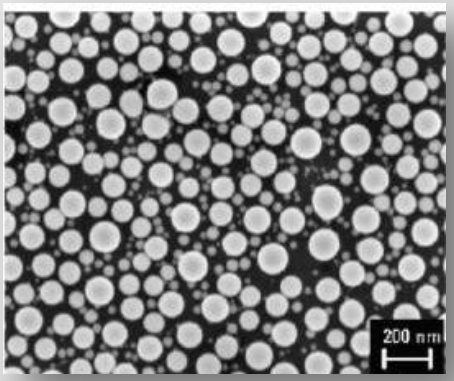
Au NPs-Graphene



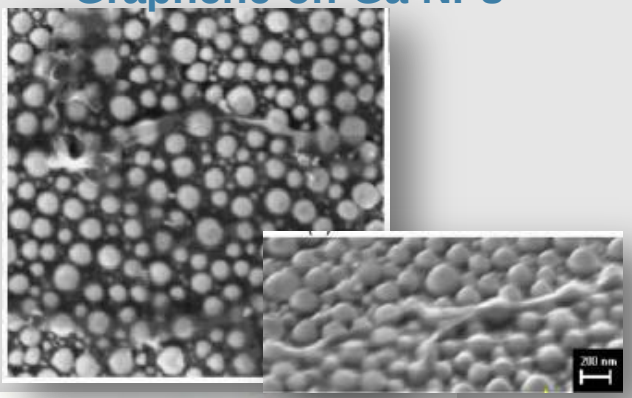
» Raman spectrum of graphene after Au NPs indicates that the graphene lattice structure is severely degraded as evidenced by the diminishing 2D peak at 2690 nm and increase of D-peak

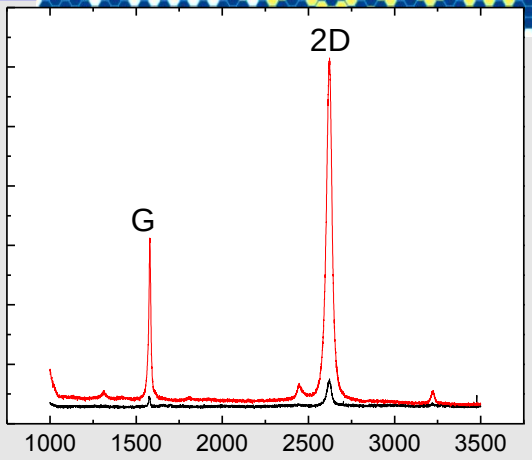
Graphene coupling with Gallium (Ga) Nanoparticles

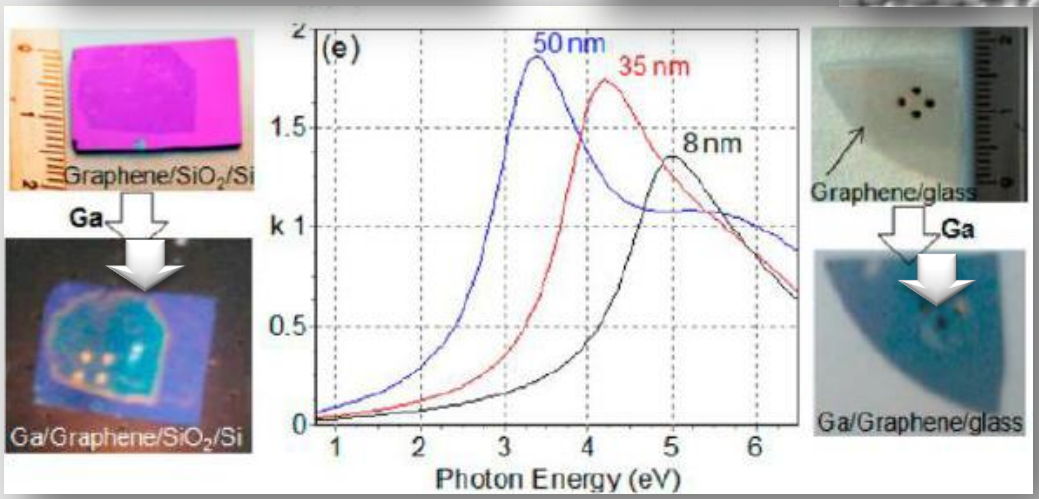
Ga NPs-on-Graphene

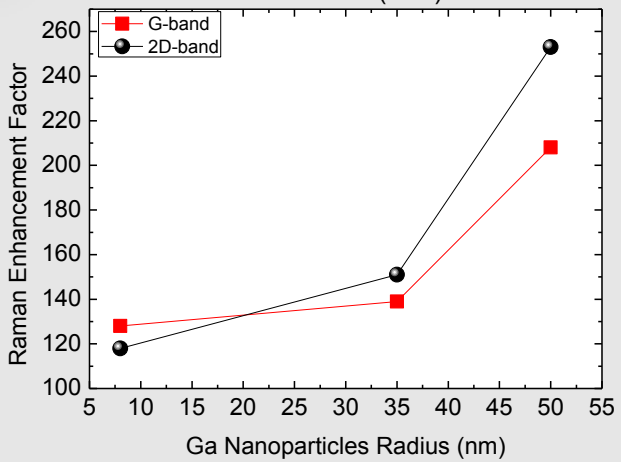


Graphene-on-Ga NPs









- Tunability of the LSPR in a broad energy range from UV to VIS NIR to match resonance
- The Raman modes of graphene are also enhanced and indicate no damage of graphene by Ga
- Graphene is permeable to the electromagnetic field enhancement [M. Losurdo et al. ACS Nano, 8, 3031 (2014)]

Ga-Graphene as a SERS Sensor for Drugs_Rhodamine

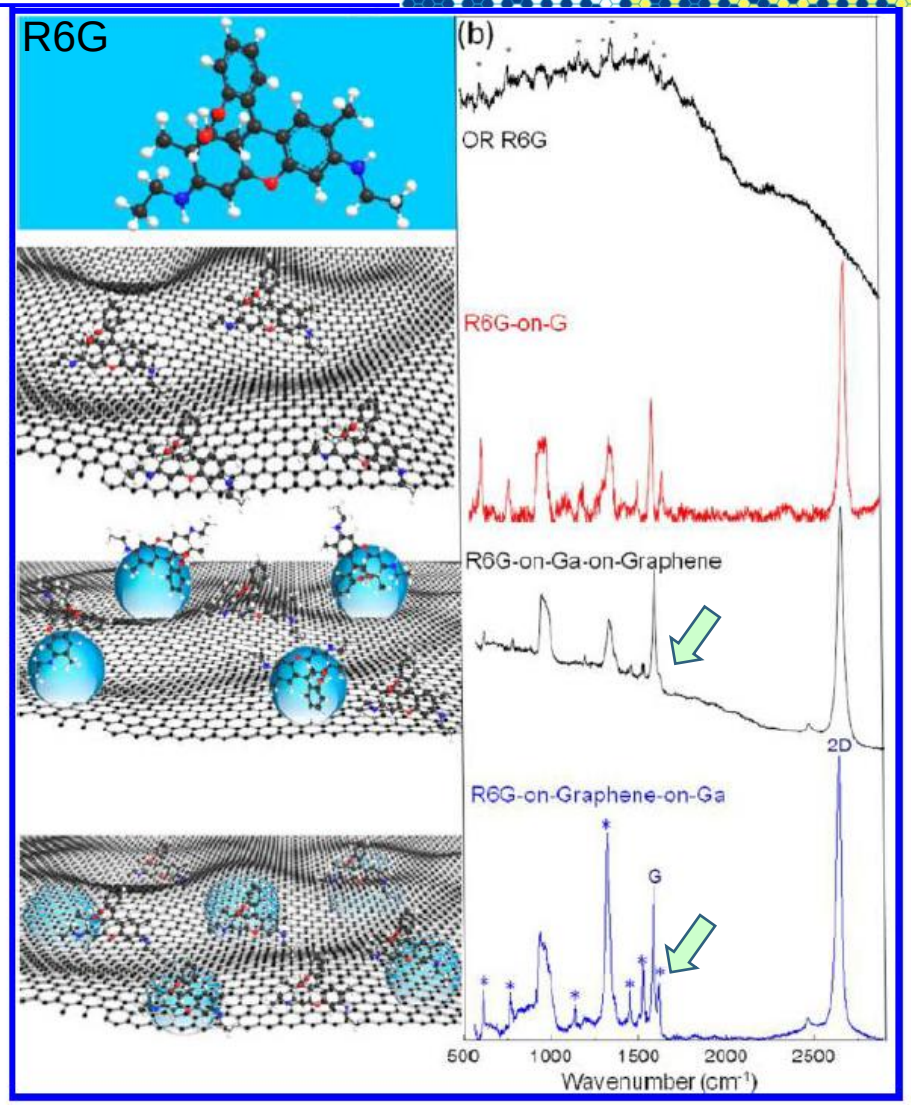
What is the most appropriate graphene SERS sensor configuration?

• The primary impact of graphene is quenching of the fluorescence background when R6G is anchored directly to graphene

• When Ga NPs are deposited on graphene, a relative increase by a factor of 10 in the intensity is observed together with a decrease in the intensity of the 1648 cm^{-1} R6G peak indicating that R6G molecules are randomly oriented on the Ga NP surface

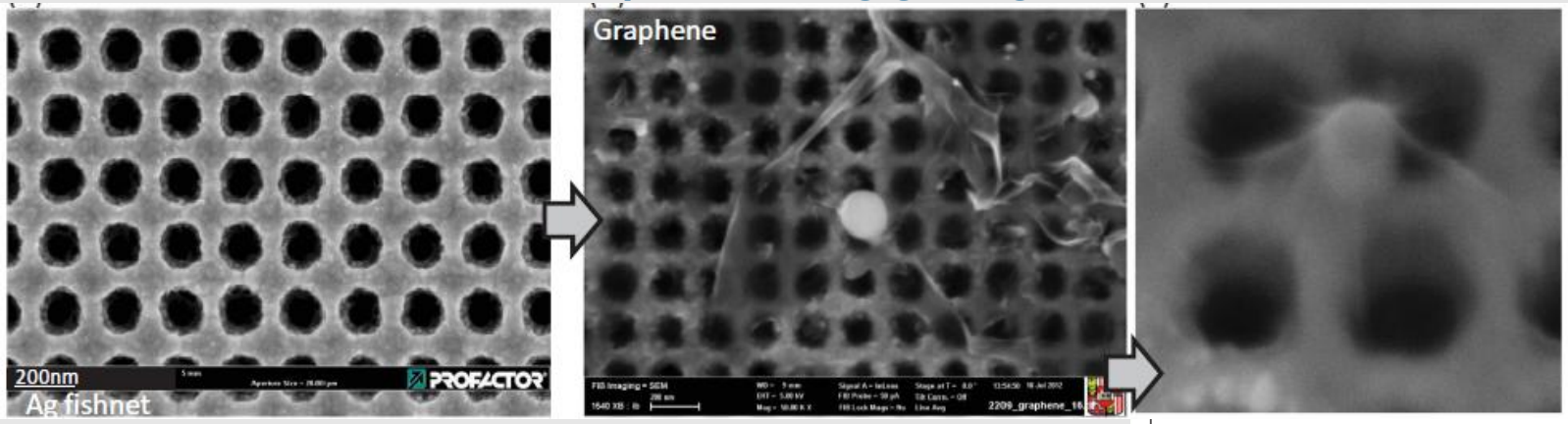
• When graphene is on top the Ga NPs, the enhancement factor is >50 and the 1648 cm^{-1} xanthene ring stretching mode iswell discerned, providing evidence for a more ordered R6G overlayer

[M. Losurdo et al. ACS Nano, 8, 3031 (2014)]

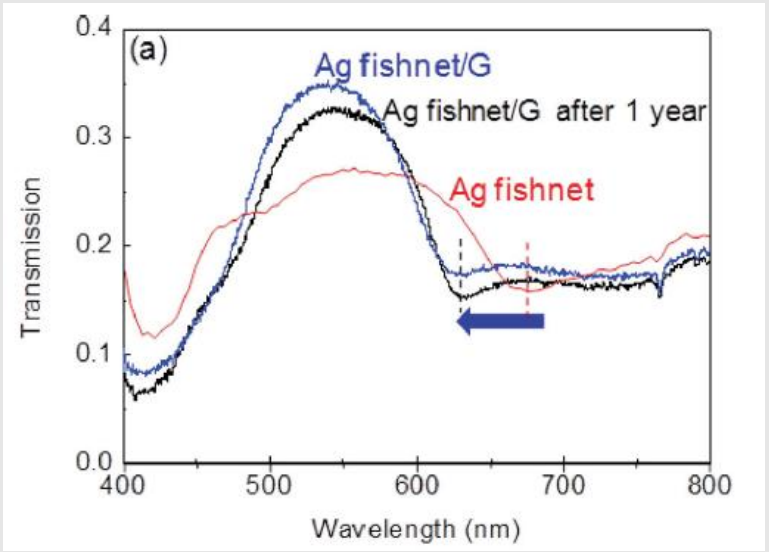


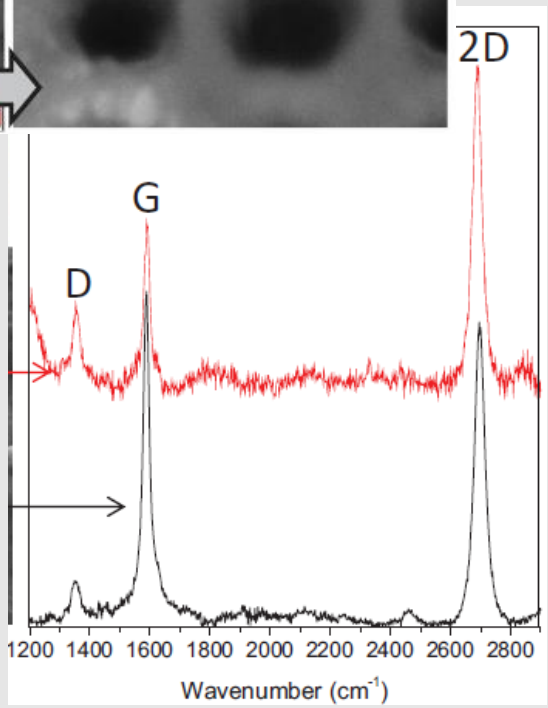
Ag-Graphene as SERS Biosensor: Impact on Air Stability of Sensor

Graphene-on-Ag grating



- **Graphene/silver hybrids** based LSPR applications and SERS sensors are significantly **more stable over a long time** period, enabling the technological development of stable plasmonic SERS toward lower wavelengths



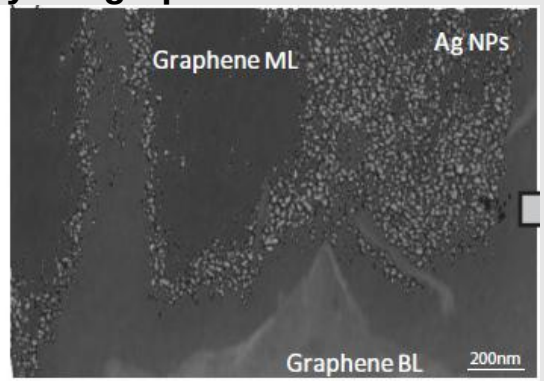


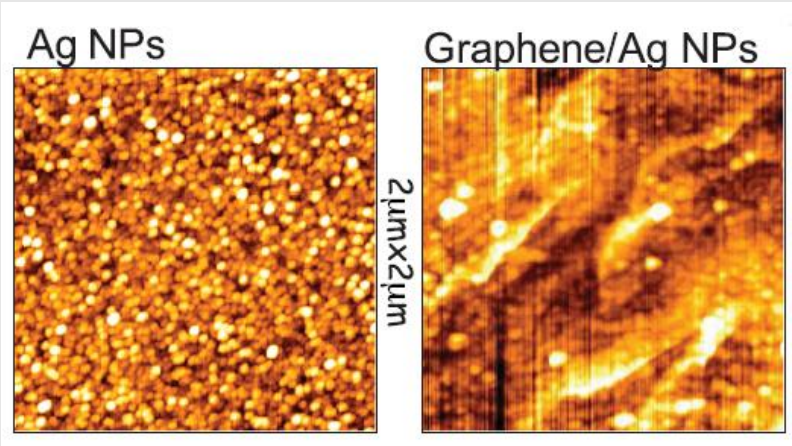
[M. Losurdo et al. Adv. Func. Mater, 24, 1864 (2014)]

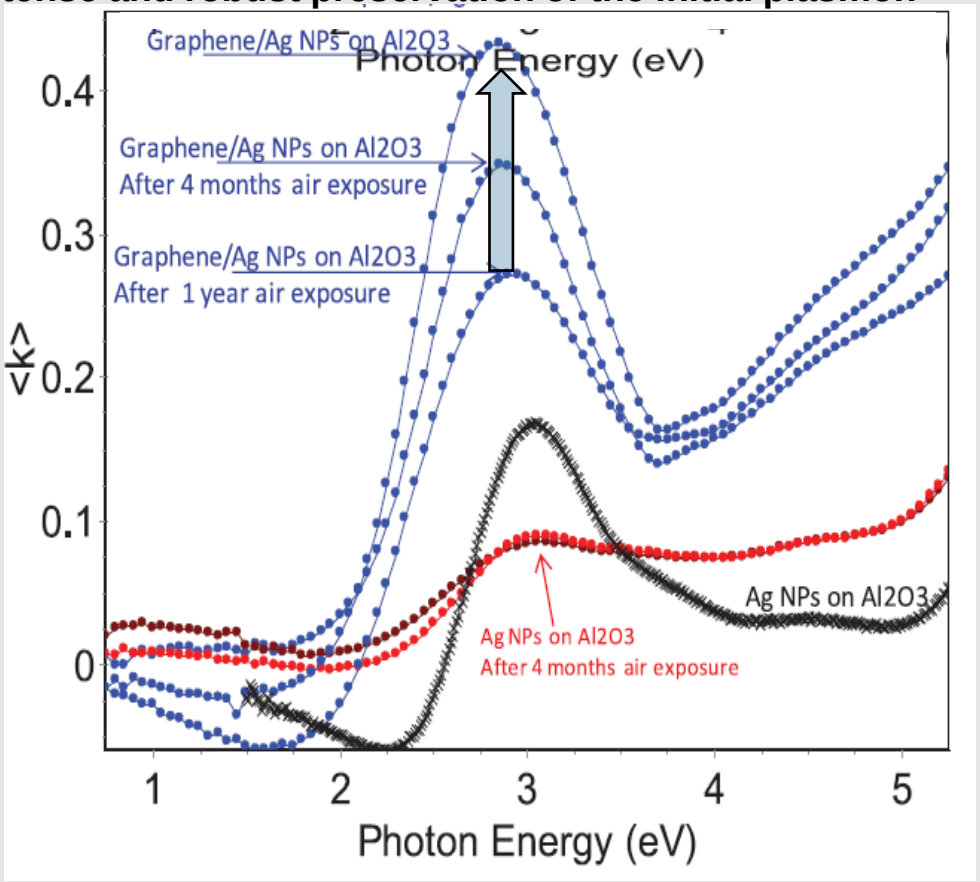
Ag NPs-Graphene as SERS Biosensor: Field Enhancement

The optical spectra of the nanoparticle arrays were measured over a period of one year of air exposure to study the effectiveness of the graphene passivation.

Over a four-months the resonant peak damped dramatically for Ag NPs. In contrast, **the Ag NPs that were covered by the graphene showed a much more intense and robust preservation of the initial plasmon**

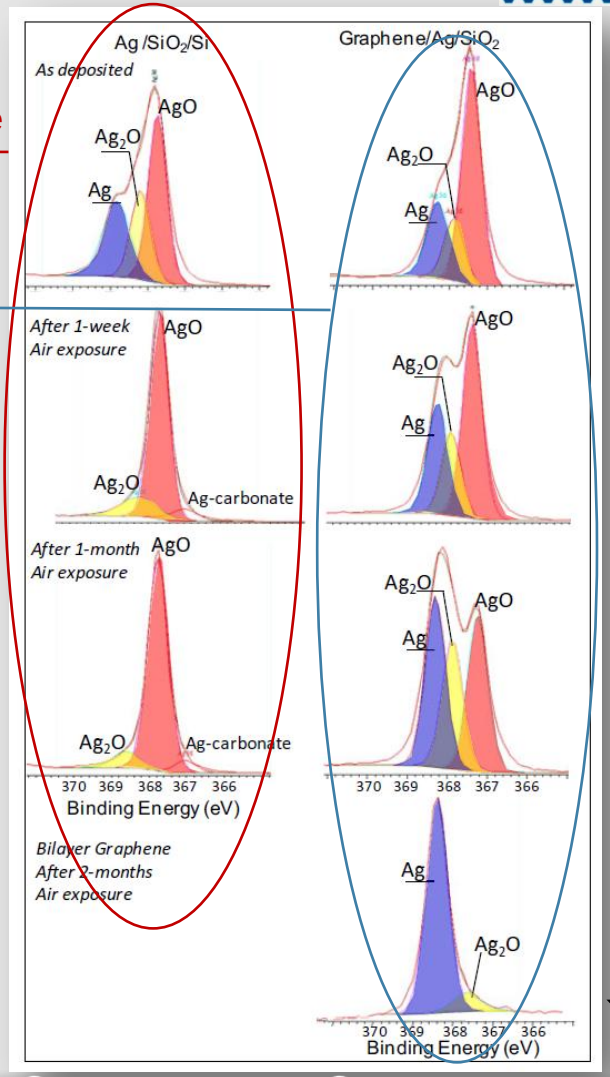


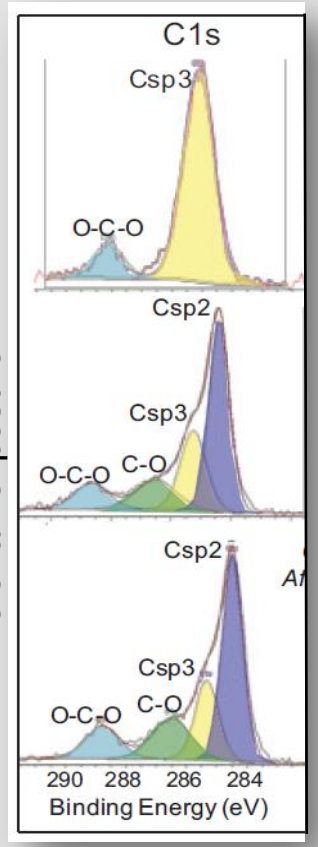




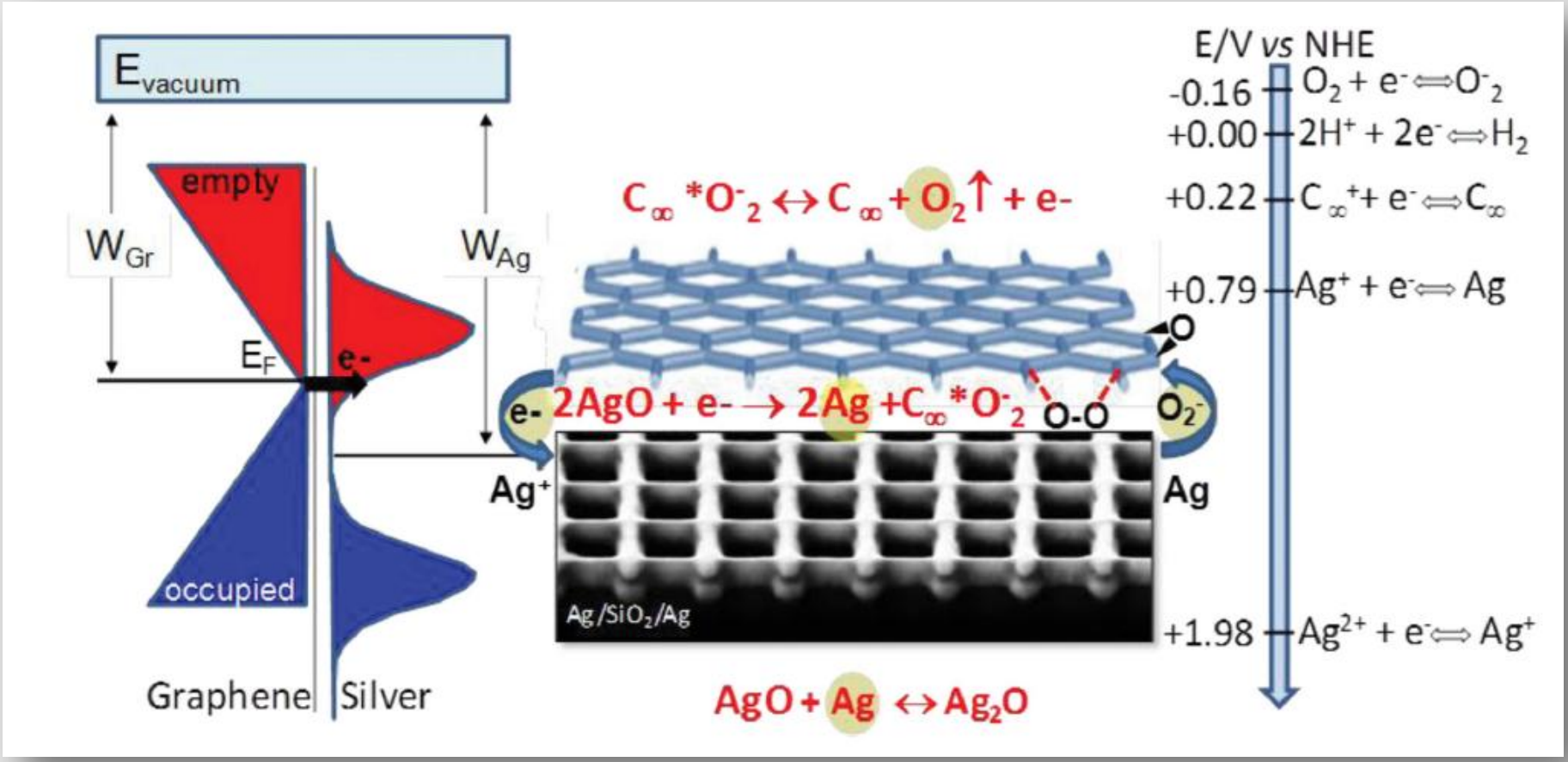
Electron Transfer from Graphene to Ag/AgO and AgO reduction

- Silver oxidizes by air exposure ← No Graphene
- When silver is covered by a graphene monolayer, silver remains metallic even after months of air exposure.
- The metallic Ag^0 component shifts to lower binding energies when it is in contact with graphene
  - Indication ef electron transfer from graphene to Ag
- When graphene is in contact with silver, new C1s components due to C-O appear
  - Indication of oxygen transfer from silver to graphene

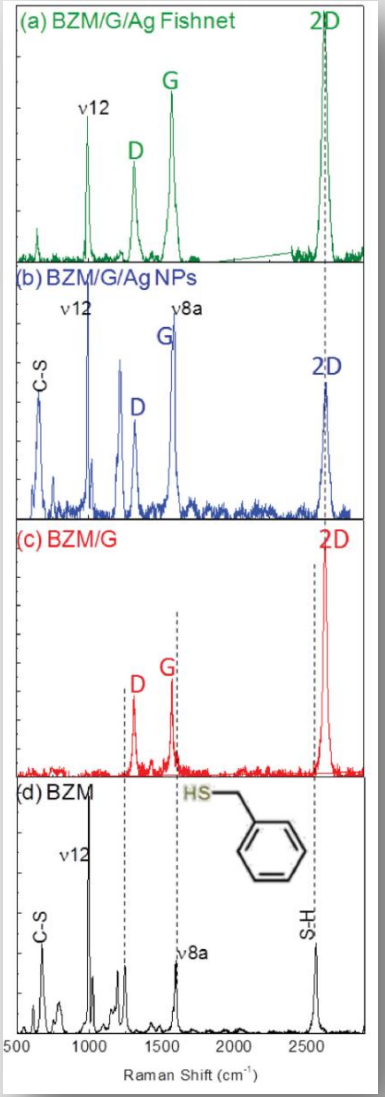




Mechanism for Ag Deoxidation Promoted by Graphene



Ag-Graphene as stable SERS sensing platform



•The stability of the plasmon resonance of the Ag NPs and fishnet structure is relevant to the realization of more stable and robust SERS sensors

•Ag NPs/graphene and graphene/Ag-fishnet has been evaluated and compared using the BZM thiol as probing molecule π -system can electronically interact with that of graphene

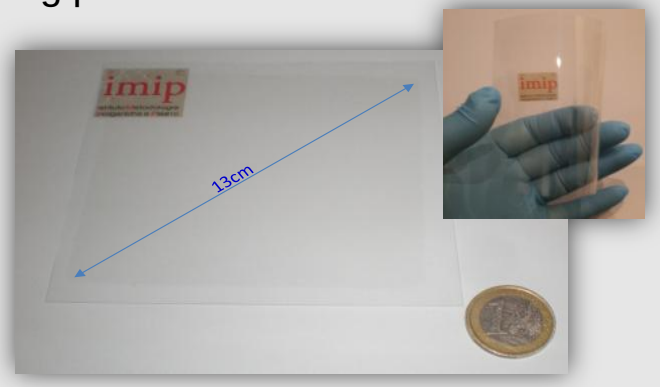
•For the SERS enhancement, EF, we considered the v12 mode and found **EF values of 210 for the graphene/Ag fishnet and of 300 for the graphene/Ag NPs, stable over 1 year!!**

•For comparison a CVD graphene transferred on a similar Au fishnet has demonstrated an enhancement factor of ≈40 for the methylene blue. [Q. Hao , et al., *J. Phys. Chem. C ,* 2012 , 116 **,** 7249]

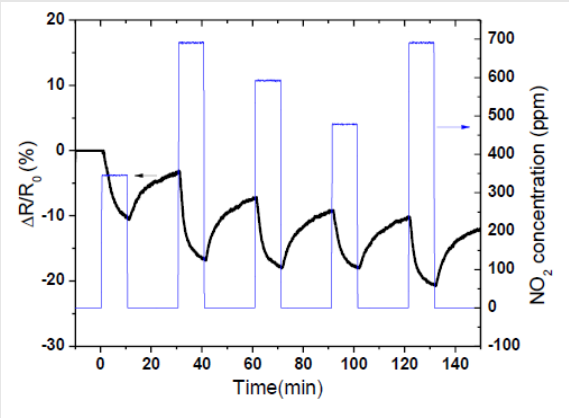
[M. Losurdo et al. Adv. Funct. Mater 24, 1864 (2014)]

Summarizing

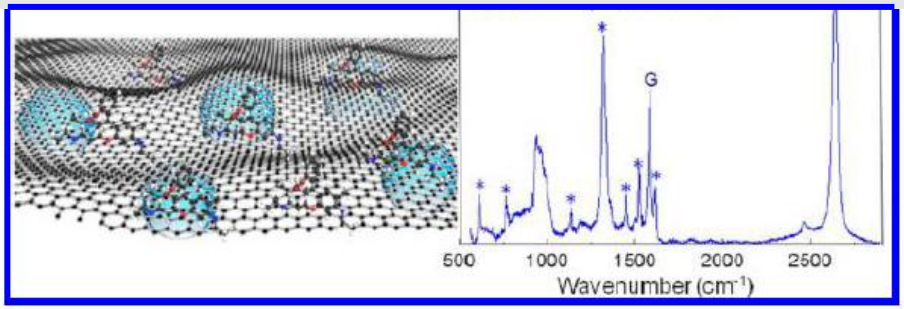
- Large area graphene by CVD is available on various supports to create catalytic and sensing platforms



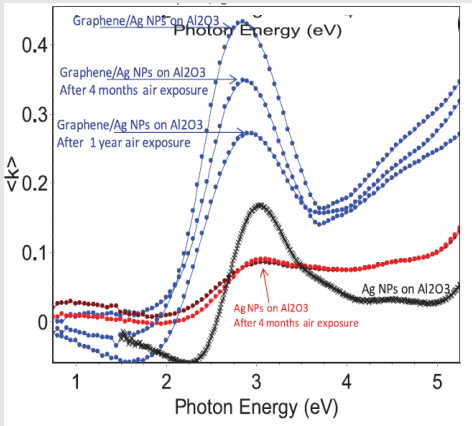
- Graphene can provide a platform for sensing NOx

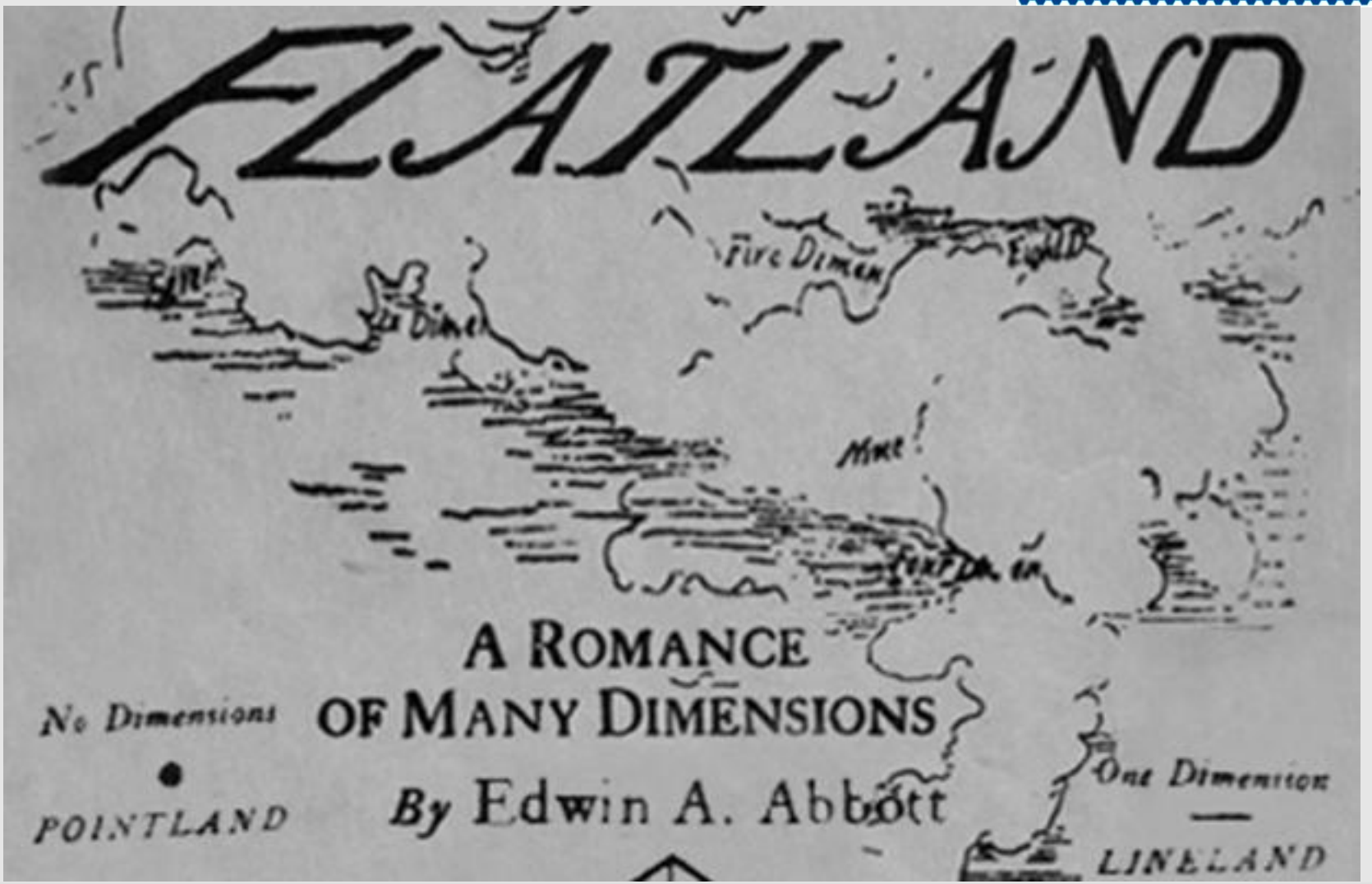


- Graphene on Plasmonic NPs provides a better sensing platform than NPs on graphene



- Coupling graphene with Ag is an effective way to have visible stable sensing SERS platform





[Published on 1889]