A two-fold active control of the plasmonic resonance of randomly distributed gold nanoparticles (GNPs) has been achieved. GNPs have been immobilized on an Indium Tin Oxide (ITO) coated glass substrate and then covered with a liquid crystalline compound. The system has been investigated by means of atomic force and scanning electron microscopy, revealing the presence of isolated and well distributed GNPs. The application of an external electric field to the sample has a two-fold consequence: the re-orientation of the hybrid-aligned liquid crystal layer and the formation of a carrier accumulation layer in the proximity of the ITO substrate. The refractive indices of both liquid crystal and accumulation layers are influenced by the applied field in a competitive way and produce a “dancing behavior” of the GNP’s plasmonic resonance spectral position.

Nanophotonic devices have the capability to concentrate light in the nanoscale range and are of great interest for many applications such as integrated optics, plasmonic circuits, biosensing and quantum information processing. One promising way to localize the optical radiation into a nanometer-sized volume has been obtained by using the unique properties of plasmonic nanomaterials. They act as an effective bridge between bulk materials and atomic or molecular structures and exhibit a very intense color, which is absent in the bulk material as well as in individual atoms. The physics behind this behavior can be explained by considering the collective oscillation of the free conduction electrons induced by the interacting external electromagnetic field: the so-called Localized Plasmon Resonance (LPR). In fact, the plasmonic coupling between metallic nanoparticles and light enables a universal range of interesting optical phenomena, such as Surface Enhanced Raman Spectroscopy (SERS),

Resonance Light Scattering (RLS) and Surface Plasmon Resonance (SPR). The control of plasmonic resonances is a hot-topic and various approaches such as controlling the size and shape of the NPs or varying the distance between the metallic structures have been used. In this way, it is possible to realize “static means” for controlling the properties of the hard matter. A more effective method to influence the plasmonic resonance is to vary the refractive index of the medium surrounding the NPs; the use of reconfigurable matter as the surrounding medium could hence provide an “active way” for controlling the plasmonic resonance. The outstanding properties of Liquid Crystals (LCs) make them an ideal candidate for this role: they are excellent examples of an active medium, where the refractive index can be finely controlled by means of external stimuli (electric field, optical field, temperature variation, etc.). This intriguing route has already been tracked and several examples of voltage and optical control of the plasmonic resonance properties have been reported in the last few years. A significant example is also provided by the work of Liu et al., where electron-beam lithography has been exploited to realize a uniform gold nanodisk array covered with a dual frequency Nematic Liquid Crystal (NLC) for controlling the plasmonic response.

Following this strategy, in this work we report on the realization and characterization of large-scale (~cm²) GNP arrays immobilized on a conductive substrate layered with an NLC film, used as an “active” surrounding medium. The step-forward of our approach with respect to the one reported in ref. 15 is represented by the possibility to realize large area layered arrays of GNPs by combining bottom-up and self-assembly processes, without the need of using any nanotechnology facility.

GNPs have been prepared according to the Turkevich method, which has been previously described in detail. One feature of nanoparticles fabricated by using this technique is their characteristic negative surface charge, which arises from the mono-layer of citrate capping molecules. This property is exploited when a substrate, suitably functionalized to possess a positive surface charge, is immersed in a solution of GNPs. The electrostatic interaction that is induced results in a single layer of GNPs deposited on the substrate surface. Briefly, the ITO-coated glass substrates were functionalized by first exposing them to a solution of H₂O₂ (30%) for 30 minutes before washing with copious amounts of Milli-Q water (18.2 MΩ cm). After drying in a stream of compressed air, the substrates were immersed in a 5% (v/v) solution of N-[3-(trimethoxysilyl)propyl]ethylenediamine in ethanol for 30 minutes and were again rinsed with water, then dried and set in an oven at 120 °C for a further 30 minutes. Electrostatic interactions were utilized to assemble a series of charged polymer layers on an initial array of GNPs, thus giving rise to a system whereby a second GNP array, separated by a well-defined distance, can be adsorbed on a glass substrate coated with ITO. In the actual case, seven polymer layers, consisting of the positively and
negatively charged poly(allylamine hydrochloride) and poly(sodium 4-styrenesulfonate) respectively, were assembled in-between the two GNP arrays. Polymers had a concentration of 5 mg mL\(^{-1}\) in 0.1 M NaCl and were deposited for one minute before rinsing with water and drying under a stream of compressed air. All measurements, excluding the SEM image, which was taken on a single GNP array, were conducted on two GNP arrays separated by seven poly-electrolyte layers.

Fig. 1a and b show the Scanning Electron Microscopy (SEM) image of the GNP distribution; they are well dispersed and approximately equally spaced with an average radius of about 10 nm. However, GNP arrays appear randomly distributed and no discernible organization is observed. The Atomic Force Microscopy (AFM) topography reported in Fig. 1c shows an average radius of about 15 nm with a modulation depth of 22 nm (see color scale, Fig. 1c). The discrepancy in the measured radius between the SEM and the AFM characterization is attributed to the convolution between the AFM tip (~tens of nm) and the average size of the GNP, that is of the same order of magnitude; conversely, due to the high vertical resolution (up to 0.1 nm) the modulation depth represents an accurate measurement of the interlayer distance.

We have investigated the spectral response of the GNP arrays by probing the sample with unpolarized white light (wavelengths in the range 300-900 nm) impinging at normal incidence. In Fig. 1e a pronounced extinction peak at \(\lambda = 522\) nm with a measured extinction coefficient of ~ 10\% is observed. Both the spectral position and the narrow width of the peak confirm the existence of a LPR due to the presence of well dispersed GNP.

Recently, it has been shown that, by means of polyelectrolyte (PE) layers, it is possible to carefully adjust the distance between adjacent GNP arrays and hence control the spectral position of the LPR. This multi-step process is known as “layer-by-layer assembly” and allows the realization of layered arrays of GNP.\(^{18}\) In order to exploit the organizational reconfigurability properties of the LC, used as a surrounding medium for the GNP, and achieve an active control of their plasmonic resonance, we have realized a glass cell by combining a conductive cover glass, treated with a thin polyimide layer for surrounding medium for the GNPs, and achieve an active control of their plasmonic resonance, we have realized a glass cell by combining a conductive cover glass, treated with a thin polyimide layer for inducing a planar alignment of the LC, with a substrate containing GNP layers. Glass and GNP-coated substrates were kept at a controlled distance by 4 \(\mu\)m glass microspheres and the NLC in the isotropic phase (65 °C, E7, by Merck) was introduced by capillary action. In order to realize a good NLC alignment, the sample was slowly cooled down to room temperature through a low-slope linear ramp.\(^{19}\)

The NLC possesses a hydrophobic alkyl chain and a hydrophilic cyanohydroxy group\(^{18}\) and, in the bulk of the cell, its director exhibits a hybrid configuration due to a competition between the homeotropic alignment, induced by the electrostatic interaction with GNP on one side of the cell, and the planar alignment due to the functionalized top cover glass on the other side (Fig. 2a). This hybrid configuration provides an intriguingly interesting environment for the realization of electro-optic effects. We performed electro-optical experiments by placing the sample between crossed polarizers with its director axis (red arrow, Fig. 2a) placed at 45° with respect to the polarizer/analyzer axes, and monitoring the transmitted intensity of a monochromatic light source (He–Ne laser, \(\lambda = 633\) nm) while applying an external voltage (frequency 1 kHz, square wave); the probe wavelength has been chosen far from the resonance peak of GNP in order to avoid affecting the NLC order, as a consequence of a local heating that could be caused by a resonant probe wavelength.

The oscillating behavior reported in Fig. 2c recalls the optical response of a planar aligned LC cell under the influence of an external electric field. In that case, the transmittivity between crossed polarizers is related to the birefringence of the cell, which depends on the presence of external fields and on the sample temperature.\(^{12}\) Under the influence of an electric field applied to the planar cell, the NLC director is reoriented (along the field direction, Fig. 2b), thus changing the effective birefringence of the device and modulating the transmitted light intensity. However, in our case, due to the presence of a hybrid alignment, we cannot expect that the same formalism used in ref. 12 can be used to explain exactly the behavior of our cell reported in Fig. 2c. In any case, we have used an optical compensator to measure directly the initial birefringence of the cell, which is responsible for that behavior. We found \(\Delta n = (0.10 \pm 0.02)\), which is a typical value in a hybrid NLC configuration. However, to go deeper into details, by using the compensator method we have been able to measure the birefringence \(\Delta n\) while increasing the external electric field.

We underline that, due to the induced NLC molecular reorientation, \(\Delta n\) can be easily varied and eventually switched to zero.

**Fig. 1** SEM view (a) and its high magnification (b), AFM topography (c) and its high magnification (d) of the GNP distribution. Spectral response of the sample (e).
To check how much the alignment of the NLC is spatially uniform, we performed optical observations by means of a Polarized Optical Microscope (POM) equipped with a CCD color camera connected to a PC; results are reported in Fig. 3(b)–(g). The fact that the whole area changes contrast uniformly suggests both that the electric field is applied uniformly over the whole sample and that the NLC director alignment has not been affected by the presence of particles (which could have been somehow removed from the layer, thus giving rise to NLC defects). Therefore, all experimental observations confirm that the GNPs are very well immobilized on the glass substrate.

In order to check the influence of the birefringence variation on the plasmonic resonance of the GNP array, we have observed the spectral response of the sample by probing it with unpolarized white light (wavelengths in the range 300–900 nm) at normal incidence for different values of the applied voltage; obtained results are reported in Fig. 4.

It is worth noting that, by increasing the applied voltage, the plasmonic absorption peak exhibits a “dancing behavior” with a continuous blue-red shift of its position (Fig. 4a). This behavior, which is very well evident in the high magnification of Fig. 4b, is in contrast with the optical behavior predicted by the Mie theory for a dispersion of isolated spherical particles. In fact, this theory predicts a linear dependence of the resonance wavelength (assumed to correspond to the local minimum of the transmission) on the value of the refractive index of the surrounding medium (a monotonic red or blue shift for increasing or decreasing values of the refractive index, respectively), when considered in a specific small range. In our case, a decrease, roughly estimated from 1.6 to 1.5, of the NLC refractive index value, obtained under the influence of the external electric field, should yield a blue-shift of the plasmon resonance wavelength; what we measured is instead a quite surprising non-linear modulation of the resonance wavelength (Fig. 4c). This unusual behavior might be explained by taking into account the influence of the ITO layer underlying the GNP array. Indeed, Feigenbaum et al. have recently demonstrated that, by shifting the plasma frequency of free carrier accumulation layers, it is possible to observe unity-order refractive index variations. This effect takes place when an external electric field is applied to a system where an ITO layer is separated from a gold one by a dielectric layer (SiO₂, in their case). Under these conditions, a 5 nm thick accumulation layer appears at the dielectric/ITO interface, and the field increases the carrier concentration from 10²¹ to 10²² cm⁻³. It is worth noting that no refractive index modulation is observed unless the SiO₂ layer is present. This remarkable result has been exploited to obtain an electro-optical and all-optical control of plasmon modes of individual nano-antennas using the nonlinear response of nanonanenna–ITO hybrids. Because of the

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**Fig. 2** Electro-optic response (c) of the large area (1 cm²) sample (d) with a hybrid NLC configuration. The sketch of the NLC configuration inside the cell without (a) and with (b) application of an external electric field.

**Fig. 3** Birefringence variation versus the applied electric field (a). The POM view of the sample while increasing the applied electric field (b–g).
organosilane layer used to functionalize the glass/ITO substrate (according to the method described above), our system is similar to the one described by Feigenbaum. As such, it is reasonable to expect, also in our case, the formation of an accumulation layer at the organosilane/ITO interface and then a refractive index variation on field application; as a result, due to the refractive index variation, the accumulation layer behaves as an additional “active” medium. In order to verify our hypothesis concerning an effect of the free carrier accumulation layer on the plasmonic resonance, we performed electro-optical experiments by using an empty glass cell (similar to the previously described one, but having air instead of NLC). Obtained results are reported in Fig. 5a.

By increasing the applied voltage from 0 V to 10 V, a monotonic red-shift of about 9 nm is observed, as reported in Fig. 5b, where we draw the variation of the plasmonic resonance wavelength (local minimum of the transmission) versus the external voltage for the empty glass cell. This result suggests that, under the influence of the external electric field, the carrier accumulation and the NLC layers enter somehow in competition as “active” media surrounding the GNP layer. The exact way they contribute to the position of the plasmonic resonance wavelength is not yet clear and will be further investigated; most probably, depending on the value of the applied voltage, they combine their effects causing either an increase or a decrease of the value of the effective refractive index of the medium surrounding the GNP layer. This corresponds to the observed “dancing behavior” of the plasmonic response peak (Fig. 4c). It is worth noting that, despite a similar initial approach, our results cannot be compared with the ones reported in ref. 15; indeed, in that case, the absence of a dielectric interface between gold nanodisks and the ITO layer prevents the creation of a charge accumulation layer, which can induce a change in the local refractive index.

In conclusion, we have realized an active plasmonic structure where the resonance properties of a large area substrate containing GNPs can be controlled by means of an external electric field. The exhibited “dancing behavior” of the plasmonic resonance peak can be interpreted as an overlapping of the effects produced by a carrier accumulation layer and a NLC layer: they both behave as “active” media surrounding the GNP array. The local refractive index changes of both the hybrid-aligned NLC layer and the accumulation layer allow us to control the plasmon resonance of the GNPs, with a tunability range of about 20 nm. This is, in our opinion, a new route towards the realization of “active plasmonics” devices that establish a strong bridge between “hard and soft matter”. The possibility of exploiting several kinds of liquid crystalline materials will also be investigated.

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References
1 V. M. Shalaev and S. Kawata, Nanophotonics with Surface Plasmons
3 J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and
6 S. Nie and S. R. Emory, Science, 1997, 275, 1102.