Graphene to Enhance Chemical and Optical Stability of Plasmonic Properties of Silver based Plasmonic- and Meta-Materials

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Graphene, with its extensive π-electron conjugation and delocalization giving rise to the extreme physical strength and chemical inertness, is a very versatile material that can be used for a number of applications in electronics, sensing, catalysis, batteries, photovoltaics, and recently also in plasmonics.
A very recent work has proposed plasmon polaritons—coupled excitations of photons and charge carriers—in graphene as a promising way to achieve electric control of light. Furthermore, the tuning of the plasmon is possible through electrical or chemical modification of the charge carrier density [1].
On the other hand, silver is an appropriate plasmonic material for the visible range. A main drawback of silver comes from its chemical instability leading to silver oxidation in time, with shift and quenching of optical resonances [2].
In this plasmonic perspective, we address the following question: what is the potential of combining together the attractive materials of graphene and silver nanostructures for plasmonic- and meta-materials?
The study of corrosion/oxidation processes and their inhibition by organic inhibitors is a very active field of research. Many factors can contribute to the inhibition effect, such as gas permeability and electron density of inhibiting atoms and orbital character of donating electrons. The pioneering work from Ruoff [3] showed that graphene grown on metals (copper and nickel) effectively suppresses metal oxidation by posing a high energy barrier to diffusion of oxygen. Indeed, when graphene is transferred to a metal, it is interesting to explore how the electronic properties of the graphene/metal hybrid change. Understanding the electronic interaction between graphene and Ag is important from many points of view and for many applications. As an example, even in explaining the SERS and variation of the Raman signals of graphene coupled to Ag, the splitting of the G band can be attributed to the interaction between Ag and graphene, which induces a change in the graphene electronic structure [4].
Here, we present a study on graphene-coated silver plasmonic nanostructures, which are ultrathin films, nanoparticles arrays and 3D fishnet nanostructures. High-quality, single-layer graphene (SLG) was synthesized by chemical vapour deposition (CVD) on copper foil and transferred to the silver nanostructures. Ag nanoparticles are formed by evaporation of silver while Ag periodic fishnets are fabricated by nanoimprint lithography (Figure 1).
A novel type of hybrids functional materials, which are oxidation resistant and with stable plasmon resonance in the visible range over almost a year of air exposure are enabled.
The interface chemistry and electronic phenomena of charge transfer underpinning the coupling of graphene with silver gratings and fishnet structures is extensively characterized chemically and optically by X-ray photoelectron spectroscopy, Raman spectroscopy, and spectroscopic ellipsometry, in conjunction with microscopies of SEM and AFM also in Kelvin mode to probe local changes of surface potential.

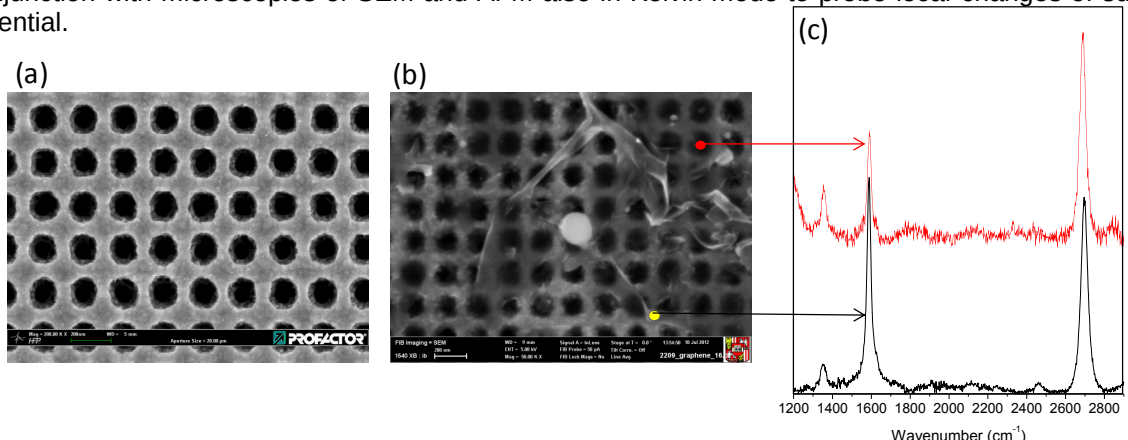

Figure 1. Scanning electron microscope (SEM) images of a silver fihnet structure fabricated by nanoimprint lithography to have optical resonances in the visible range (a) as deposited and (b) with graphene transferred on it; (c) Raman spectra acquired in two different points of the graphene/Ag fishnet hybrid using a 514 nm laser with a power of ~1mW/μm a 10 s integration time, and one accumulation.

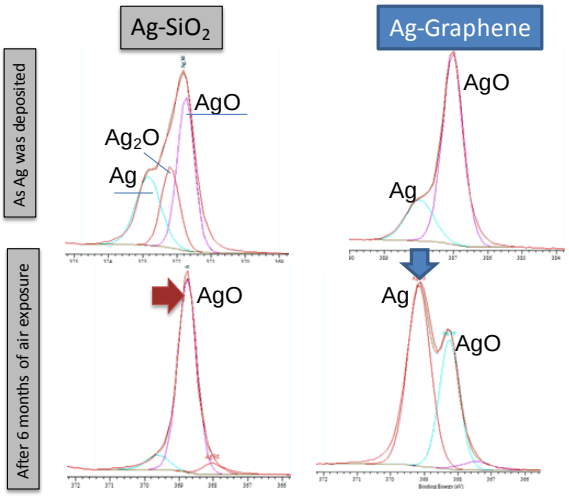

Figure 2. XPS spectra of Ag3d for the Ag fishnet on SiO2 without and with graphene ontop measured soon after fabrication (top) and after 6 months of air exposure (bottom).

In this case, the graphene coupled to 30 nm Ag nanoparticles results in an increase of the localized plasmon resonance (LSPR) of silver/graphene, which remains stable and intense over months of air exposure. Differently, a complete damping of the plasmon resonance occurs on a similar Ag nanoparticles sample without graphene (Figure 3).
Applications of this research on graphene/metals will likely have a large impact in a variety of fields, such as optical metrology, SERS sensors, renewable energy, metamaterials, high transparent and electrically conductive thin films research, through the development of novel graphene/silver composites.

Consequently, the graphene passivated silver fishnet and nanoparticles can provide much more stable SERS substrates. Here, we also show the effectiveness of the new Ag/graphene hybrids as SERS substrates and sensors using benzyl mercaptane and hemin as the probe molecules.

We demonstrate that electron transfer from graphene can activate reduction of silver oxides to metallic silver in a dynamic way and preserve temporally stable silver plasmonic properties. A chemical model for the electron transfer from graphene to silver is given to rationalize the oxidation resistance behavior of silver-coupled-to-graphene and the new chemical/optical properties of the hybrid [Figure 2].
Specifically, the $Ag/SiO_2/Si$ sample shows fit-components due to Ag, Ag_2O and AgO, indicating a fast surface oxidation soon after deposition; after a week of air exposure, the only component detected is AgO, and it stays after a month the same, indicating complete oxidation of the Ag silver layer. Conversely, for the Ag/graphene, a significant part of silver stays as metallic silver even after six months of air exposure. A similar reduction of Ag-oxide to metallic Ag has also been verified for 30 nm Ag nanoparticles passivated by graphene.

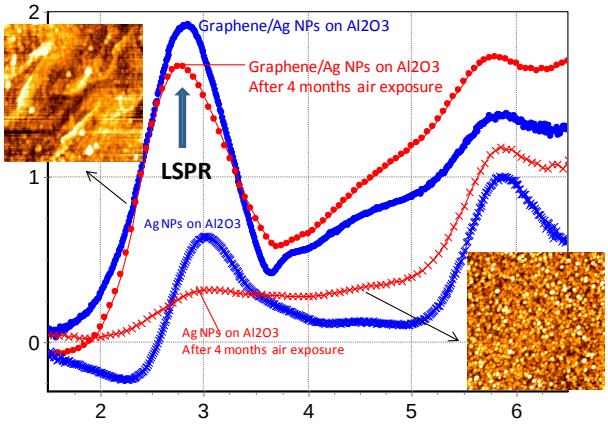

Figure 3. Spectra of the extinction coefficient of 30nm Ag nanoparticles deposited on sapphire with (top spectra) and without (bottom spectra) graphene ontop. The 30nm Ag NPs have a LSPR at 3 eV that is enhanced by graphene and stays stable over 4 months of air exposure, whereas it completely dampens for the nacked Ag NPs. (Blue curves refer to "as-fabricated" sample, while red curves are after 4 months of air exposure. The insets are the 2μmx2μm AFM images of graphene-passivated (top) and naked Ag NPs

The SERS enhancement mechanism of the SLG-coated substrates is discussed, and the different enhancement factors (EFs) between graphene-coated nanoparticles and nanoholes are understood based on the different morphologies of graphene on the two substrates using numerical simulation.
Ultimately, the performance of a novel sensor based on Hemin/graphene/silver to detection of the nitric oxide, NO, is demonstrated.

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