Plasmonic properties of nanostructured graphene with silver nanoparticles

Novikov, S. M.; Popok, V. N.; Fiutowski, J.; Arsenin, A. V.; Volkov, V. S.

Published in:
Journal of Physics: Conference Series

DOI (link to publication from Publisher):
10.1088/1742-6596/1461/1/012119

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Plasmonic properties of nanostructured graphene with silver nanoparticles

IOP Conf. Series: Journal of Physics: Conf. Series **1461** (2020) 012119 doi:10.1088/1742-6596/1461/1/012119

Plasmonic properties of nanostructured graphene with silver nanoparticles

S M Novikov[1], V N Popok[2], J Fiutowski[3], A V Arsenin[1] and V S Volkov[1,4]

[1]Center for Photonics and 2D Materials, Moscow Institute of Physics and Technology, Dolgoprudny 141700, Russia
[2]Department of Materials and Production, Aalborg University, Skjernvej 4A, 9220 Aalborg, Denmark
[3]Mads Clausen Institute, University of Southern Denmark, NanoSYD, Alsion 2 DK-6400 Sønderborg, Denmark
[4]SDU Nano Optics Mads Clausen Institute University of Southern Denmark Campusvej 55, DK-5230, Odense, Denmark

Novikov.s@mipt.ru

Abstract. Ensembles of size-selected silver nanoparticles (NPs) deposited on nanostructured graphene using cluster beam technique are studied. Graphene is nanostructured by focused ion beam (FIB) to form arrays of holes. It is found that the deposited NPs are tended to collect in and around the holes in graphene. The graphene with NPs is covered by Rhodamine 6G and examined by Raman spectroscopy. It is shown that amount of so-called hot spots increases dramatically for the nanostructured graphene with Ag NPs in comparison with continuous graphene covered by the NPs at the same conditions. Hereby, combining 2D material, FIB and cluster beam deposition techniques allows to form nanostructured surfaces with advanced plasmonic properties to be applied in sensor technologies and surface enhanced Raman scattering.

1. Introduction

Light interaction with nanostructures, especially those fabricated of noble (gold, silver) metals, gives rise to various fascinating optical phenomena [1]. One of the current research directions in nano-optics is the development of metal nanostructures that efficiently interconvert propagating and localized surface plasmons and thereby facilitate the generation of strongly enhanced local electrical fields. [2]. Strong field enhancement (FE) is important for practical applications, for example, in sensing and in surface-enhanced Raman scattering (SERS) [3, 4]. Noble metal nanostructures are also very promising for the formation of surface plasmon resonators, which have demonstrated enormous enhancement of the fluorescence of quantum emitters, thus, facilitating the development of ultra-bright and stable single-photon sources. Silver is one of the metals exhibiting excellent plasmonic properties that can be used in the above-mentioned applications [5-6]. There are many strategies for the fabrication of plasmonic structures using silver. Different approaches such as particle formation by evaporation or sputtering, high-fluency ion implantation, chemical and photo reduction, production from colloids *etc*. were suggested. Many of them allow formation of nanomaterials with attractive efficiency. However, rapid sulfidisation of silver in ambient atmosphere dramatically decreases all bonuses of this metal [7, 8] and

causes complications in terms of practical applications. Recently, it has been shown that metal nanoparticles (NPs) formed by gas aggregation in vacuum [9] and collimated into cluster beams for deposition are monocrystalline, thus, exhibiting great stability of plasmonic properties ensuring strong FE on long time scale (plasmon band intensity decreases only for about 20% after 30 days in ambient atmosphere) [10, 11]. Cluster beam deposition allows to control size and surface coverage of NPs but making arrays of NPs requires combining the cluster technique with other methods. Recently, it has been shown that electron beam lithography can be one of those [12]. In this work, we form arrays of holes in graphene by focused ion beam (FIB) and show that the deposited NPs predominately collect in these holes or around them, thus, allowing to create periodic areas with enhance surface coverage of NPs, i.e. periodic plasmonic (hot) spots. Formation of such arrays of hot spots gives rise of SERS signal intensity near 6-7 times in comparison with randomly deposited NPs. We anticipate that the obtained results are very promising for further manipulation of NPs and their application in SERS, e.g. for single molecule spectroscopy.

2. Nanostructured surface with Ag NPs

The PVD grown graphene was transferred on the Si substrate using standard procedure. The quality of graphene monolayer was assessed by Raman spectroscopy. The arrays of holes were formed in graphene by FIB. The radius of holes is ~80 nm, the period is 160 nm. The size-selected (approximately 15 nm in diameter) silver NPs were produced and deposited on graphene utilizing magnetron sputtering cluster apparatus (MaSCA) [13]. Figure 1 shows SEM images of the fabricated samples. One can see that the particles on flat graphene (Figure 1a) are located randomly, while in the case of nanostructured graphene (Figure 1b) NPs are tended to collect diffuse towards the nearest holes where they became trapped by defects. This type of behavior is well known from earlier experiments of cluster deposition on graphite surfaces [14].

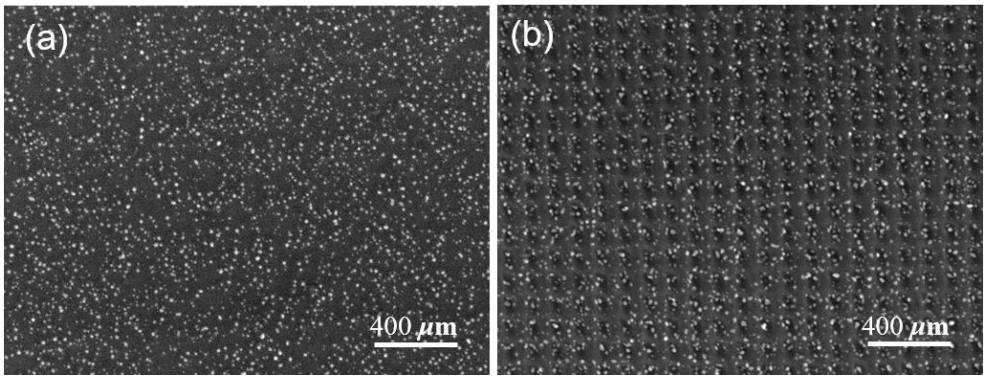

Figure 1. SEM images of silver NPs a) randomly deposited on continuous graphene and b) on graphene with hole arrays.

3. SERS characterizations

In order to estimate applicability of the samples for SERS, the Raman measurements are performed. We used Horiba LabRAM HR Evolution confocal Raman microscope. The measurements are conducted with a visible laser light (λ = 632.8 nm) at incident power ~0.35 mW, integration time 0.5 sec and 100×/N.A.=0.90 microscope objective. The measurements are carried out on the sample kept in ambient atmosphere for 14 days after the fabrication. Sample is covered by 10^{-6} M solution of Rhodamine 6G in ethanol and dried under ambient conditions. The typical SERS images and spectra obtained from the continuous graphene with Ag NPs and nanostructured one with Ag NPs are shown in Figure 2. Spectra in Figure 2 (a) demonstrate considerably higher intensities for the case of nanostructured surfaces.

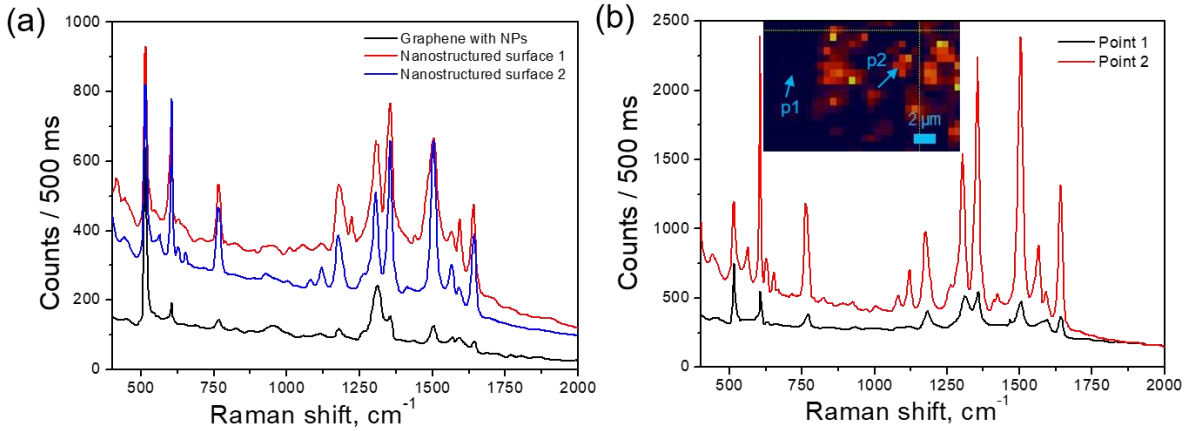

Figure 2. a) Average Raman spectra obtained from continuous and nanostructured graphene with NPs, b) Raman spectra from the points indicated by the arrows in the inserted figure. P1 – point out of array, P2 – hot spot from the array.

SERS images show rather homogeneous signal distribution across the continuous graphene surface with Ag NPs except a few fluctuations in intensity related to NP aggregation around surface defects of graphene. On the nanostructured surfaces, an increase of the SERS signals has a relatively simple explanation. Due to weak interaction between the silver NPs and graphene, the particles can diffuse across the surface [15] until they meet trapping centers, which are hole edges in our case. Thus, around the holes, the clusters make aggregates, i.e. these are the areas with increased NP coverage (see Figure. 1b) forming densely packed hot spots (in assumption that every individual Ag NP represents a hot spot) producing enhanced local field on interaction with the laser light. To compare a signal increase in SERS, with that in ordinary Raman keeping the same experimental parameters, the analytical enhancement factor (EF expression) is used [16]. The average EF is estimated to be ~0.47×10^5 for the continuous graphene with NPs and ~2.82×10^5, for the nanostructured surface, respectively. We would like to stress that in this case we have used non-resonant dye for our laser, whereas for resonant cases the enhancement estimation would be near one order of magnitude higher. Considering the high stability of plasmonic properties of our silver NPs, the fabricated nanostructured systems can be interesting for the sensor technologies and SERS applications.

Acknowledgments
This research was funded by Russian Science Foundation, grant number 18-19-00684. We thank the Shared Facilities Center of the Moscow Institute of Physics and Technology (grant no. RFMEFI59417X0014) for the use of their equipment.

References
[1] Gramotnev D K, Bozhevolnyi S I 2010 *Nat. Photon.* **4** 83.
[2] Maier S. *Plasmonics: Fundamentals and Applications.* Springer 2007 New York.
[3] Beermann J, Novikov S M, Albrektsen O, Nielsen M G, Bozhevolnyi S I 2009 *J. Opt. Soc. Am. B.* **26** 2370.
[4] Samal A K, Polavarapu L, Rodal-Cedeira S, Liz-Marzán L M, Pérez-Juste J, Pastoriza-Santos I 2013 *Langmuir* **29** 15076.
[5] Brazhe N A, Evlyukhin A B, Goodilin E A, Semenova A A, Novikov S M, Bozhevolnyi S I, Chichkov B N, Sarycheva A S, Baizhumanov A A, Nikelshparg E I, Deev L I, Maksimov E G, Maksimov G V, Sosnovtseva O 2015 *Sci. Rep*. **5** 13793.
[6] Vishnupriya S, Chaudhari K, Jagannathan R, Pradeep R. 2013 *Part. Part. Syst. Char*. **30** 1056.
[7] Cao W, Elsayed-Ali H E 2009 *Mater. Lett*. **63** 2263.

[8] Scuderi M, Esposito M, Todisco F, et. al. 2016 *J. Phys. Chem.* C **120**, 24314.
[9] Hartmann H, Popok V N, Barke I, V. von Oeynhausen and Meiwes-Broer K-H 2012 *Rev. Sci. Instrum*. **83** 073304.
[10] Novikov S M, Popok V N, Evlyukhin A B, Hanif M, Morgen P, Fiutowski J, Beermann J, Rubahn H-G, Bozhevolnyi S I 2017 *Langmuir* **33** 6062.
[11] Novikov S M, Popok V N, Evlyukhin A B, Hanif M, Morgen P, Fiutowski J, Beermann J, Rubahn H-G, Bozhevolnyi S I 2018 *J. Phys. Conf. Ser.* **1092**, 012098.
[12] Ceynowa F A, Chirumamilla M, Zenin V A, Popok V N 2018 *MRS Advances* **3** 2771.
[13] Popok V N, Hanif M, Ceynowa F A, Fojan P 2017 *Nucl. Instrum. Meth. Phys. Res. B* **409**, 91.
[14] Carrol S J, Seeger K, Palmer R E 1998 *Appl. Phys. Lett.* **72** 305.
[15] Guerra R, Tartaglino U, Vanossi A, Tosatti E 2010 *Nature Mat.* **9** 634.
[16] Le Ru E C, Blackie E, Meyer M, Etchegoin P G 2007 *J. Phys. Chem. C* **111** 13794.