

Low-cost and large-size nanoplasmonic sensor based on Fano resonances with fast response and high sensitivity

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Abstract: We have developed a low-cost, fast and sensitive plasmonic sensor with a largesize for easy handling. The sensor is formed by a Au nanobelt grating fabricated by soft lithography with a period of 780 nm and a width of 355 nm in an even and uniform area of $\sim 2 \times 2 \text{ cm}^2$. The sensor uses the Fano-shaped third order mode localized plasmon resonance of the Au nanobelts, which appears in the visible part of the transmission spectrum. We have found a detection resolution of 1.56×10^{-5} refractive index units with a temporal resolution of 1 s in a sensing area of $0.75 \times 0.75 \text{ mm}^2$. The high uniformity and size of the sensor permit the detection using a simple optical system, which provides the device with the potential to be used as an easy to handle, portable and disposable sensor.

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References and links

- J. Homola, "Surface plasmon resonance sensors for detection of chemical and biological species," Chem. Rev. 108(2), 462–493 (2008).
- A. G. Brolo, R. Gordon, B. Leathem, and K. L. Kavanagh, "Surface plasmon sensor based on the enhanced light transmission through arrays of nanoholes in gold films," Langmuir 20(12), 4813–4815 (2004).
- A. A. Yanik, A. E. Cetin, M. Huang, A. Artar, S. H. Mousavi, A. Khanikaev, J. H. Connor, G. Shvets, and H. Altug, "Seeing protein monolayers with naked eye through plasmonic Fano resonances," Proc. Natl. Acad. Sci. U.S.A. 108(29), 11784–11789 (2011).
- K.-L. Lee, P.-W. Chen, S.-H. Wu, J.-B. Huang, S.-Y. Yang, and P.-K. Wei, "Enhancing surface plasmon detection using template-stripped gold nanoslit arrays on plastic films," ACS Nano 6(4), 2931–2939 (2012).
- S. H. Wu, K. L. Lee, A. Chiou, X. Cheng, and P. K. Wei, "Optofluidic platform for real-time monitoring of live cell secretory activities using fano resonance in gold nanoslits," Small 9(20), 3532–3540 (2013).
- 6. B. Zeng, Y. Gao, and F. J. Bartoli, "Rapid and highly sensitive detection using Fano resonances in ultrathin plasmonic nanogratings," Appl. Phys. Lett. **105**(16), 161106 (2014).
- B. Caballero, A. García-Martín, and J. C. Cuevas, "Hybrid magnetoplasmonic crystals boost the performance of nanohole arrays as plasmonic sensors," ACS Photonics 3(2), 203–208 (2016).
- C. Valsecchi and A. G. Brolo, "Periodic metallic nanostructures as plasmonic chemical sensors," Langmuir 29(19), 5638–5649 (2013).
- B. Luk'yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen, and C. T. Chong, "The Fano resonance in plasmonic nanostructures and metamaterials," Nat. Mater. 9(9), 707–715 (2010).
- F. López-Tejeira, R. Paniagua-Domínguez, and J. A. Sánchez-Gil, "High-performance nanosensors based on plasmonic Fano-like interference: probing refractive index with individual nanorice and nanobelts," ACS Nano 6(10), 8989–8996 (2012).
- 11. J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, and R. P. Van Duyne, "Biosensing with plasmonic nanosensors," Nat. Mater. 7(6), 442–453 (2008).
- M. Svedendahl, S. Chen, A. Dmitriev, and M. Käll, "Refractometric sensing using propagating versus localized surface plasmons: a direct comparison," Nano Lett. 9(12), 4428–4433 (2009).

- M. A. Otte, B. Sepúlveda, W. Ni, J. P. Juste, L. M. Liz-Marzán, and L. M. Lechuga, "Identification of the optimal spectral region for plasmonic and nanoplasmonic sensing," ACS Nano 4(1), 349–357 (2010).
- B. Auguié and W. L. Barnes, "Collective resonances in gold nanoparticle arrays," Phys. Rev. Lett. 101(14), 143902 (2008).
- N. Verellen, Y. Sonnefraud, H. Sobhani, F. Hao, V. V. Moshchalkov, P. Van Dorpe, P. Nordlander, and S. A. Maier, "Fano resonances in individual coherent plasmonic nanocavities," Nano Lett. 9(4), 1663–1667 (2009).
- V. Giannini, Y. Francescato, H. Amrania, C. C. Phillips, and S. A. Maier, "Fano resonances in nanoscale plasmonic systems: a parameter-free modeling approach," Nano Lett. 11(7), 2835–2840 (2011).
- F. López-Tejeira, R. Paniagua-Domínguez, R. Rodríguez-Oliveros, and J. Sánchez-Gil, "Fano-like interference of plasmon resonances at a single rod-shaped nanoantenna," New J. Phys. 14(2), 023035 (2012).
- N. Verellen, F. López-Tejeira, R. Paniagua-Domínguez, D. Vercruysse, D. Denkova, L. Lagae, P. Van Dorpe, V. V. Moshchalkov, and J. A. Sánchez-Gil, "Mode parity-controlled Fano- and Lorentz-like line shapes arising in plasmonic nanorods," Nano Lett. 14(5), 2322–2329 (2014).
- J. B. Lassiter, H. Sobhani, J. A. Fan, J. Kundu, F. Capasso, P. Nordlander, and N. J. Halas, "Fano resonances in plasmonic nanoclusters: geometrical and chemical tunability," Nano Lett. 10(8), 3184–3189 (2010).
- 20. Y. Xia and G. M. Whitesides, "Soft lithography," Annu. Rev. Mater. Sci. 28(1), 153-184 (1998).
- C. Vericat, M. E. Vela, G. Benitez, P. Carro, and R. C. Salvarezza, "Self-assembled monolayers of thiols and dithiols on gold: new challenges for a well-known system," Chem. Soc. Rev. 39(5), 1805–1834 (2010).
- P. B. Johnson and R.-W. Christy, "Optical constants of the noble metals," Phys. Rev. B 6(12), 4370–4379 (1972).
- A. Vitrey, L. Aigouy, P. Prieto, J. M. García-Martín, and M. U. González, "Parallel collective resonances in arrays of gold nanorods," Nano Lett. 14(4), 2079–2085 (2014).
- A. G. Nikitin, "Diffraction-induced subradiant transverse-magnetic lattice plasmon modes in metal nanoparticle arrays," Appl. Phys. Lett. 104(6), 061107 (2014).
- M. A. Otte, M.-C. Estévez, L. G. Carrascosa, A. B. González-Guerrero, L. M. Lechuga, and B. Sepúlveda, "Improved biosensing capability with novel suspended nanodisks," J. Phys. Chem. C 115(13), 5344–5351 (2011).
- D. Meneses-Rodríguez, E. Ferreiro-Vila, P. Prieto, J. Anguita, M. U. González, J. M. García-Martín, A. Cebollada, A. García-Martín, and G. Armelles, "Probing the electromagnetic field distribution within a metallic nanodisk," Small 7(23), 3317–3323 (2011).
- 27. L. Hoyt, "New table of the refractive index of pure glycerol at 20 C," Ind. Eng. Chem. 26(3), 329-332 (1934).
- M. E. Stewart, N. H. Mack, V. Malyarchuk, J. A. Soares, T.-W. Lee, S. K. Gray, R. G. Nuzzo, and J. A. Rogers, "Quantitative multispectral biosensing and 1D imaging using quasi-3D plasmonic crystals," Proc. Natl. Acad. Sci. U.S.A. 103(46), 17143–17148 (2006).
- K.-L. Lee, J.-B. Huang, J.-W. Chang, S.-H. Wu, and P.-K. Wei, "Ultrasensitive biosensors using enhanced Fano resonances in capped gold nanoslit arrays," Sci. Rep. 5(1), 8547 (2015).
- Y. Gao, Q. Gan, Z. Xin, X. Cheng, and F. J. Bartoli, "Plasmonic Mach-Zehnder interferometer for ultrasensitive on-chip biosensing," ACS Nano 5(12), 9836–9844 (2011).
- M. Piliarik and J. Homola, "Surface plasmon resonance (SPR) sensors: approaching their limits?" Opt. Express 17(19), 16505–16517 (2009).
- K. Yamanaka and M. Saito, "Nanoimprinted Plasmonic Biosensors and Biochips," in Nanobiosensors and Nanobioanalyses (Springer, 2015), pp. 71–80.

1. Introduction

Surface plasmon based sensing is widely used in real-time and label-free detection of a wide variety of substances and especially for the analysis of biospecific interactions. The initially analyzed system, based on continuous metal thin films and propagating surface plasmons excited through prism coupling, has given rise to a well-established family of sensors denoted as surface plasmon resonance (SPR) sensors and commercially available from several companies [1]. In the last decades, alternative configurations have also been explored in the search of increased sensitivity/lower limits of detection and more flexible and easy-to-use devices. For example, metal films perforated with arrays of nanoholes or nanoslits, which do not require the use of prisms, have been analyzed [2-7] showing a sensitivity comparable to that of continuous films, *i.e.* allowing to detect changes on the refractive index (RI) of the sensing medium as small as 10^{-7} [8]. In some of these systems [3, 5, 6], the achieved high sensing performance is due to the presence of Fano resonances, asymmetric peaks resulting from the interference between a broad continuum and a discrete state [9]. Indeed, the linewidth of Fano resonances is narrower than that of the original discrete resonance, making them more interesting for sensing purposes [9, 10]. A further improvement in surface plasmon based sensing has been the use of localized collective oscillations confined to the

surface of metal nanoparticles [11]. Such oscillations, generally referred as localized SPRs (LSPRs), can be directly excited by external illumination without the need of any additional coupling-in technique for particles smaller than the incident wavelength. The use of LSPRs and the understanding of its high dependence on size, shape and refractive index of the environment can be exploited to improve the sensitivity of this type of sensors [11]. So far, several works have compared the performance of SPR and LSPR sensors and established that each of them can be highly competitive in the appropriate regime [12, 13]: SPR offers higher sensitivity for bulk sensing while LSPR is more adequate for surface sensing, which is more relevant for detecting biological binding events. Fano resonances are also present in nanoparticle systems [9, 14–18], and they have been demonstrated to possess promising capabilities for sensing too [19]. In particular, it has been shown theoretically that individual metallic nanobelts (*i.e.* metallic nanowires or nanostripes with rectangular cross-section) present Fano-like peaks associated with their localized odd parity surface plasmon modes with reasonable good properties for sensing [10].

Another significant point for the development of competitive plasmonic sensors is the use of low cost and large area fabrication techniques in order to obtain large sensing areas with reasonable cost, as well as to avoid the need of complex optics or high magnification microscopes. Within this context, soft lithography [20] is an interesting option that allows to fabricate gratings of Au nanobelts on glass in a simple manner. In this work we present an easy to handle, large-area sensor $(2 \times 2 \text{ cm}^2)$ made of a grating of Au nanostripes fabricated by low-cost soft-lithography. We show, both theoretically and experimentally, that the Fanolike third order mode of the nanobelts has good properties for sensing also in the case of gratings. The fabricated sensor offers a fast temporal resolution of 1 s (a relevant feature for monitoring kinetics of surface binding events) and a detection resolution of 1.56×10^{-5} RIU (RIU stands for refractive index units), comparable with the state of the art in nanoplasmonic sensors using gold nanogratings [6]. In addition, increasing the size of the sensor allows an easy handling and improved portability of the device that can work without a powerful microscope. All of the mentioned suggests that this sensing platform has considerable promise for sensitive, low-cost, disposable and portable biosensors that could significantly impact point-of-care diagnostics for personal healthcare.

2. Design and numerical analysis

The use of single metallic nanobelts on substrate for sensing has been analyzed in the literature [10]. However, a grating of nanostripes offers further advantages as the amount of signal is increased and no high magnification microscope is needed to localize and focus on a single nanostructure. Therefore, we first analyze numerically the optical properties of a grating of metallic nanobelts to identify the modes present and characterize the expected sensing performance. Au has been chosen as the metallic element as it presents a high chemical stability and the functionalization and immobilization protocols for sensing and biosensing are firmly established for it [21].

The numerical simulations were performed using the Finite Element Method (FEM, Comsol Multiphysics). A 2D rectangular simulation domain was used to emulate a single unit cell in the grating. The rectangle was divided into two sub-domains representing the substrate (glass) and the superstrate (with varying refractive index from n = 1 to n = 2). Periodicity was simulated imposing Bloch boundary conditions on the lateral sides. The system is excited from the top with a port that generates a normally incident, TM-polarized plane wave, that is, with the electric field parallel to the simulation plane and therefore also parallel to the nanostripe width. Additional ports are used on the top and bottom boundaries to calculate the reflected and transmitted powers into the different diffraction orders, including the specular reflection and direct transmission. The Au nanobelts were modeled as rectangles lying on top of the substrate with material parameters taken from Ref [22].

Figure 1 shows the results of the FEM numerical simulations for the specular reflection from a grating of Au nanobelts of 375 nm width and 20 nm thickness placed over a glass (n = 1.5) substrate with a periodicity of 750 nm; several spectra are shown for varying indices of refraction of the surrounding medium over the substrate, as a function of both energy (Fig. 1(a)) and wavelength (Fig. 1(b)). In the case of a single nanobelt, we would expect two modes [10]: a broad dipolar mode (λ /2-resonance) in the near infrared range, and a narrower peak at higher energies, corresponding to the third order mode $(3\lambda/2$ -resonance). However, three main peaks can be identified in the spectral range used for the calculations in the case of a grating. This results from the interaction of the plasmon resonances with the diffracting orders of the grating, which generate the so called collective resonances [14, 15, 23, 24]. In fact, at wavelengths close to a Rayleigh anomaly (RA), which corresponds to the transition from an evanescent to a propagative diffraction order in an array, the LSPRs can couple between them through these grazing diffracted waves originating a collective mode which is indeed a Fano resonance. The position of the Rayleigh anomaly, λ^{RA} , can be easily obtained from the Bragg condition $n_{in} 2\pi/\lambda^{RA} \sin \theta_{in} + m 2\pi/P = n_{out} 2\pi/\lambda^{RA} \sin \theta_{out}$, with n_{in} the RI of the incident medium, n_{out} the RI of the output medium, θ_{in} the incidence angle, which is fixed in our case at 0° for normal incidence, θ_{out} the output angle, fixed at 90° for grazing orders, m the grating order (usually 1) and P the period of the nanobelt grating. This results in $\lambda^{RA} = n_{out} P$. Although initially the collective modes were only shown for systems where the polarization of the incident light was perpendicular to the plasmonic grating periodicity [14], it has been recently demonstrated that they are also possible for configurations with collinear periodicity and incident light polarization, and they were specifically denoted as parallel or transverse collective resonances [23, 24].

In our case, where the grating is surrounded by a substrate and a superstrate with different RI values, we obtain two RA, one for the light diffracting towards the substrate (glass), and the other one for the light diffracting towards the superstrate. The position of the first RA is then fixed at $\lambda^{RA}(glass) = 1125$ nm, while the position of the second RA evolves with the RI of the superstrate from $\lambda^{RA}(superstrate) = 750$ nm with n = 1.0 to $\lambda^{RA}(superstrate) = 1500$ nm with n = 2. This allows us to identify in Fig. 1 the broad peak located around $\lambda \sim 1.1$ µm (\cong 1.13 eV) with the interaction of the dipolar mode of the nanobelt with the diffracting order towards the glass, while the peak that shifts from $\lambda \sim 0.8 \ \mu m \ (\cong 1.55 \ eV)$ to $\lambda \sim 1.5 \ \mu m \ (\cong 0.83)$ eV) corresponds to the interaction of the dipolar mode with the diffraction towards the superstrate. The near-field maps shown in Figs. 1(d) and 1(e) reveal the dipolar character of those resonances, with the characteristic maxima of field located at each side of the nanostructure, as well as the coupling to the indicated RA for each case, visible as a delocalization of electromagnetic near field towards the indicated outside medium (glass or superstrate). The pattern appearing in the superstrate in Fig. 1(e) results from the combined effect of the interference between the incident and reflected beams in the vertical direction and that of the counter-propagating diffracted beams parallel to the substrate, both with a periodicity matching half of the illumination wavelength. The interference between the narrow diffraction peaks and the broad $\lambda/2$ resonance originates the asymmetric Fano-like lineshapes that can be observed. Note that, for the increasing value of the RI of the superstrate, both the background dipolar mode and the associated diffracting order are redshifted, as expected. Additional calculations, not shown here, also confirm that the width of the nanobelts modifies the spectral position and the width of the $\lambda/2$ resonance, changing therefore the overlap with the diffraction modes and modifying the overall spectral shape.





Moreover, another narrow resonance appears at higher energies, highlighted in the box in Fig. 1(b) and zoomed in on Fig. 1(c). This resonance can be attributed to the $3\lambda/2$ -resonance of a single nanobelt [17] confirmed also by the near-field map shown in Figs. 1(f) and 1(g), which show the four field lobes (3 nodes) expected for this kind of resonance [17, 18]. Such peak is very narrow and also redshifts remarkably as the RI of the surrounding medium

increases [10]. The asymmetric Fano-like profile of this mode is not due to interaction with the diffraction orders as there is not spectral overlap between them. In this case, it can be explained in terms of mode-parity-controlled interference through a simple antenna-like emission model, experimentally verified for single nanorods [18].

As both the $3\lambda/2$ -resonance and the parallel collective mode associated with diffraction towards the superstrate have a Fano lineshape and a remarkable dependence on the RI of the superstrate, the two of them could be thought as good candidates for sensing. However, we focus on the $3\lambda/2$ -resonance for two main reasons. On the one hand, this resonance is placed in the visible range, which is more interesting in terms of low cost sensing as the needed optics and detectors are usually cheaper. On the other hand, it is known that the electromagnetic field associated with the parallel collective resonances is highly extended in the vertical direction [23] (see Figs. 1(d) and 1(e)). This improves the ability of these modes for bulk sensing, but in principle diminishes its performance in the case of surface sensing [13].



Fig. 2. (a) Specular transmission, obtained from FEM numerical simulations, from a 750 nm period grating of Au nanobelts of 375 nm width and 20 nm thickness, placed over a glass (n = 1.5) substrate and with a superstrate of refractive index varying from n = 1.0 to n = 2.0. (b) Resonance position as a function of the superstrate refractive index. Inset: Table containing the calculated sensitivity and figure of merit (FOM) of this resonance to RI changes.

Figure 2(a) shows the shift of the $3\lambda/2$ -resonance, as seen in transmission, as a function of the RI. The shift of the peak center position with RI can be fitted to a straight line (Fig. 2(b)) with different slope depending on whether the index of refraction is larger or smaller than that of the substrate. To evaluate its performance for sensing, the magnitude S_{λ} (wavelength shift in nm per RIU) is shown as an inset Table for both n-regions (and also overall for the sake of completeness). Such magnitude is significant, but not remarkable. However, the relevant magnitude for sensing is the figure of merit (FOM) defined as the plasmon resonance sensitivity divided by the peak full width at half-maximum, FWHM. Since this $3\lambda/2$ resonance is actually very narrow, remarkable FOMs are thus obtained, in the range predicted by López-Tejeira et al. [10]. The better performance of the system for RI of the superstrate larger than that of the substrate can be understood in general terms as a consequence of the inhomogeneous distribution of the electromagnetic field inside a plasmonic nanostructure deposited onto a substrate [25, 26], compared to that of a plasmonic nanostructure embedded in a homogeneous medium. The field is more intense at the interface of the plasmonic structure with the medium of higher refractive index. This can be clearly seen comparing the near field maps plotted in Figs. 1(f) and 1(g), where the substrate is glass in both cases but the RI of the superstrate is 1.0 and 2.0, respectively. It can be expected that the medium with higher concentration of electromagnetic field will be more sensitive to modifications on its properties. In this way, if the substrate has a higher refractive index than the superstrate, the sensitivity would be lower than in the case that the superstrate has a higher RI than the substrate (being here the superstrate the medium with changing properties).

3. Experimental sensing demonstration

The Au nanobelt gratings can be obtained with low cost fabrication techniques over large areas. Figure 3(a) shows the fabrication process used for our sensor. First, a 20 nm-thick Au film was deposited by e-beam evaporation on a glass substrate (Menzel-Gläser cover slips 18 \times 18 mm², 130 to 160 μ m thick). Then, 40 nm of SiO_x were deposited by plasma enhanced chemical vapor deposition (PECVD) as hard mask. The Au nanobelts were patterned by soft lithography [20]. A droplet of 5µl of resist (5% PMMA 996K in gamma-butyrolactone (GBL)) was dropped over the SiO_x layer with a micropipette. The resist is then covered with the PDMS stamp and pressed between two glasses. The resist is cured under vacuum for 3 hours. All the procedure is extremely easy and cheap and permits the fabrication of large areas, in our case with a size around 2×2 cm². Reactive ion etching (RIE) with CHF₃ plasma was used to transfer the pattern onto the SiO_x hard mask. The remains of resist were removed with acetone and oxygen plasma. RIE etching with Ar plasma was done to transfer the pattern onto Au. Finally, RIE etching with CHF_3 was used to remove the SiO_x over Au nanobelts. The end part of Fig. 3(a) shows an AFM image of the nanobelts finally obtained. Figure 3(b) shows the measured (J.A. Woollam M-2000FI ellipsometer) and simulated optical transmission spectra for light normally incident on a 20 nm thick Au nanobelt grating, with a 780 nm period and 355 nm linewidth, in air. The experimental illumination spot has a diameter of 2 mm. The peaks are very well defined, demonstrating the high uniformity of the sample. The agreement between the experimental and the simulated spectra is quite good, and allows us to clearly identify each peak nature. The $3\lambda/2$ -resonance corresponds to the peak located around $\lambda \sim 600$ nm. The experimental peaks are broader than the calculated ones, probably due to local inhomogeneities throughout the grating.



Fig. 3. (a) Fabrication process for Au nanosensor, based on soft-lithography, including at the end the AFM image of the obtained Au nanobelt grating over glass. (b) Measured and simulated optical transmission through a 20 nm thick Au nanobelt grating with a period of 750 nm and linewidth of 355 nm fabricated on glass.

To measure the sensitivity and the detection resolution we used an Olympus BX51 microscope for convenience, although a simpler optical system without any large magnification can be used. Light from a halogen lamp (100 W) passes through a polarizer and it is loosely focused onto the sensor surface with a condenser lens with very low numerical aperture (< 0.1) to obtain close-to-normal incidence. The transmitted light was collected through a low-magnification 2x objective (N.A. = 0.06) and focused onto an optical fiber of 1 mm core diameter connected to a portable spectrometer (Ocean Optics USB4000). In this way, the active area of the sensor, the area from which the light is collected, corresponds to a spot diameter of 750 μ m. The spot could be much larger but for initial testing purposes is sufficient. The chip is bonded with optical glue to a plastic container (Ibidi) with two openings used to flow the gas or liquid to be detected. The polarization of the incident light is

kept perpendicular to the Au nanobelts (TM). To calibrate the fabricated sensor, a solution of DI water with glycerol with different concentrations (0%, 3%, 6%, 9%, 12% and 15%) was injected. Each concentration provides a different RI, from water (0%) with RI = 1.331 to glycerol 15% with RI = 1.355. The RI of each concentration was calculated from the values taken from Ref [27]. Figure 4(a) shows the transmission spectra for each of the solutions. As it can be seen, the peak redshifts as n increases, as predicted by the numerical results. The obtained experimental sensitivity resulting from this shift is $S_{\lambda} \sim 150$ nm/RIU, in good agreement with the theoretically obtained value. However, due to the inhomogeneous broadening of the experimental peak, the accuracy in the determination of the peak position is reduced, degrading the detection resolution of the sensor based only of peak wavelength shift. A common and efficient method for the real time detection is the use of multispectral data analysis [5, 6, 28]. This method calculates the integrated response (R)like: $R = \sum_{\lambda}^{\lambda_2} \left(\left| I(\lambda) - I_0(\lambda) \right| / I_0(\lambda) \right) \times (\lambda_2 - \lambda_1) / N_{\lambda} \times 100\%$, where λ_1 and λ_2 define the integrated wavelength range for the relative intensity changes (defined as $(I(\lambda) - I_0(\lambda))/I_0(\lambda)$, the normalized variation of the transmission intensity of the solution compared to that of water) and N_{λ} corresponds to the number of wavelengths comprised within the integration range. The wavelengths λ_1 and λ_2 are chosen to select the spectral region where the signal to noise is highest. Here, λ_1 and λ_2 are 650 and 750 nm respectively. Figure 4(b) shows the relative intensity change for the different values of the RI. Figure 4(d) plots the obtained values of R as a function of RI and the sensibility (S_R) of the sensor calculated from the slope of the plot: The value of the sensibility obtained was $S_R = 1.05 \times$ $10^{4\%} \times \text{nm/RIU}$. Figure 4(c) shows the integrated response R as a function of time. We used N = 200 spectrum frames averaged with an integration time of $\tau = 5$ ms for each spectrum. From those measurements it is possible to calculate the noise level of the signal and its standard deviation $\sigma = 0.16\% \times \text{nm}$ over 15 data points. With that we can calculate the detection resolution of our sensor, $\sigma/S = 1.56 \times 10^{-5}$ RIU. This value is comparable with the state of art of gold nanobelt sensors. In recent works other authors have achieved values of 1.93×10^{-5} RIU [4] and 3.74×10^{-5} RIU [29], which are similar to our result. However, while in other works the temporal resolution is 10 s [30] or even 30 s [4] we achieved a temporal resolution of 1 s, one order of magnitude in improvement. The temporal resolution could be further improved using a lower N but this could produce an increment in the noise of the signal [31]. Despite the sensibility of our sensor is not a record value, a fast detection in a wide dynamic range is possible.



Fig. 4. (a) Optical transmission spectra of the sensor for the solutions prepared with different RI. (b) Relative intensity change spectra for the different RI. (c) Integrated response (R) of the sensor for each RI as function of time. (d) Integrated response of the sensor for each dissolution as function of RI. The sensibility of R, S_R , is obtained from the slope of the linear fit.

In summary, the fabricated sensor has an advantage for tagging-free, point-of-care testing based on its large size, which makes it of easy handling and allows for the use of a low-magnification, simple optical system for detection. The fabrication process is low-cost as it is based on the combination of soft nanoimprinting techniques and plasma etching, therefore making it suitable for mass production [32]. With these advantages, our novel Au nanobelt plasmonic sensor may find a practical use in applications that require a fast, sensitive, portable and disposable detection without the need of complicated optical devices, making it as a good candidate for sensing in developing countries and remote locations.

4. Conclusions

We have fabricated a low-cost and easy to handle large-area $(2 \times 2 \text{ cm}^2)$ nanoplasmonic sensor that uses Fano resonances for detection. The sensor is formed by a grating of ultra-thin 20 nm-thick Au nanobelts. By using the third-order mode LSPR of the nanobelts, with a Fano-like profile, we have obtained a sensor with a high sensibility of $1.05 \times 10^{4\%} \times \text{nm/RIU}$. The sensor achieved a detection resolution of 1.56×10^{-5} RIU with a fast temporal resolution of 1 s, on an effective measured spot of 0.75 mm in diameter. The detection and temporal resolutions along with the simple optical system used for the measurements make this sensor as very promising for its use as a disposable and portable sensor.

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