Optical field enhancement in composite plasmonic nanostructures: gold dots with graphene and dye R6G

V. G. Kravets, F. Schedin, R. Jalil, L. Britnell, K. S. Novoselov, and A. N. Grigorenko

School of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, UK,
Email: vasyl.kravets@manchester.ac.uk

Abstract

We present composite plasmonic nanostructures designed to achieve cascaded enhancement of electromagnetic fields at optical frequencies. Our structures are made with the help of electron beam lithography and comprise a set of self-similar metallic nano-discs placed one above another. The optical properties of reproducible arrays of these structures are studied using scanning confocal Raman spectroscopy. We observe significant (up to 1000 times) enhancements of resonant Raman scattering from a graphene layer generated by near-fields of a plasmonic nanoarray. This enhancement is quantitatively explained by the electromagnetic mechanism.

1. Introduction

An excitation of localized plasmon resonances (LPR) in metal nanoparticles can lead to a strong enhancement of electromagnetic fields near the surface of particles in visible and near-infrared range of spectrum. [1-3] Recent experimental and theoretical works on plasmonic enhancement effects focused on surface enhanced Raman scattering (SERS) with sensitivity down to a single molecule, biosensing applications as well as photoelectron-chemistry [1,4]. On the other hand, graphene, a flat monolayer of carbon atoms, also continues to attract an immense interest [5]. Our previous experiments with a single graphene layer covered by gold nanoparticles showed that it is possible to significantly increase the intensity of main Raman peaks of graphene [6]. These results are important because Raman spectroscopy based on inelastic light scattering is main instrument for identification of single layer graphene (SLG) and allows one to monitor doping, defects, disorder, edges and chemical modification of SLG [5,7].

In this work we study properties of a graphene sheet placed directly above a regular plasmonic nanoarray. We show that the resonant SERS of graphene can be enhanced by three orders of magnitude by near-fields of plasmonic nanostructures and demonstrate that this enhancement is described well by the electromagnetic mechanism. We also experimentally demonstrate a cascaded enhancement in nanofabricated self-similar gold nanostructures of original design [2,3] that exhibits a maximal field enhancement ratio of > 120 for visible light. The self-similar nanostructures robustly demonstrate dramatic enhancement of the Raman signals when compared to those measured from constituent elements.

2. Sample Preparation.

A set of square arrays of gold nanoparticles have been nanofabricated using high-resolution electron-beam lithography. The arrays have the following parameters: the lattice constant a=320nm, the diameter of dots D=100-120nm, the dot height h=90nm and the dot separation in the pair s=140nm. The structures typically covered an area of $200\times200\mu m^2$ and contained $\approx10^6$ nanodots. To perform electron beam lithography, a 5nm layer of Cr has been evaporated onto a glass substrate. We have employed double-layered resist in order to improve lift-off. The single layer graphene was prepared by a micromechanical cleavage of graphite placed on the top of an oxidized Si substrate (300nm SiO_2). SLG was separated from the substrate and transferred on top of square arrays of Au nanoparticles using wet transfer procedure. As a result, a graphene flake rested on the tops of gold nanoparticles as a relatively rigid sheet.

We also fabricated arrays of nanostructures comprised two or three coaxial gold discs of different diameter stacked one on top of another and separated by dielectric spacers. We used the tower-

ISBN 978-952-67611-2-1

type design [2,3] which features a larger metallic disc of diameter D that has a cylindrical hole of diameter d filled with a dielectric column produced by overexposed PMMA, a smaller metallic disc also of diameter d placed on the top of the column, and a still smaller disc of diameter δ placed on top of that. Raman spectroscopy has been employed to investigate optical and chemical properties of SLG on the top of Au dots and the total field enhancement afforded by our double and triple structures. We coated the nanostructures with a layer of a dye, rhodamine 6G (R6G), randomly dispersed in a polymer host. The dye concentration in the solution was 10^{-6} M, which implies that the average distance between dye molecules was about 120nm, and the probability to have one R6G molecule within ~30nm from the top disc was about 20%, which indicates that we were working at the limit of a single molecule Raman spectroscopy for R6G.

3. Results and discussions.

The Raman signature of graphene consists of a set of distinct peaks: the G peak at 1580cm^{-1} due to the in-plane vibrational E_{2G} mode at the Brillouin zone center and the 2D peak at about 2670cm^{-1} due to two phonon inter-valley scattering [5-7]. We found that the Raman signals from SLG placed at the top of regular arrays of Au nanoparticles are dramatically enhanced by the plasmonic resonances of the nanostructure. The enhancement factor for both G and 2D bands of graphene layer was about $F\approx$50-100 for 514nm and $F\approx$1000 for 633nm laser excitations, respectively (Fig. 1). The enhancement factor of G and 2D peaks (F_G and F_{2D}) are different for different excitation wavelengths (514.5nm or 632.8nm). Indeed, the G peak at 1580cm^{-1} is strongly enhanced under 633nm excitation wavelength, while the intensity of the 2D peak strongly increases for 514nm excitation. This is explained by the position of LPR of our structures. The extinction spectrum of the composite structure has the resonance peak in the red region (~600nm) which corresponds to the excitation of localized plasmons. The enhancement of Raman signals is governed by the increase of local field produced by nanoparticles and therefore is larger when both excitation and scattered light are close to LPR. For 633nm excitation the G peak produces light closer to LPR than the 2D peak and hence shows larger plasmonic enhancement ($F_G>F_{2D}$); and for 514nm excitation the 2D peak will generate light closer to LPR than the G peak and hence shows larger plasmonic enhancement ratio ($F_{2D}>F_G$). It is important to note that the Raman enhancement by more than 3 orders of magnitude for graphene layer allows one to observe the defect peak and hence quantify the amount defect on SLG surface. Raman spectra show an additional D peak at ~1350cm^{-1} for laser excitation of 633nm. It is difficult to detect the D peak in normal Raman scattering because of high purity of the graphene lattice. Thus, the ability to probe a fine structure of Raman scattering is an advantage of SERS. A chemical reaction of atomic hydrogen with graphene gives rise to changes in electronic and phonon properties [5,7]. As a result, hydrogenated graphene shows an additional sharp Raman D peak at about 1340cm^{-1} activated by defects.

The experimental results shown in Fig. 2 were typical for arrays of double and triple structures. We found that the majority of the studied double structures showed fluorescence enhancement while the triple structures showed large Raman signals. By comparing the signals from the triple and double nanostructures, we estimate that the ratio of the field enhancement observed for triple and double structures (the cascaded enhancement factor) is ~ 4 for the wavelength of 633nm. This estimate is based on the root of 4th power from the ratio of Raman peaks for the triple and double structures, it represents a conservative lower limit of the enhancement factor since it does not take into account the greater number of R6G molecules that contribute to the double structure Raman signal due to the larger size of the top disc of the double structure (110nm) compared to the top disc of the triple structure (30nm). By comparing signals from single dots and double structures, we have evaluated the total local field enhancement for the double structure with the studied size as $g > 30$ [2,3]. Therefore, we estimate the field enhancement ratio for the optimal triple structures as $g_{tot} > 120$.

As a check on our measurements of the cascaded field enhancement, we performed finite-element modeling. Simulations of the electromagnetic fields produced by the triple structures suggested that the field enhancement ratio g_{tot} strongly depends on the thickness of dielectric spacers between the discs. It was found that the sharp dependence of g_{tot} on the top

ISBN 978-952-67611-2-1

spacer thickness *s*, with maximal values of g_{tot} being > 100, can be reached for the thickness of the top spacer 7-10nm.

4. Conclusion

We have shown that nanofabricated regular arrays of three-tier composite plasmonic nanostructures that exhibit cascaded optical-field enhancement. The cascaded enhancement is a reproducible phenomenon which is observed for the reproducible arrays of fabricated nanostructures. The field enhancement was probed using a thin layer of dye molecules. It was demonstrated that the graphene could become a test object of choice for studying SERS and elucidating its mechanisms. Indeed, the well-defined 2D geometry of graphene and relative ease with which it is possible to identify the position of the plane of graphene flake allows one to calculate the electromagnetic fields at the graphene plane quite accurately and hence to make a judgment on the prevailing mechanism of SERS.

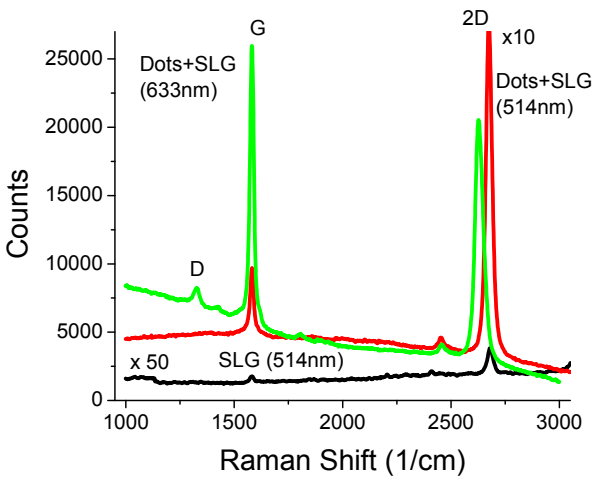

Fig. 1: The experimental enhancements for main Raman bands of graphene layer on top of Au nanodots.

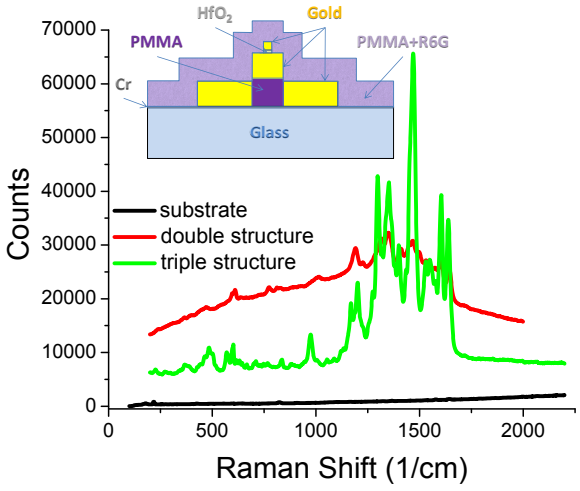

Fig. 2: The Raman spectra (laser power ~ 200μW, τ≈60s). Inset: schematic of the cross-section of the structure with a coating of PMMA/dye.

References

[1] Kuiru L., M.I. Stockman and D.J. Bergman, Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens, *Physical Review Letters*, vol. 91, p. 227402, 2003.

[2] V.G. Kravets, G. Zoriniants, C.P. Burrows, F. Schedin, A.K. Geim, W.L. Barnes, and A. N. Grigorenko, Composite Au Nanostructures for Fluorescence Studies in Visible Light, *Nano Letters*, vol. 10, pp. 874879, 2010.

[3] V.G. Kravets, G. Zoriniants, C. P. Burrows, F. Schedin, C. Casiraghi, P. Klar, A.K. Geim, W. L. Barnes, and A. N. Grigorenko, Cascaded Optical Field Enhancement in Composite Plasmonic Nanostructures, *Physical Review Letters*, vol. 105, p. 246806, 2010.

[4] S. Nie, S.R. Emory, Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering, *Science*, vol. 275, p. 1102, 1997.

[5] D.C. Elias, R.R. Nair, T.M. Mohiuddin, S.V. Morozov, P. Blake, M.P. Halsall, A.C. Ferrari, D. Boukhvalov, M.I. Katsnelson, A.K. Geim, K.S. Novoselov, Control of Graphenes Properties by Reversible Hydrogenation: Evidence for Graphane, *Science*, vol. 323, p 610, 2009.

[6] F. Schedin, E. Lidorikis, A. Lombardo, V.G. Kravets, A.K. Geim, A.N. Grigorenko, K.S. Novoselov, A.C. Ferrari, A. C. Surface- Enhanced Raman Spectroscopy of Graphene. *ACS Nano*, vol. 4, p. 5617, 2010.

[7] V.G. Kravets, F. Schedin, R. Jalil, L. Britnell, K.S. Novoselov, and A. N. Grigorenko, Surface Hydrogenation and Optics of a Graphene Sheet Transferred onto a Plasmonic Nanoarray, *J. Phys. Chem. C* vol.116, p.3882, 2012.

ISBN 978-952-67611-2-1