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Control of the plasmonic resonance of a graphene coated plasmonic nanoparticle array combined with a nematic liquid crystal

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We report on the fabrication and characterization of a switchable plasmonic device based on a conductive graphene oxide (cGO) coated plasmonic nanoparticle (NP) array, layered with nematic liquid crystal (NLC) as an active medium. A monolayer of NPs has been immobilized on a glass substrate through electrostatic interaction, and then grown in place using nanochemistry. This monolayer is then coated with a thin (less than 100nm) cGO film which acts simultaneously as both an electro-conductive and active medium. The combination of the conductive NP array with a separate top cover substrate having both cGO and a standard LC alignment layer is used for aligning a NLC film in a hybrid configuration. The system is analysed in terms of morphological and electro-optical properties. The spectral response of the sample characterized after each element is added (air, cGO, NLC) reveals a red-shift of the localized plasmonic resonance (LPR) frequency of approximately 62nm with respect to the NP array surrounded by air. The application of an external voltage (8Vpp) is suitable to modulate (blue shift) the LPR frequency by approximately 22nm. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4959869>]

Plasmonics is a subfield of nano-optics that uses metallic nanoparticles to control light at the nanoscale. Plasmonic nanoparticles (e.g. gold, silver) are able to squeeze down an electromagnetic wave at the nanoscale.^{1,2} Indeed, visible light can induce the oscillation of the bulk free electrons localized at the metallic/dielectric interface. Such coherent and dipolar oscillation is called the Localized Plasmonic Resonance (LPR). The LPR frequency can be tuned by varying the nanoparticle (NP) shape, size, composition and roughness.^{3,4} It turns out that all these parameters can be controlled during the synthetic phase of NPs enabling a “static” control of the LPR frequency. A very effective way to tune the LPR frequency is to vary the refractive index of the medium surrounding the NPs. In this framework, liquid crystals (LCs) are smart anisotropic materials and possess an electrical-variable birefringence controllable with a quite low driven voltage.^{5,6} The large change (~0.2) of the LC refractive index is a compelling solution for tuning the LPR frequency upon the application of an external electric field. The opportunity has been well studied and investigated for different plasmonic architectures such as thin metal films,⁷ gold nanoparticle arrays^{8,9} and gold nanorods.^{10,11} In order to exploit the LC reconfigurability for realizing switchable plasmonic devices, the utilization of a transparent electrical conductor is required. In the past years indium tin oxide (ITO) has been largely used for all these purposes. Despite ITO is an excellent material, it

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exhibits many drawbacks such as expensive deposition methods, requires high temperature for good quality deposition and its optical transparency fails in the infrared range. Graphene is a fascinating alternative material - made of a single atomic layer of carbon possesses excellent electrical and optical properties.¹² Atomic layer graphene absorbs only 2-3% (fundamental losses) of the light in the visible spectral region. The deposition of an atomic layer of graphene on a substrate (e.g. glass, plastic, etc..) can be obtained via chemical vapour deposition (CVD)¹³ or single crystal (SiC) epitaxial growth.¹⁴ Both of these processes are quite expensive and do not enable simple uniform deposition on large area substrates ($>1\text{cm}^2$). Graphene oxide (GO) is an alternative opportunity to realize inexpensive and high quality coated substrates. Unfortunately GO is an insulator and therefore not usable in many applications such as optics, electronics, photonics and plasmonics. Enabling the electrical conductivity of GO can be achieved by chemically modifying the GO¹⁵ which when done properly results in a conductive GO (cGO) thin film exhibiting good optical and electrical properties.

In this communication, we report the fabrication and characterization of an electrically switchable plasmonic device realized by using a large area ($\sim 1\text{ inch}^2$), cGO coated, NPs array immobilized on a glass substrate which is used as one part of a hybrid LC cell.

The NP solution has been prepared by following the Turkevich method described in detail elsewhere¹⁶ while the NP array immobilized on the glass substrate along with the procedure of growth of NPs have been realized by using a slightly modified process reported in Ref. 17. Indeed, a single layer of citrate capped gold NPs (exhibiting a negative surface charge) are electrostatically bonded on a positively charged glass substrate by exploiting a dipping method. As a consequence, due to the electrostatic repulsion between NPs, there is a random self-organization of non-interacting NPs. Figure 1(a) is a Scanning Electron Microscopy (SEM) image of the substrate- NPs are homogeneously distributed with an average radius of about $(29\pm 3)\text{ nm}$. Visually, such a film has a pinkish tint (Figure 1(b)) and when characterized with unpolarized white light (normal incidence), the presence of an absorption peak at $\lambda = 572\text{ nm}$ is present (Figure 1(c)) due to the LPR mechanism.

A commercially available (*by BeamCo*), water based, cGO solution was spin-coated onto the NP coated-substrate at 5000 rpm for 30 s followed by baking in an oven at $100\text{ }^\circ\text{C}$ for 10 min to evaporate the residual water. Despite the starting solution being black (Figure 2(b)), a thin film of cGO exhibits (Figure 2(c)) both good optical transparency and surface homogeneity as confirmed by spectral characterization (transmittance $> 95\%$) reported in Figure 2(a) (blue curve) and optical microscopy analysis (Figure 2(d)). A four point probe method was used to measure the sheet resistance (R_s) of the cGO layer at $\sim 2\text{ K } \Omega/\text{sq}$. Remarkable, R_s can be reduced to $200\text{ } \Omega/\text{sq}$ (Figure 2(e)) by increasing the number of cGO layers (up to 4 layers) while keeping its transmittance higher than 90% as it is evident in the spectral characterization (transmission vs the number of deposited cGO layers) reported Figure 2(a) (red, magenta and green curves).

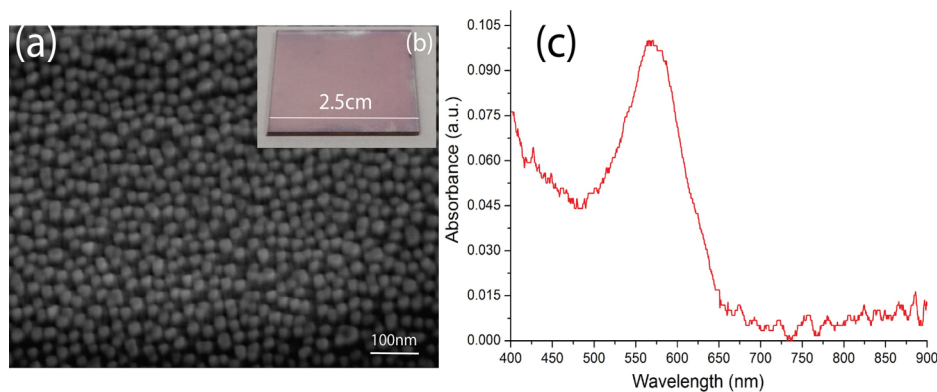


FIG. 1. SEM view (a) of the GNPs distribution immobilized on glass substrate (b) along with the spectral response of the sample (c).

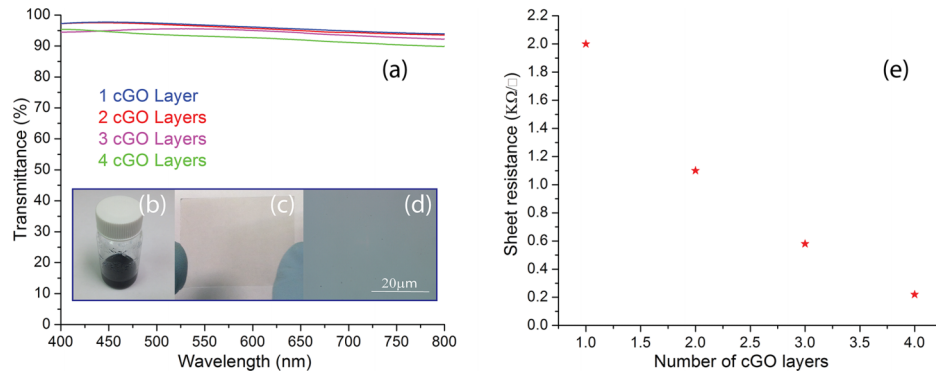


FIG. 2. Spectral response (a) of the cGO solution (b) spin-coated on a glass substrate (c) along with its optical microscope analysis (d). Sheet resistance of the glass substrate versus the number of deposited cGO layers (e).

The cGO solution spin-coated ($<$ than 100 nm) onto the NP monolayer affects the refractive index of the medium surrounding the NPs [from air ($n=1$) to cGO ($n=1.5$)] as evidenced by the red shift of the LPR peak reported in Figure 3 (from 572 nm (red) to 597nm (blue) and depicted in the sketch reported in the inset of. This behaviour can be explained in the framework of Mie theory¹⁸ which provides an analytical solution of Maxwell's equations for the absorption/scattering of electromagnetic radiation for small (≤ 100 nm) and isolated spherical NPs. According to this theory, the LPR frequency depends on the value of the refractive index of the surrounding medium. Indeed, the LPR frequency exhibits a red or blue shift for increasing or decreasing values of the refractive index surrounding the NPs.

The electrical properties of the cGO film overlaying the NP-coated substrate was measured. Rs was unchanged with respect to bare (glass) substrate covered by cGO. The presence of the cGO layer enables both electrical conductivity and modification of the LPR frequency. In order to exploit the refractive index change of the LC under the influence of an external voltage, a cell was fabricated by combining the cGO coated NP monolayer with a conductive (cGO coated) top cover glass treated with a Photo-Alignment Layer (PAL). The PAL layer (PAAD-22 synthesized by BeamCo) is an azo-dye dissolved in dimethylformamide; it possesses a broad absorption range centered at 367 nm. A PAL/DMF solution was spin-coated onto a cGO coated glass substrate at 3000 rpm for 30s and then baked in a hot-plate at 100°C for 10 min to remove the residual solvent. The substrate was illuminated with a polarized UV source for 20 min, inducing a molecular director alignment perpendicular to the light polarization direction.

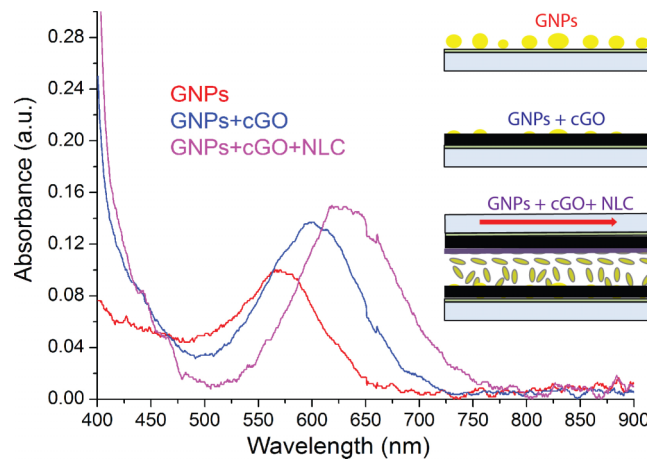


FIG. 3. Spectral response of the NPs arrays surrounded by different media, air (red curve), cGO (blue curve), cGO +NLC (magenta curve). In the inset is depicted the sample fabrication and characterization procedure.

A glass cell with a 4 μm cell gap was realized by combining the functionalized glass and NP-coated substrate; subsequently the cell was infiltrated with NLC in isotropic phase (65 $^{\circ}\text{C}$, E7, by Merck) by capillary flow. The E7 NLC molecules due to their chemical composition (hydrophobic alkyl chain and a hydrophilic cyano head group) tends to orient in a hybrid configuration due to a competition between the homeotropic alignment induced by the electrostatic interaction with NPs on one side of the cell and the planar alignment due to the treated top cover glass on the opposite side (inset of Figure 3, lower image). The LPR field possesses an evanescent behaviour at the surface of the NP monolayer;¹⁹ so that, the LPR wavelength shift exhibits a typical exponential decay with increasing distance from the surface of the NP given by:

$$S = \delta n \Delta n (1 - \exp(-2l/a)) \quad (1)$$

where S is the LPR shift, δn is the refractive index sensitivity of the NPs, Δn is the change in the refractive index, l is the adsorbate layer thickness and a is the decay length of the electric field. In the actual case, did not functionalize the NPs substrate with the PAL layer in order to minimize the interdistance between the NLC molecules and the NPs. As such, we have obtained a hybrid configuration rather than a full planar aligned NLC sample. Due to the increasing value of the refractive index surrounding the NPs [from the cGO layer to the hybrid NLC film ($n_{\text{average}} \sim 1.6$)], the LPR frequency is further red-shifted by approximately 32 nm (Figure 3, magenta curve). This behaviour is well in agreement with Mie theory previously described.¹⁸

The effective red-shift of the LPR wavelength is also affected by the adsorbate layer thickness. The cGO layer ($n=1.5$) is less than 100nm thick while the NLC film ($n_{\text{average}} \sim 1.6$) is 4 μm thick. Thus a refractive index change of 0.5 between air and cGO induces a red-shift of approximately 25 nm while a refractive index change of only 0.1 between cGO and the NLC generates a further red shift of about 32nm. This higher sensitivity obtained with the NLC film (despite the lower refractive index change) can be ascribed to the fact that the evanescent field “feels” more the refractive index change due to a bulk effect induced by the thicker NLC layer as reported in equation (1).

In order to check the influence of the refractive index change on the LPR wavelength, the spectral response for different values of the applied voltage have been measured. The layout of the NLC reorientation under the influence of the applied voltage is sketched in Figure 4(e). Indeed, since the NLC (E7) molecules possess a permanent dipole along the long axis ($\Delta\epsilon > 0$) tend to orient along the electric field direction (blue arrow, Figure 4(e)). As a consequence, due to the gradual reorientation of the NLC ($n \sim 1.6$) to homeotropic ($n \sim 1.5$), there is a blue shift of the LPR wavelength of approximately 22 nm (again in agreement with Mie theory¹⁸). It is important to stress that the refractive index change of the NLC (evidence that the cGO based layer is conductive) is accompanied by a visual colour change (due to the birefringence variation) of the sample inspected

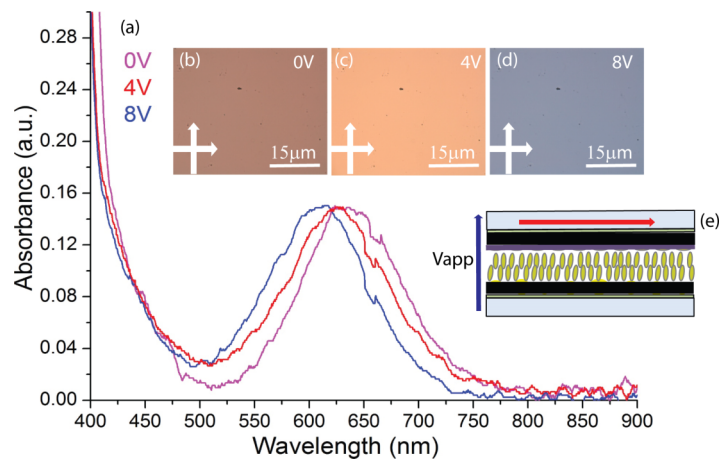


FIG. 4. Spectral response (a) and POM view of the sample (b, c, d) for different values of the external voltage. Sketch of the NLC sample under the influence of the applied voltage (e).

between cross polarizers (Figures 4(b), 4(c), 4(d)). The LPR spectral shift and associated coloration is reversible.

To summarize, a switchable plasmonic device fabricated by utilizing a cGO coated NP-coated film as one substrate in a hybrid NLC film was realized. A monotonic red-shift (62nm) of the LPR frequency due to the variation (increasing) of the refractive index surrounding the NPs (from air to cGO and from cGO to NLC) is observed. The application of a low external voltage induces the NLC reorientation decreasing its refractive index (from hybrid to homeotropic) with a resulting blue shift of the LPR wavelength of approximately 22nm. This represents a different opportunity for graphene based technologies since it enables “ITO-free” switchable and large area devices useful for applications ranging from plasmonics to photonics. Improvement of the performance of the system (in terms of LPR tuning range) can be obtained by employing NLC with higher birefringence or utilization of NPs with higher refractive index sensitivity (e.g. nanorods).

- ¹ V. M. Shalaev and S. Kawata, *Nanophotonics with Surface Plasmons*, (Advances in Nano-Optics and Nano-Photonics) (Elsevier, 2007).
- ² T. W. Ebbesen, C. Genet, and S. I. Bozhevolnyi, *Phys. Today* **61**(5), 44 (2008).
- ³ L. M. Liz-Marzán, *Mater. Today* **7**, 26 (2004).
- ⁴ C. Lumdee, B. Yun, and Pieter G. Kik, *Nanoscale* **7**, 4250 (2015).
- ⁵ L. M. Blinov, *Electro-optical and magneto-optical properties of liquid crystals* (Wiley, Chichester, 1983).
- ⁶ P. G. De Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford Science Publications, 1993).
- ⁷ Y. Wang, *Appl. Phys. Lett.* **67**(19), 2759 (1995).
- ⁸ L. De Sio, A. Cunningham, V. Verrina, C. M. Tone, R. Caputo, T. Büergi, and C. Umeton, *Nanoscale* **4**, 7619 (2012).
- ⁹ P.A. Kossyrev, A. Yin, S.G. Cloutier, D.A. Cardimona, D. Huang, P.M. Alsing, and J.M. Xu, *Nano Lett.* **5**, 1978 (2005).
- ¹⁰ K. C. Chu, C. Y. Chao, Y. F. Chen, Y. C. Wu, and C. C. Chen, *Appl. Phys. Lett.* **89**, 103107 (2006).
- ¹¹ L. De Sio, G. Klein, S. Serak, N. Tabiryan, A. Cunningham, C. M. Tone, F. Ciuchi, T. Büergi, C. Umeton, and T. Bunning, *J. Mater. Chem. C* **1**(45), 7483 (2013).
- ¹² A. K. Geim and K. S. Novoselov, *Nat.Mater.* **6**, 183 (2007).
- ¹³ Y. Zhang, L. Zhang, and C. Zhou, *Acc. Chem. Res.* **46**(10), 2329 (2013).
- ¹⁴ R. Ming, Y. Hu, Z. Guo, R. Dong, J. Palmer, J. Hankinson, C. Berger, and W. A. De Heer, *Materials Research Bulletin* (Elsevier, 2012), Vol. 37, p. 1138.
- ¹⁵ D. R. Dreyer, S. Park, C. W. Bielawski, and R. S. Ruoff, *Chem. Soc. Rev.* **39**, 228 (2010).
- ¹⁶ A. Cunningham, S. Mühlig, C. Rockstuhl, and T. Büergi, *J. Phys. Chem. C* **115**, 8955 (2011).
- ¹⁷ U. Cataldi, R. Caputo, Y. Kurylyak, G. Klein, M. Chekini, C. Umeton, and T. Büergi, *J. Mater. Chem. C* **2**, 7927 (2014).
- ¹⁸ G. Mie, *Ann. Phys* **25**, 377 (1908).
- ¹⁹ J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. Van Duyne, *Nat. Mater.* **7**, 442 (2008).