Antisymmetric plasmon resonance in coupled gold nanoparticles as a sensitive tool for detection of local index of refraction

A. N. Grigorenko,[a] H. F. Gleeson, Y. Zhang, and N. W. Roberts
Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL United Kingdom

A. R. Sidorov
General Physics Institute, 38 Vavilov Street, Moscow 117942, Russia

A. A. Panteleev
Troitsk Institute of Innovation and Thermonuclear Investigations, Troitsk 142190, Russia

A nanofabricated regular array of coupled gold nanopillars is employed to detect local indices of refraction of different liquids using a shift of an antisymmetric plasmon resonance peak observed in the reflection spectra. The peak's spectral position is found to be a unique function of the local refractive index for a wide range of indices. We discuss possible applications of the fabricated nanostructured arrays in bio- and chemical sensors. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2187432]

Plasmon resonances (selective excitation of localized vibrations of the electron plasma in metals by electromagnetic field) turned out to be a valuable tool in the development of new optical devices. Surface plasmons[1] produced in different configurations (e.g., in Kretschmann[2] or Otto[3] geometries) have been extensively used in a large variety of tools and techniques for bio- and chemical sensing, such as surface plasmon resonance (SPR) sensors,[4] commercially available from Biacore, surface plasmon microscopy,[5] colorimetric detection of DNA by gold nanoparticles,[6] etc. The sensitivity of surface plasmon techniques has been improved to just one atomic monolayer by using interferometry,[7,8] and dark-field techniques.[9]

Most of the initial success of plasmonic optics was achieved by exploiting plasmon resonances in thin metallic films. However, the advent of nanofabrication allowed one to create controlled arrays of nanoparticles and nanostructures, also possessing plasmon resonant modes of electron vibrations. These plasmon modes retain the high sensitivity of plasmon resonances to the environment but provide a local response and compatibility with the high-throughput techniques required by biophysics. As a result, plasmonic optics has benefited from the discovery of plasmon-assisted extraordinary transmission of light,[10] detection of polynucleotides based on distance-dependent optical properties of nanoparticles,[11] light concentration in self-similar chains of metal nanospheres,[12] and detection of local refractive index from individual nanoparticles.[13] Nanoparticles with resonant plasmonic modes made it possible to create novel artificial materials based on metallic "nanoatoms" and "nanomolecules" with unique optical properties unachievable in natural materials.

Recently we have fabricated a new artificial nanomedium formed by regular arrays of nanomolecules—pairs of coupled identical gold nanopillars with plasmon resonances in the visible part of the spectrum.[14] In this material, which may be referred to as optomagnetic,[14,15] a plasmon resonance mode of a nanoparticle splits into two resonant modes for a particle pair: a symmetric mode, characterized by an overall dipole response and contributing to the medium's permittivity, and an antisymmetric mode, in which the dipoles oscillate in antiphase canceling the dipole response and leaving the overall magnetic response contributing to the magnetic permeability.[15,16] The purpose of this work is to show that the antisymmetric plasmon resonance mode of the coupled nanopillars can be used to detect local changes of the refractive index with high sensitivity in a wide range of refractive indices. Combined with a relatively simple design, controlled nature of resonance splitting, compatibility with high-throughput screening, and a simple optical scheme for plasmon excitation, the proposed medium has a potential to find a wide range of applications in bio- and chemical sensors.

Figure 1(a) shows an electron micrograph of one of our samples. The prepared structures were regular arrays of Au pillars fabricated by high-resolution electron-beam lithogra-
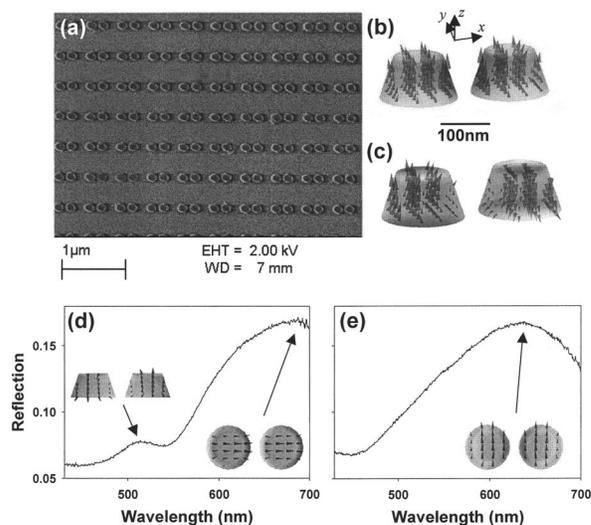

FIG. 1. Fabricated optomagnetic medium and its spectra. (a) A micrograph of the sample ($a=500$, $s=200$ nm, and $d=160$ nm) on which all data presented were collected. (b) The distribution of electric currents (conical arrows) inside a pair of pillars for the resonant symmetric z mode. (c) Same for the antisymmetric z mode. (d), (e) Experimental reflection spectra measured for TM and TE polarizations, respectively. The insets show the current distribution calculated by solving Maxwell equations for the actual experimental geometry at the resonant wavelengths.

[a]Author to whom correspondence should be addressed; electronic mail: sasha@man.ac.uk
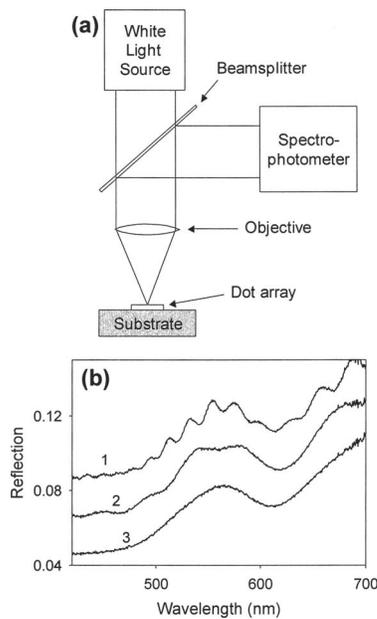
FIG. 2. (a) Optical scheme for measurements of the reflection spectra. (b) The dynamics of the reflection spectra of the sample covered with a thin layer of glycerol ($n=1.47$): 1—the initial spectrum; 2—the spectrum after 15 min; 3—after 1 h. The spectra are offset for clarity. Drying was assisted by a fan and illumination.
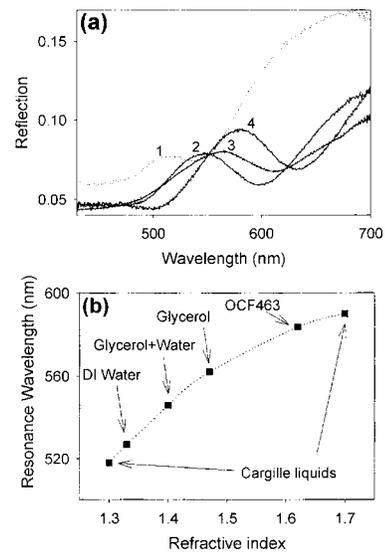

FIG. 3. (a) Reflection spectra registered in the presence of optically thin layers of liquids: 1—clean sample; 2—glycerol+water; 3—glycerol; 4—OCF463. (b) The antisymmetric resonance wavelength as a function of the refractive index of an optically-thin liquid layer.

phy on a glass substrate and grouped in tightly-spaced pairs.[14]

Figures 1(d) and 1(e) show typical reflection spectra measured from the sample of Fig. 1(a) under the condition of normal light incidence for TM light (with the electric-field vector along the x axis) and TE light (with the electric field vector along the y axis), respectively. The reflection spectra were collected by a conventional spectrophotometer from an area of 100×100 μm^2. There are two distinct resonance peaks in the TM spectrum indicated by arrows and only one peak in the TE spectrum. The symmetry analysis and the numerical solution of Maxwell equations for the experimental geometry with Femlab software,[14] [the results are shown in the insets of Figs. 1(d) and 1(e) for the resonant wavelengths] proves that the weaker resonance peak (observed at green wavelength) corresponds to the antisymmetric z-mode and the stronger peaks of Figs. 1(d) and 1(e) (observed at red wavelengths) correspond to the symmetric x and y modes of plasmonic resonances, respectively.

The plasmonic resonances shown in Figs. 1(d) and 1(e) are excited by light of normal incidence [see schematic view of the experimental setup in Fig. 2(a)] and do not require an elaborate optical scheme of Kretschmann or Otto geometries. This implies that our medium can be easily combined with sensing techniques based on any kind of reflection or microscopy. We demonstrate this by employing our structures to detect local refractive indices of optically thin liquid layers. Figure 2(b) shows the TM spectra of the sample of Fig. 1(a) covered with a thin layer of liquid taken at intervals as the liquid was drying (curves 1–3). Initially, the reflection spectrum (curve 1) shows an interference pattern produced by the interference of light reflected from the top and the bottom of the liquid layer. The positions of minima in the interference pattern can be found from the condition[17] $nD=(2m+1)\lambda/4$, where n is the refractive index of the liquid layer, D is the layer thickness, and $m \geq 0$ is an integer. As the liquid dries up, D decreases and the interference pattern gradually disap-

pears (compare curves 1 and 2) eventually leaving spectrum 3 without any trace of interference (which implies that $D \ll \lambda/4n$). The final spectrum (curve 3) shows the peaks of the plasmon resonances due to the nanostructured media and did not change for several hours after initial drying (even days for some liquids). Using Fresnel reflection coefficients[17] to model the change of the interference pattern of Fig. 2(b), we can obtain a rough estimate of the average effective thickness of dried liquid as <50 nm. We believe, however, that the liquid is mostly concentrated "inside" the nanomolecules (between pillars in a pair) and is dried completely in areas between nanomolecules. Below we shall refer to the final stable spectrum as the spectrum of samples covered with optically thin layers of liquid. Before every series of measurements, the samples were cleaned by rinsing in acetone and propanol and blowing dry by compressed nitrogen. The cleaning procedure removed the liquid completely and restored the original reflection spectrum of the samples shown in Figs. 1(d) and 1(e).

The important property of the spectra of structures covered with an optically-thin layer of liquid is an increase of the amplitude of the antisymmetric resonance and a substantial redshift of the resonance peak. (It is worth noting that the symmetric resonance peak was also redshifted albeit decreased in the amplitude.[14]) These features are emphasized in Fig. 3(a), where the spectra measured in normal TM light for the sample of Fig. 1(a) covered with different liquids are presented. One can notice that the change in reflection around the antisymmetric resonance for, e.g., spectrum 4 of Fig. 3(a) is $\approx 6\%$ (the spectrum corresponds to optical coupling fluid OCF463). This change is about three times greater than that for the spectrum of the clean sample [Fig. 1(b), $\approx 2\%$]. It is also clear that the resonance peak is redshifted in Fig. 3(a) by ≈ 30–60 nm with respect to the original spectral peak's position in TM spectrum of Fig. 1(b). We extracted the spectral position of the antisymmetric resonance peak from the spectra and plotted it as a function of the refractive index of the liquid in Fig. 3(b). Figure 3(b) demonstrates the main experimental result of this letter: in a wide range of refractive indices (from 1.3 to 1.7) there exists a unique
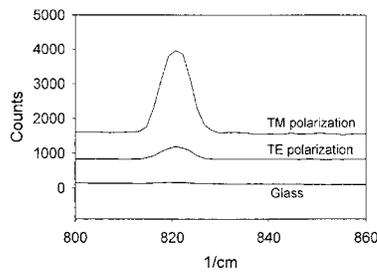
FIG. 4. Fragment of the Raman spectra measured for the sample and the glass substrate covered with a thin layer of 2-propanol in TM and TE polarizations. The spectra are offset for clarity.

(close to linear) dependence between the refractive index of an optically thin liquid layer covering the fabricated metamaterial and the shift of the antisymmetric resonance. The observed shift was about 2.8 nm per 0.01 index of refraction. This is comparable with the redshifts recorded previously for the quadrupole resonance of an individual nanoparticle[13] (1.6 nm per 0.01) but less than that for the conventional SPR technique ($\approx 5-7$ nm per 0.01).[1,2]

We briefly discuss the dependence of the resonance shifts on the refractive index of the environment. The wavelength of the antisymmetric resonance λ_{anti} can be found from the implicit formula[15]

$$\lambda = 2h \operatorname{Re}\left[\sqrt{\epsilon\left(1 + \frac{i\lambda \zeta_{xx}}{4\pi d \ln(2s/d)}\right)} \right], \qquad (1)$$

where ϵ is the local permittivity, c is the speed of light, and $\zeta_{xx} = \zeta_{xx}(\lambda)$ is the element of the surface impedance matrix. For the intermediate skin effect, which is applicable to our structures, (1) is simplified to $\lambda \approx \lambda_r n(1 - \lambda/\Lambda)$, giving the resonance wavelength as

$$\lambda_{anti} \approx \lambda_r \frac{n}{1 + an}, \qquad (2)$$

where $a = \lambda_r/\Lambda$ and Λ is a constant. The simple expression (2) describes well the measured dependence presented in Fig. 3(b). It is necessary to stress that (2) is calculated near the limit of the applicability of the theory.[15] For this reason, we regard Eqs. (1) and (2) only as a useful analytical approximation that is proved to work reasonably well for the studied structures.

The lateral resolution with which the reflection spectra were recorded in our experiments was about 100 μm. It can be reduced to 10 μm by using stronger objective lenses and/or by engineering microarrays of cells (based on the proposed metastructures) either with electron lithography or microcontact printing.[18] This would allow one to study the refractive index of an unknown liquid and to perform high-throughput screening[19] on an almost micrometer scale. The spatial resolution of the analysis can be improved further down to 1 μm by using other methods of surface microscopies. For example, it is known that electromagnetic fields are greatly enhanced near the metal in the presence of plasmonic modes, which leads to surface enhanced Raman scattering (SERS).[20,21] This implies that the fabricated nanomedium might be useful as a substrate for SERS. Indeed, Fig. 4 shows a fragment of the Raman spectra measured using Renishaw Raman Microscope (System 2000) for the structures of Fig. 1(a) (illuminated by TM and TE light of wavelength $\lambda = 532$ nm) and the glass substrate covered by

2-propanol. In all measurements, the SERS spectra were collected from a 1 μm spot (using $\times 50$ objective). The magnitude of the SERS peak for the structure is about 4000 times larger than for the glass substrate, which gives a rough estimate of the local field enhancement of 8, confirmed by the Femlab numerical calculations described above. We also note that the SERS peak for TM polarization (where the antisymmetric mode of the plasmon resonance is excited at $\lambda = 532$ nm) is about seven times greater than for TE polarization, in agreement with the reflection spectra of Fig. 1(b). It is apparent that SERS is superior in resolution and sensitivity, as compared to measurements of the reflection spectra. However, the practicality of its use for cheap high-throughput screening is doubtful.

In conclusion, we have demonstrated that the shift of the antisymmetric plasmon resonance of the media produced by pairs of identical gold nanopillars can be applied to detect local refractive indices of optically thin layers of liquids. This method provides a micrometer spatial resolution and a very high sensitivity (≈ 3 nm per 0.01 of the refractive index) in a wide range of refractive indices (from 1.3 to 1.7). The simple optical scheme for plasmon excitation and compatibility with high-throughput analysis suggest that the media can be successfully used for bio- and chemical sensing.

[1]V. M. Agranovich, *Surface Polaritons* (North-Holland, Amsterdam, 1982).
[2]E. Kretschmann and H. Reather, Z. Naturforsch. A **23A**, 2135 (1968).
[3]A. Otto, Z. Phys. **216**, 398 (1968).
[4]B. Liedberg, C. Nylander, and I. Lundström, Sens. Actuators **4**, 299 (1983).
[5]B. Rothenhäusler and W. Knoll, Nature (London) **332**, 615 (1988).
[6]C. A. Mirkin, R. L. Letsinger, R. C. Mucic, and J. J. Storhoff, Nature (London) **382**, 607 (1996).
[7]A. N. Grigorenko, P. I. Nikitin, and A. V. Kabashin, Appl. Phys. Lett. **75**, 3917 (1999).
[8]P. I. Nikitin, A. N. Grigorenko, A. A. Beloglazov, M. V. Valeiko, A. I. Savchuk, O. A. Savchuk, G. Steiner, C. Kuhne, A. Huebner, and R. Salzer, Sens. Actuators, A **85**, 189 (2000).
[9]A. N. Grigorenko, A. A. Beloglazov, P. I. Nikitin, C. Kuhne, G. Steiner, and R. Salzer, Opt. Lett. **174**, 151 (2000).
[10]E. Altewischer, M. P. van Exter, and J. P. Woedman, Nature (London) **418**, 304 (2002).
[11]R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger, and C. A. Mirkin, Science **277**, 1078 (1997).
[12]K. Li, M. I. Stockman, and D. J. Bergman, Phys. Rev. Lett. **91**, 227402 (2003).
[13]J. J. Mock, D. R. Smith, and S. Schultz, Nano Lett. **3**, 485 (2003).
[14]A. N. Grigorenko, A. K. Geim, H. F. Gleeson, Y. Zhang, A. A. Firsov, I. Y. Khrushchev, and J. Petrovic, Nature (London) **438**, 335 (2005).
[15]L. V. Panina, A. N. Grigorenko, and D. P. Makhnovskiy, Phys. Rev. B **66**, 155411 (2002).
[16]V. A. Podolskiy, A. K. Sarychev, and V. M. Shalaev, J. Nonlinear Opt. Phys. Mater. **11**, 65 (2002); V. A. Podolskiy, A. K. Sarychev, E. E. Narimanov, and V. M. Shalaev, J. Opt. A, Pure Appl. Opt. **7**, S32 (2005).
[17]M. Born and E. Wolf, *Principles of Optics* (Cambridge University, Cambridge, 1980).
[18]Y. Xia, D. V. Qin, J. Tien, and G. M. Whitesides, Langmuir **14**, 363 (1998).
[19]S. M. Senkan, Nature (London) **394**, 6691 (1998).
[20]M. I. Stockman, V. M. Shalaev, M. Moskovits, R. Botet, and T. F. George, Phys. Rev. B **46**, 2821 (1992).
[21]K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, Phys. Rev. Lett. **78**, 1667 (1997).