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Generation of Surface Plasmons at Waveguide Surfaces in the Mid-Infrared Region

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Abstract A technique is proposed to extend the application of surface-plasmon-based spectroscopy into the mid-infrared spectral regime, which is of substantial interest in the field of chemical analysis and biosensing. Surface plasmons can be excited for wavelengths of the order of 6 μm at corrugated waveguides for a given combination of materials and thicknesses, and for refractive indices of the surrounding medium corresponding to those of organic solvents. This approach can easily be extrapolated to other values of any of these parameters. Based on these considerations, a new generation of mid-IR SPR sensors can be developed with a diverse range of potential applications in chem/bio sensing.

Keywords Surface plasmons · Corrugated waveguides · Mid-infrared

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Introduction

Surface plasmon resonance (SPR) is a well-studied physical mechanism, commonly used in chemical and biological sensing, where it has repeatedly proven its versatility, accuracy, and practical operativity [1]. Many methods have been employed to excite plasmons. Most of them are based on attenuated total reflection (ATR) in a refractive element, the so-called Kretschmann configuration [2, 3]. There also exists a tremendous variety of operative SPR fiber sensors, some of them based on so-called tapered fibers. [4, 5]

However, it is quite surprising to note that the effective spectral range where SPR-based devices have been developed is rather confined to date, roughly between the red limit of the visible spectrum to around 1.6 μm in the near infrared (NIR). This fact is remarkable, because many other spectral regions are of substantial interest in the field of chem/bio spectroscopy and sensing and have largely been ignored with respect to designing novel SPR configurations.

In particular, it is well-known that spectroscopy in the mid-infrared (mid-IR; 3–20 μm) is a most important spectral regime in terms of identification of constituents of chemical and biological interest, e.g., in environmental analysis or bioanalytics. Mid-IR spectroscopy permits to detect the fingerprints of many compounds, and significant efforts have been made to develop more accurate techniques to provide identification and precise measurement of particular substances. However, since the molecular information is contained in weak vibrational modes, electric field enhancement techniques are frequently needed [6]. Consequently, it would be a great opportunity to exploit the advantageous characteristics of SPR devices in the mid-IR thereby facilitating the translation of mid-IR SPR into a valuable routine technique comparable to NIR-based devices.

The number of papers in the literature that explore the possibility of mid-IR SPR sensors is surprisingly small and quite often their claims are limited. In particular, to the best of our knowledge, the existing references on SPR sensing in the mid-IR range are mainly theoretical developments based on gratings generated by doping of silicon substrates [7, 8], although some experimental work based on ATR configurations have been presented [6, 9]. However, all the proposed and tested setups reported in literature are angularly interrogated, which is a drawback for the development of e.g., lab-on-a-chip devices.

To extend the SPR technology to the mid-IR, the authors propose instead the design and fabrication of waveguides that enable waveguide-based SPR sensors operating at mid-IR frequencies. Such devices will offer several important advantages including compactness, ruggedness, and versatility in fabrication, along with the subsequent benefit of integration into complex optoelectronic circuits.

Mid-IR Waveguides for SPR Sensing

In order to get an integrated operative device based on the surface plasmon resonance in the mid-IR, the first challenge is to find a waveguide transparent in the desired range 3–20 μm. Currently it is easy to find optical fibers based on either sulfide or selenide glasses up to 9 μm and silver halide fibers transparent on a wide bandwidth up to about 15 μm. These later fibers have been used in fact as the basis of silver halide slab waveguides for measuring refractive indices of outer media through evanescent wave interaction [10]. Also operative semiconductor waveguides in the mid-IR range up to 13 μm have been recently reported [11].

The use of silver halide slabs is quite cumbersome from the technical point of view, and although they could be suitable to design and fabricate a device based on this principle, it is not so easy to get a single-mode waveguide with the technique reported in [10]. Thus a fabrication based on semiconductor techniques and facilities would be more adequate.

Furthermore, the main feature of these waveguides is the relatively high effective propagation index of the fundamental TM mode, above 2.4. For instance a slab waveguide made from GaAs grown at an $Al_{0.2}Ga_{0.8}As$ buffer [11] presents an effective refractive index of around 3.30 at a wavelength of 6 μm, for an outer refractive index around 1.56, which is in the range of some organic solvents such as e.g., aniline or benzyl-alcohol.

Indeed, in order to get a surface plasmon resonance suitable for determining outer refractive indices, a metallic medium should be added to the waveguide along with phase-matching between the effective refractive index of the structure and the surface plasmon. Since surface plasmons (SP) can be understood as confined surface waves in a multi-layered structure including metallic media, it is straightforward to calculate the dispersion relations of the guided modes for a planar structure including a substrate [12] (which in this case must be the waveguide itself), a metallic layer, and an outer medium. The values that can be calculated for the SP effective refractive index are substantially below the value of the TM_0 mode in the slab waveguide, thereby no possibility of phase-matching exists.

The usual method to get the resonance of a surface plasmon in such conditions is based on the deposition of an additional dielectric layer on top of the structure [5, 12] for modifying the real part of the effective index of the supported surface plasma wave, whose value is mainly affected by the outer refractive index one. Although in the case of mid-IR waveguides the large difference between the effective refractive indices of the fundamental TM mode and the surface plasmon makes this approach unsuitable if a high sensitivity is required. Thus a different approach has to be made.

Generation of Surface Plasmon Resonance in Corrugated Waveguides

It is well-known that a grating can be used to modify the incident wavevector at the surface [13]; hence, in order to excite a surface plasmon, the use of grating-assisted waveguides appears to be a viable solution toward integrated sensors based on SPR. With this kind of waveguides, the guided mode is diffracted, and the phase matching with the surface plasmon wavevector can be accomplished.

To get a plasmon resonance, the waveguide grating must be designed to couple radiation from the fundamental TM mode of the waveguide to an SP mode. The grating period Λ can then be calculated from the phase-matching condition [14, 15]

$$\Lambda = \frac{\lambda}{\mathrm{Re}\left(n_{\mathrm{eff},W}\right) - \mathrm{Re}\left(n_{\mathrm{eff},\mathrm{SP}}\right)}, \tag{1}$$

where λ is the desired resonance wavelength, $n_{\mathrm{eff},W}$ is the effective index of the fundamental TM mode for the waveguide and $n_{\mathrm{eff},SP}$ is the effective refractive index for the surface plasmon mode. A variation in the outer refractive index of the structure then becomes a change in the $n_{\mathrm{eff},SP}$.

Following this approach, we have focused on corrugated waveguides made from state-of-the-art materials that can be fabricated and structured rapidly and easily, thereby providing a proof-of-principle for the feasibility of transferring SPR technology into the mid-IR region. The technical feasibility, simplicity, and versatility of the selected approach render this concept a natural extension of the devices that have been working quite successfully in other spectral regions. Consequently, rather than a specific sensor, a concept is proposed that can be easily applied also for other materials and measurement situations due to its scalability for different frequency ranges.

A scheme of the proposed waveguide is shown in Fig. 1. It consists of a guiding layer of GaAs with a mean thickness h, and a superficial corrugation with a height of Δh and a period of Λ. Both the material and the dimensions are appropriate for state-of-the-art fabrication facilities. On the top of the corrugated waveguide a gold layer with a thickness of d is deposited. Gold is selected, as it is by far the most common material for SPR sensing due to the standardized techniques available for its deposition, structuring, and functionalization in order to obtain specific recognition of analytes dissolved in the outer (sample) medium. In this context, the inherent molecular selectivity of absorptions in the mid-IR is considered a major advantage for SPR devices operating in the 3–20 μm range, as less specificity of the molecular recognition interface may be compensated with the SPR tuned to a selective absorption band of the analyte to be determined, where the authors have shown the variation of refractive index is enhanced [16]; in moderately complex samples, the (bio)recognition interface may be omitted at all.

In any case, the presence of the metallic layer is the key to achieving plasmon excitation, and the values of h, d, and Λ must be calculated to provide excitation of plasmons for the desired ranges of operating wavelengths and outer refractive indices.

The transmittance of a corrugated waveguide with a grating period Λ and length L such as depicted in Fig. 1, can be evaluated through the equation [15]

$$T = \left| \left[\cos(\zeta L) - j \frac{\sigma}{\zeta} \sin(\zeta L) \right] e^{j\left(k\, n_{\mathrm{eff},W} - \sigma\right) L} \right|^2, \quad (2)$$

where

$$\sigma = \frac{k\left(n_{\mathrm{eff},W} - n_{\mathrm{eff,SP}}\right)}{2} - \frac{\pi}{\Lambda}, \quad (3)$$

is the detuning parameter, k the wavenumber and

$$\zeta = \left(\sigma^2 + |\kappa|^2\right)^{1/2}, \quad (4)$$

being κ the coupling coefficient of the grating [14], which can be analytically calculated for single-mode waveguides [17].

With the calculated values of the effective refractive indices for the fundamental mode of the waveguide and the surface plasmon, it is possible to calculate the value of the grating period Λ, thereby taking into account that for small corrugation, $\Delta h << h$, the $n_{\mathrm{eff,SP}}$ can be considered as the one obtained for pure planar layers.

Furthermore, the optimization of the transmittance, understood as the contrast of the transmittance dip or figure-of-merit (FOM), can be achieved for $\kappa L = (2n+1)\pi/2$, where $n = 0, 1, 2, \ldots$

Following the procedure depicted above, it is quite easy to obtain the starting parameters for designing a corrugated waveguide based on a GaAs slab 10 μm height for SPR around 6 μm wavelength. For a waveguide such as the depicted, the effective index of the fundamental mode TM_0 turn out to be like the shown in Fig. 2a in the range between 5.9 and 6.5 μm. In this range, a planar slab with GaAs as substrate, a gold layer 15 nm thick and an outer medium with refractive index of 1.56, gives a real part of the effective refractive index for the SP like the plotted in Fig. 2b. As can be seen, these values are far apart one from the other so as to directly fulfill the phase-matching condition. However, with both set of values, it is straightforward to calculate the grating pitch needed to obtain a SPR around a wavelength of 6 μm. This calculation renders a value of about 3.5 μm for the corrugation period.

Then, if one considers a corrugated waveguide such as the one depicted in Fig. 1, with the calculated period of 3.5 μm, 10 μm height and 5 mm length, and a gold layer of 15 nm thickness deposited on top of the corrugated surface, an optimized value of $\kappa L = 5\pi/2$ is obtainable from a corrugation height of approximately 10 nm. The transmittance for this structure, obtained from Eq. (1), for a range of outer refractive indices between 1.54 and 1.57 is shown in Fig. 3a. Evidently, FOM is high enough to perform an accurate identification of the resonance wavelength, for which the transmittance is a minimum.

The slope of the curve obtained by tracking the displacement of the SPR wavelengths with the outer refractive index variation (the commonly utilized analytical parameter evaluated in

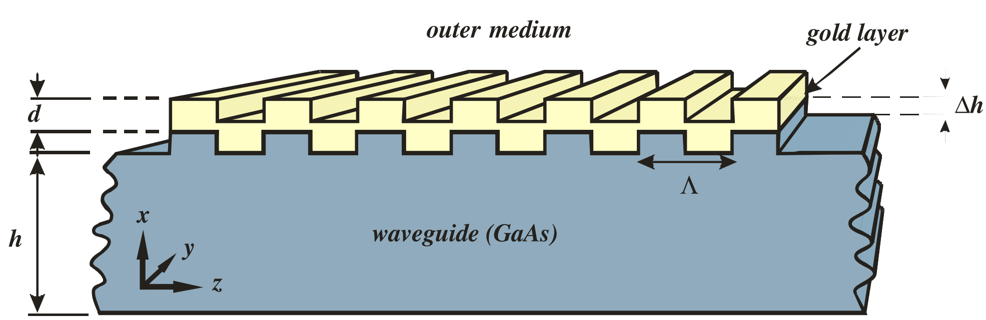

Fig. 1 Scheme of the proposed device, consisting of a corrugated waveguide of GaAs with an Au layer deposited onto it

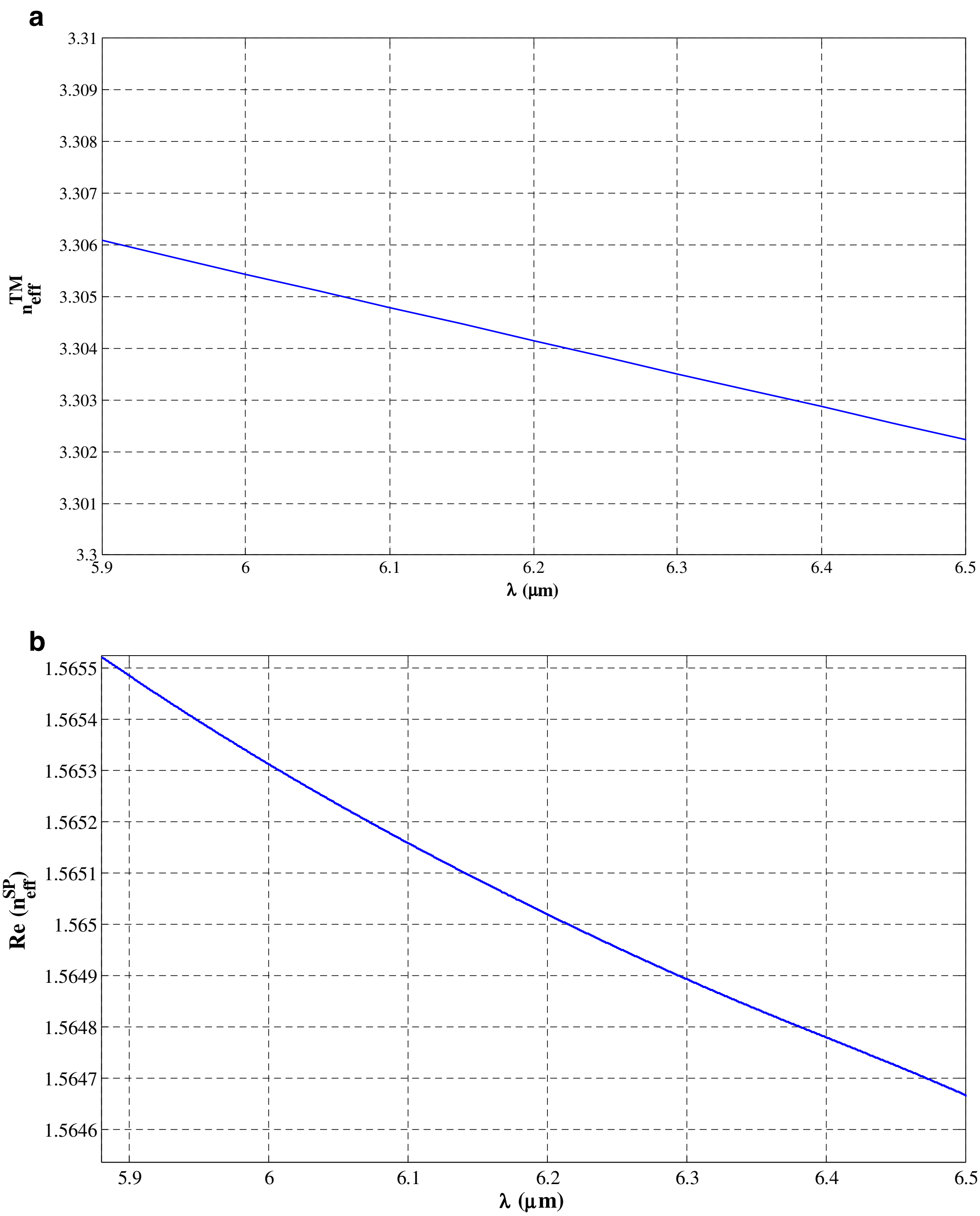

Fig. 2 **a** Effective index of the fundamental TM_0 supported mode by a GaAs slab 10 μm thick on an $Al_{0.2}Ga_{0.8}As$ buffer and a cover with a refractive index of 1.560. **b** Real part of the effective index of the supported mode by a multilayer structure GaAs-Au(15 nm)-outer medium (n_{out}=1.560)

SPR sensors) gives an estimation of the potential device sensitivity, which is approximately −3,500 nm/RIU, as shown in Fig. 3b. This value is comparable with those obtained with SPR devices reported in literature operating in the NIR.

We have chosen to study the feasibility of SPR around 6 μm because the advances in technology have made available the required elements in terms of light sources (quantum cascade lasers, QCLs) and waveguides, so an experimental verification of these calculations can be relatively easy and fast. Of course this analysis may easily be extended to other interesting region inside the MIR where QCLs or CO_2 lasers can be also used as sources. In that case, a

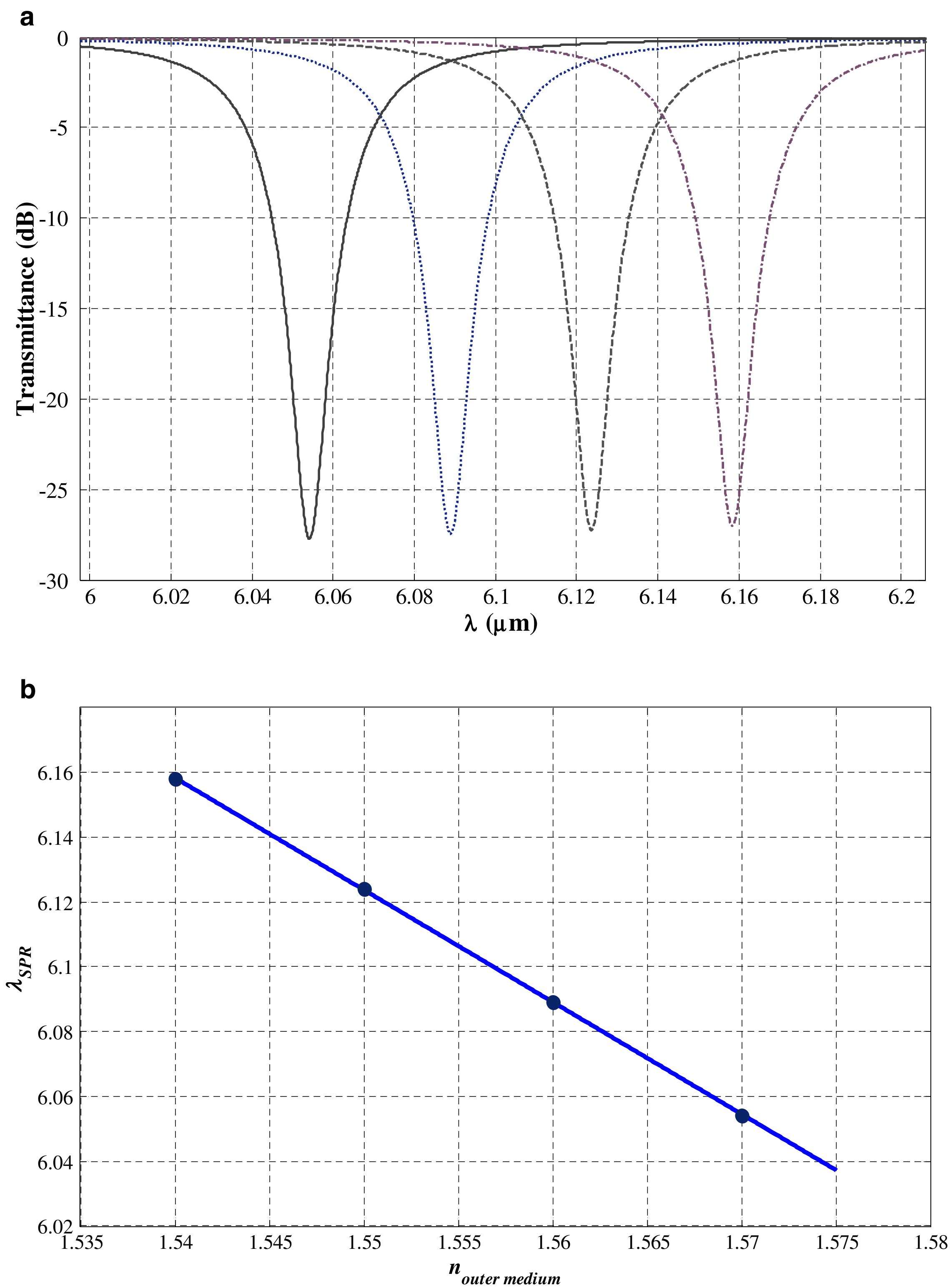

Fig. 3 **a** Transmittance of the proposed device. From left to right, the values of outer refractive index are 1.57, 1.56, 1.55, and 1.54 respectively. **b** Displacement of the plasmon resonance wavelengths with the variations of the refractive index of the outer medium. The estimated sensitivity of the device is around −3,500 nm/RIU in the range of outer refractive indices 1.54–1.57

new selection of materials and a new calculation of the parameters would be needed, but the method depicted here is fairly general and the modifications would be straightforward.

Conclusions

In this work, the concepts linked to generation of surface plasmons and their application to refractive index measurements have been extended to an unusual spectral range such is the mid-infrared. The expected sensitivity is in the same magnitude order than the currently available SPR transducers based on waveguides. Thus, the procedure for developing operative integrated SPR sensors based on semiconductor technologies has been stated.

The availability of advanced light sources such as quantum cascade lasers emitting at 6 μm renders this approach easy to implement. Furthermore, the proposed device parameters may readily be adapted for response at many other wavelengths within the mid-IR spectral band provided that appropriate light sources and detectors are available. With the proposed concept, the advantages of SPR-based spectroscopy and sensing can be transferred to the probably most relevant spectral regime in chemical and biological analysis facilitating novel diagnostic platforms with applications ranging from environmental monitoring to biomedical diagnostics and label-free assay technology. Given that the proposed technique takes advantage of conventional microfabrication techniques, a wide range of sensing platforms with unsurpassed versatility, operativity, compactness, and sensitivity may be anticipated.

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