Plasmonic gold nanoparticle deposition on pristine and functionalized graphene

Giuseppe V. Bianco, Maria M. Giangregorio, Maria Losurdo, Pio Capezzuto, Giovanni Bruno**,**

Institute of Inorganic Methodologies and of Plasmas, IMIP-CNR, via Orabona 4, 70126 Bari, Italy

giuseppevalerio.bianco@cnr.it

Nowadays, there is no doubt that materials of the graphene family (single layer graphene, SLG, few layer graphene, FLG, graphane, graphene nanoribbon, GNRs, reduced graphene oxides, RGO, graphene oxide, GO, epitaxial graphene, EG) can be successfully employed in a variety of hybrid structures that take advantage of their unique optical and electronic properties.

It is expected, among others, that the marriage between graphene and plasmonic gold nanoparticles (AuNPs) can yield novel functional nanostructured materials which can be fully exploited in a variety of applications spanning from optoelectronics, such as organic photovoltaics and light emitting devices, to sensors, such as bio-and gas sensors also in SERS devices.

In this contribution we prepare AuNPs/graphene hybrids by combining different approaches as detailed:
- three main methods have been used to fabricate graphene–AuNPs composites:
  - direct vapor growth of AuNP by PVD, both sputtering and evaporation on the graphene surface
  - solution growth of AuNP by reduction of $HAuCl_4$ on graphene.
  - anchoring of solution gold nanoparticles on functionalized graphene.
- The graphene has been obtained by both the Cu catalyzed CVD and the Si sublimation of SiC.
  - The CVD graphene sheets were obtained by CH_4/H_2 at 900 °C on Cu foil and the standard transferring method using $FeCl_3$ and PMMA on 300 nm SiO_2/Si substrate [1].
  - The Epitaxial graphene is produced on 6H-SiC by Si sublimation in a UHV reactor (Base vacuum better than 10^{-8} torr) at 1600°C.[2]

We have identified few-layer (<5 layers) graphene sheets using spectroscopic ellipsometry and attenuation SiC Raman peak method.

Raman spectroscopy has been used to fingerprint the graphene layer quality, and some representative spectra are shown in Fig. 1.

The aim is at engineering both optical properties, i.e., transparency, plasmon resonance energy and amplitude, and electrical properties, i.e., conductivity and carrier density by exploiting the charge transfer processes in the Au NPs/graphene hybrids.

Here we show for the first time the dynamic of the surface plasmon resonance (SPR) of AuNPs/graphene/ obtained by Au sputtering onto EG and CVD-graphene, allowing tailoring the SPR energy and amplitude to the target application (SERS-sensor or PV) (Figure 2). For this kind of hybrids, an upshift for both the G and 2D peaks of graphene is observed which is consistent with a p-type doping of graphene as reported by others [3]. We present the correlation existing between the Au NPs size and graphene p-type doping mutual affecting the SPR characteristics. A comparative discussion about Au NPs effects and doping realized by the wet $HAuCl_4$ chemistry will be presented.

Furthermore, we also investigated and present data on the assembling of colloidal Au NPs on molecular functionalized graphene. Specifically, in order to allow uniform coating of AuNP on the pristine graphene, functionalization is necessary to induce uniform surface groups as active anchoring sites. We discuss the effect of various functionalizing molecules including CTAB, aliphatic (dodecanthiol) and aromatic (BZT) the difference in between the categories being the additional coupling of the aromatic system of the functionalizing layer with graphene. Specifically, the Benzyl thiol (BZT) is an excellent candidate for selective functionalization of graphene surfaces owing to its planar conjugated ring (BZ) system and its thiol (-SH) functionality. While BZ partition adheres to graphene, likely via π-π stacking and hydrophobic forces, the terminal thiol group reacts with gold to strong covalent AuS bond. The Raman analysis on those systems shows that the aromatic BZT link between the graphene and the Au NPs enhances the charge transfer and p-type doping of graphene. We also observe an enhanced SERS effect of both graphene modes and BZT mode providing evidence of an effective coupling of the SPR of Au NPs. On the other hand, in the case of the CTAB linker, there is no effective charge transfer to Au NPs and n-type molecular doping by the CTAB self-assembled monolayer occurs confirmed also by the downshift of the G-band. Thus, the plasmonic properties of Au NPs and doping effects can be tailored independently.

References

[1]   X. Li, W, Cai, J. An, S. Kim, J. Nah, D. Yang, L. Colombo, R.S. Ruoff, Science **324** (2009) 1312.

[2]   C. Berger, Z. Song, T. Li, X. Li, A.Y. Ogbazghi, R. Feng, Z. Dai, A.N. Marchenkov, E.H. Conrad, P.N. First, W.A. de Heer, J. Phys. Chem. B, **108** (2004) 19912.

[3]   F. Schedin, E. Lidorikis, A. Lombardo, V. G. Kravets, A. K. Geim, A. N. Grigorenko, K. S. Novoselov, A. C. Ferrari, ACS Nano, **4** (2010), pp 5617–5626

[4]   S. Shivaraman et al. J. Electron. Mater. **38** (2009) 725

Epitaxial Graphene on SiC

CVD Graphene on SiO₂
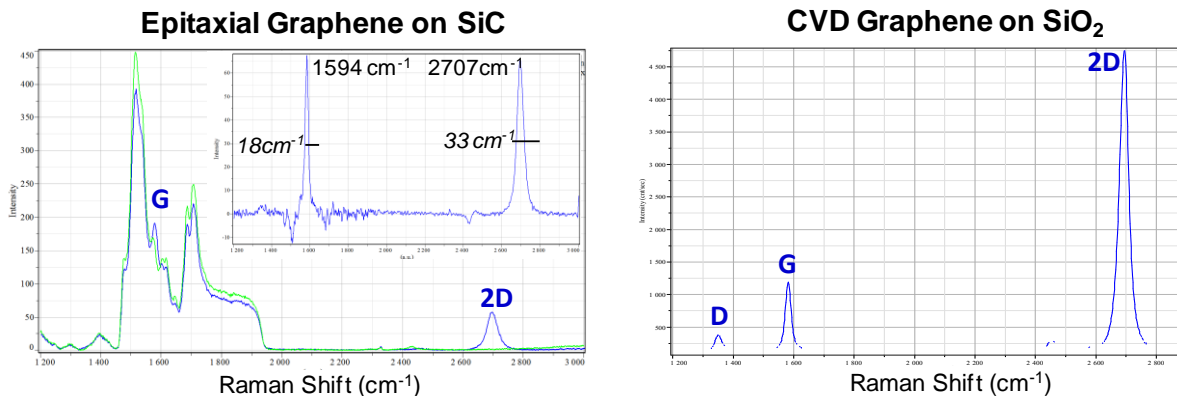
Figure 1: Raman spectra of (a) EG on C-face SiC by the SiC sublimation method; the inset shows the difference spectrum between SiC substrate and EG/SiC and of (b) on Cu-foil by CVD from CH4-H2. For EG/SiC the attenuation of substrate Raman intensity is S=0.88 corresponding to estimated thickness = 4 layers [4]

Au NP/Graphene/SiC

Au NP/Graphene/Al₂O₃
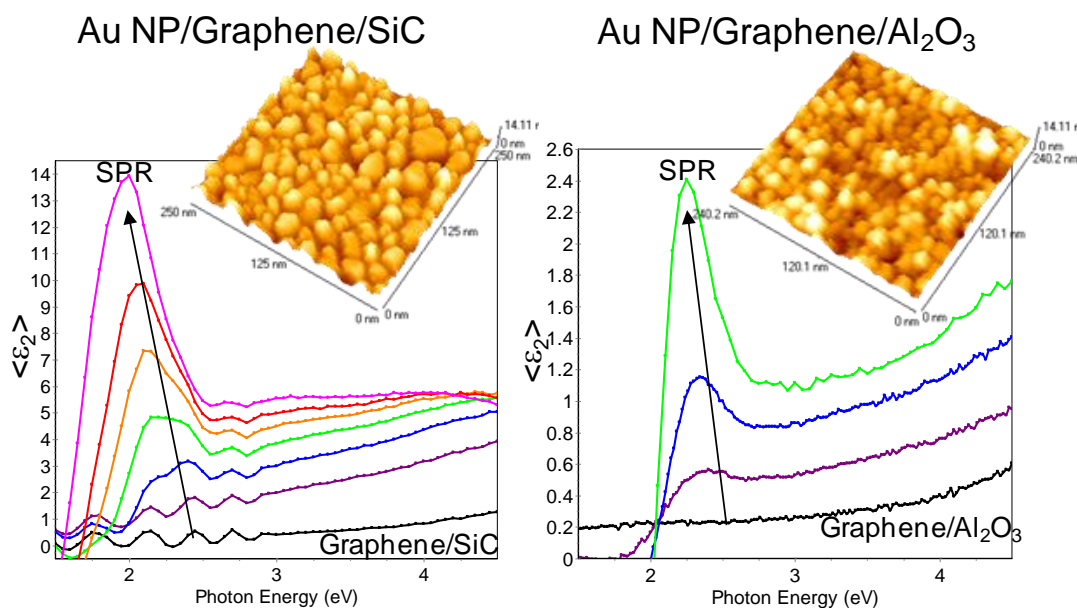
Figure 2: Real time dynamics of the surface plasmon resonance (SPR) peak of Au nanoparticles deposited on epitaxial graphene/SiC and on CVD graphene transferred on Al₂O₃ monitored by ellipsometric spectra of the imaginary part of the dielectric function. The AFM morphologies show the different aspect ratio of the AuNPs grown on the different graphene.
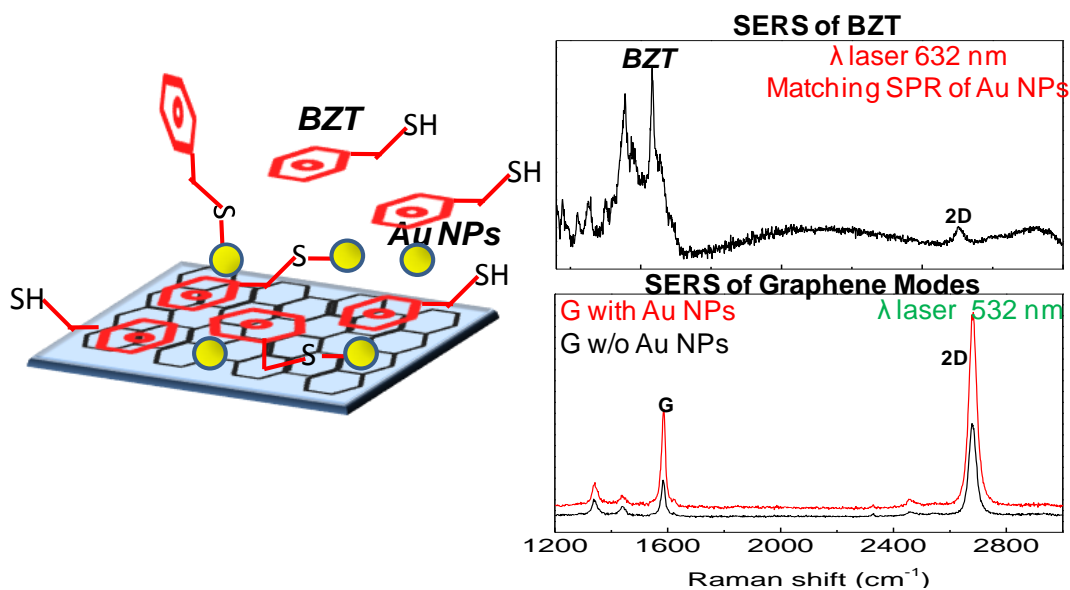
Figure 3: Colloidal Au NPs linked to graphene through the BZT self assembled layer; the Raman spectra show the SERS enhancement of the graphene modes (green laser at 532 nm) and the SERS enhancement of the BZT thiol modes (red laser at 633 nm) matching Au NPs SPR.