

Long-range plasmons in lossy metal films on photonic crystal surfaces

Valery N. Konopsky* and Elena V. Alieva

Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow region, 142190, Russia

*Corresponding author: konopsky@isan.troitsk.ru

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A one-dimensional (1D) photonic crystal structure with a terminal palladium layer supporting long-range surface plasmon polariton (LRSP) waves in any gaseous environment is described. We show that LRSP propagation may be achieved not only along “good plasmonic” metals such as Ag and Au but also along lossy metals such as Pd, which does not usually support plasmon propagation in the visible spectral range with ordinary Kretschmann excitation. The possibility of the LRSP propagation along catalytically active metals such as Pd or Pt opens up new perspectives for studying of (photo)chemical surface reactions and offers the potential for more applications in the general area of catalysis, photocatalysis, and plasmon-mediated chemistry. We present experimental results that demonstrate the hydrogen sensitivity of this photonic structure incorporating a catalytically active 8-nm-thick Pd final layer. A 3% hydrogen concentration in nitrogen is detected with a signal-to-noise ratio of approximately 300, with a response time of about 10 s at room temperature. © 2009 Optical Society of America

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Surface plasmon polaritons (SPPs) are *p*-polarized optical surface waves propagating along a metal–dielectric interface [1]. The maximum electromagnetic (EM) field strength of the SPPs is located at the interface, and this leads to high surface sensitivity of these waves. The sensitivity of SPPs has been used in many surface plasmon resonance (SPR) applications, where a shift of a SPR dip is measured, from biosensors used for detecting biomolecules in a liquid to gas sensors for detecting impurity traces in the air [2]. A limiting factor for SPR sensitivity in these applications is the limited propagation length of SPPs due to a strong intrinsic damping of their EM field in metal. Even for using the “best plasmonic” metals such as silver and gold, the SPP propagation length is only about 10 μm in the optical frequency range. Other metals do not practically support any SPP propagation at visible frequencies.

One way to increase the SPP propagation length and, consequently, the SPR sensitivity is to use long-range SPPs (LRSPs), which can be achieved using a thin metal film, imbedded between two dielectrics with identical refractive indexes (RIs) [3–5]. This requirement to match the RIs on both sides of the metal film poses serious complications for the practical employment of LRSPs for sensing in liquids and gaseous environments. For example, in gases ($n_e \approx 1$), a freely suspended thin metal film is required to match the RIs on both sides, and consequently ultra-thin membranes are currently the only option as its support [6].

Recently we have shown [7] that this RI-matching requirement may be circumvented by using a one-dimensional (1D) photonic crystal (PC) as a substrate for the metal film. The 1D PC is a simple periodic multilayer stack. Such 1D PC can exhibit photonic bandgaps where the propagation of optical EM waves is forbidden. By changing the bandgap parameters by modifying the thicknesses of alternating layers in the stack, the LRSP propagation can be excited in the

terminal metal layer, bordering an external medium with any RI, including $n_e \approx 1$.

In this Letter we show that LRSPs may occur in this structure, not only with “good plasmonic” metals such as Ag and Au but practically with any metal, including lossy ones, if the thickness of the final metal layer is in the nanometer range. As an example we demonstrate that LRSPs may propagate along a palladium nanofilm, which does not usually support any plasmon propagation in the visible spectral range with ordinary Kretschmann excitation. The possibility of the LRSPs propagation along catalytically active metals such as Pd or Pt opens up new perspectives for studying of (photo)chemical surface reactions. By way of illustration, a hydrogen sensor based on a 1D PC with the palladium final layer is presented in this Letter.

A sketch of the setup is shown in Fig. 1(a). The LRSPs are excited by focusing a laser beam from a diode laser through a glass prism onto the 1D PC structure (a Kretschmann-like excitation scheme). An objective with the focal length $f=40$ mm is used to focus the laser beam (with diameter $D=1.5$ mm) on the structure. The excitation source is a fiber-coupled diode laser with wavelength $\lambda=737.7$ nm and power $W=0.26$ mW. The LRSP’s angular resonance curves are measured by detecting the intensity distribution of the light reflected from the 1D PC structure using a 512 pixel Hamamatsu photodiode array (with pixel pitch 25 μm) placed 640 mm away from the prism. The 1D PC structure used in the experiments is as follows: substrate/(HL)¹⁴H’M/air, where *H* is a Ta₂O₅ layer with a thickness $d_2=112.8$ nm, *L* is an SiO₂ layer with $d_1=155.0$ nm, *H’* is a Ta₂O₅ layer with $d'_2=103.4$ nm, and *M* is the palladium layer with $d_3=d_M=8$ nm. The prism and the substrate are made from BK-7 glass. The Ta₂O₅/SiO₂ multilayer and palladium film are deposited by magnetron and cathode sputtering, respectively. The RIs of the substrate,

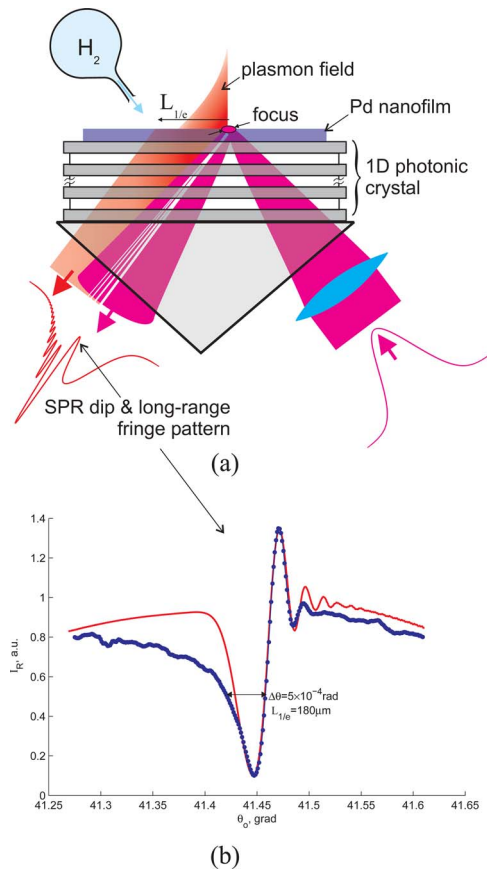


Fig. 1. (Color online) (a) Sketch of the experimental setup. An incident and then reflected focused laser beam is shown in dark gray (magenta), while the LRSPP propagated along the surface and then backcoupled into the prism is displayed in light gray (red) to distinguish between them. Both the SPR dip and the fringe pattern near the dip are the result of interference between these waves. (b) Angular SPR curves: experimental points [black (blue) dots] and theoretical calculation [light gray (red) line]. A discrepancy between calculated and observed values at angles $\theta_0 < 41.43^\circ$ is due to a strong LRSPP scattering near the total internal reflection angle.

Ta_2O_5 , SiO_2 , and Pd are respectively (at $\lambda = 737.7$ nm) $n_0 = 1.513$, $n_2 = 2.076$, $n_1 = 1.455$, and $n_3 = n_M = 1.9 + i4.8$. The RIs at other wavelengths are derived using dispersion data presented by Palik [8].

A typical experimental long-range SPR curve is presented in Fig. 1(b). The angular curve width is $\Delta\theta = 5 \times 10^{-4}$ rad, which corresponds to the SPP propagation length $L_{1/e} \approx 180 \mu\text{m}$. The propagation length of SPPs in a Pd film, using the ordinary Kretschmann configuration at optimal film thickness (15 nm of Pd deposited on the glass prism) and at the same wavelength, is about $1 \mu\text{m}$. Therefore, a 180-fold increase in SPP propagation length is achieved in our structure. The fringe pattern near the resonance dip in Fig. 1(b) is the result of this long-range propagation of SPPs. In Fig. 1(a) the origin of this fringe pattern is illustrated; the fringe pattern appears when the propagation length of the surface waves is greater than the waist of the incident Gaussian beam [7]. In our experiments the waist is $f\lambda/D \sim 20 \mu\text{m} \ll L_{1/e}$. This fringe pattern observed on the larger-angle side of the resonance dip is the dis-

tinguishing feature of long-range surface wave propagation, and a similar fringe pattern is observed not only with SPPs [7] but also with other long-range propagating surface waves [9]. The fringe pattern near the dip (also as the SPR dip itself) is the result of the interference between the divergent reflected Gaussian wave and the (more flat) LRSPP wave, which is backcoupled into the prism from the surface. This fringe pattern is reproduced well at a theoretical intensity distribution shown in Fig. 1(b) (light gray line) obtained by a numerical calculation of the reflection of a focused Gaussian beam 640 mm away from our structure. One can also see that the fringe pattern on the reflection curve presented for the purposes of illustration in Fig. 1(a) is more pronounced, because this curve is calculated at a distance of 128 mm from the 1D PC structure (five times less than in the actual experiment). It may be easily inferred that for very large distances, where wavefront curvatures of both waves equalize, the fringe pattern will disappear and the only resonance dip will be preserved [7].

In Fig. 2 the calculated dispersion of our 1D PC structure in air is presented as the logarithm of the optical field enhancement (i.e., as $\log[(E_e E_e^*) / (E_0 E_0^*)]$) in the external medium near the structure. The experimental point at $\lambda = 737.7$ nm, $\rho = 1.0012$ is designated as a white pentagram. The dispersion is presented using the coordinate $\lambda(\rho)$, where λ is the optical wavelength and ρ is the NA $\rho = n_0 \sin(\theta_0)$. The NA ρ may be used as an angle variable instead of angles θ_j in different layers. This is a unified angle variable for all layers since, according to Snell's law, $\rho = n_0 \sin(\theta_0) = n_j \sin(\theta_j)$, for any layer j . The angular parameter ρ , at which the excitation of the surface mode occurs, is equal to the effective RI of the mode n_{sw} . Therefore, the dark, red curve inside the dark bandgap in Fig. 2 presents the dispersion of the LRSPP mode (i.e., the dependence of its effective RI on the wavelength).

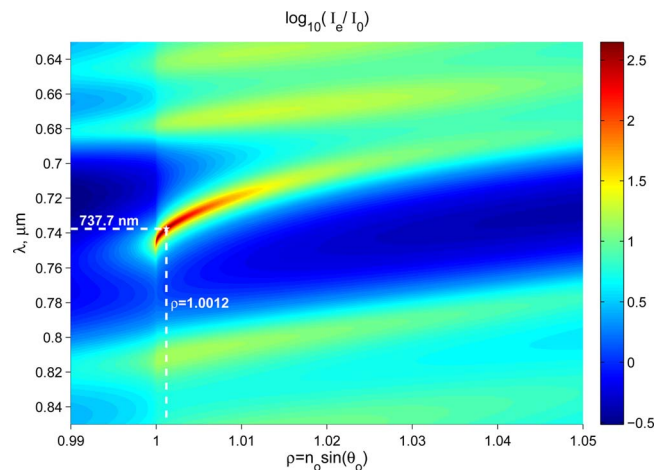


Fig. 2. (Color online) The calculated dispersion of the 1D PC structure with the terminal Pd nanolayer in air and the experimental point (white pentagram) of $\lambda = 737.7$ nm, $\rho = 1.0012$. The LRSPP mode is seen as the black core within the white stripe (dark, red curve) with an enhancement of more than 100 inside the bandgap, which is seen as dark (blue) areas with an enhancement of less than 1.

The principal reason for the long-range plasmon propagation is the presence of the electric field strength minimum inside the thin metal film, which is the result of destructive interference between SPPs from both film interfaces. It is because of this field minimum inside the film that LRSPP propagation is possible even along lossy metals, such as Pd. In a previous paper [7] we highlighted a general condition for the existence of the electric field minimum in thin films (see Eq. (1) from [7]): if a surface wave has an effective RI of $\rho = n_{sw} \approx n_e$, then this surface wave will be less sensitive to the losses in the metal, because only a small fraction of the EM energy propagates inside the metal film. It may be shown that the thinner the final metal layer, the less the EM field is inside the one (though the maximum of the EM field at the interface preserves). One can see from Fig. 2 that the LRSPP mode exists near $\rho \sim n_e$ only ($\rho \approx 1 \dots 1.0023$), where the minimum of EM field inside the metal nanolayer occurs, while at $\rho > 1.0023$ the EM damping is strongly increased in this 8-nm-thick metal film [in accordance with Eq. (1) from [7]].

Owing to the high sensitivity of narrow LRSPP resonance to changes in the thickness of the Pd nanofilm and the film environment, new potentialities appear for studying catalytic reactions on the surface. By way of illustration of these potentialities, we present experimental data of hydrogen dissociation and uptake by the palladium film in our structure. Owing to the very small thickness of Pd layer in our structure, we expect that the one can be used as a hydrogen detector with a fast response to hydrogen exposure.

Palladium is able to absorb up to 900 times its own volume in hydrogen in a reversible process where the amount of hydrogen soluble in Pd is dependent on the temperature and partial pressure of the hydrogen. Hydrogen uptake by palladium strains the Pd lattice, leading to a volumetric expansion that reaches equilibrium for a given hydrogen concentration in the environment around the material [10]. This volumetric expansion leads to an increase in the thickness of the Pd film on one hand and a decrease in the real and imaginary parts of the palladium RI, on the other hand. Our 1D PC structure is predominantly sensitive to the former effect, while the changes of RIs of the Pd film and a gas near the film give a minor contribution.

To verify the sensitivity of our 1D PC structure to hydrogen and to compare it with existing hydrogen sensors, we present experimental data showing changes in the SPR pattern position $\Delta\theta_0$ converted to changes in the effective RI of the surface wave n_{sw} , in response to exposure to 3% hydrogen. The data are shown in Fig. 3. The measurements were performed in a nitrogen environment at atmospheric pressure and room temperature (20°C). The 3% hydrogen was added to a gas chamber attached to the 1D PC structure. One can see that the response time following hydrogen injection was about 10 s. The noise floor

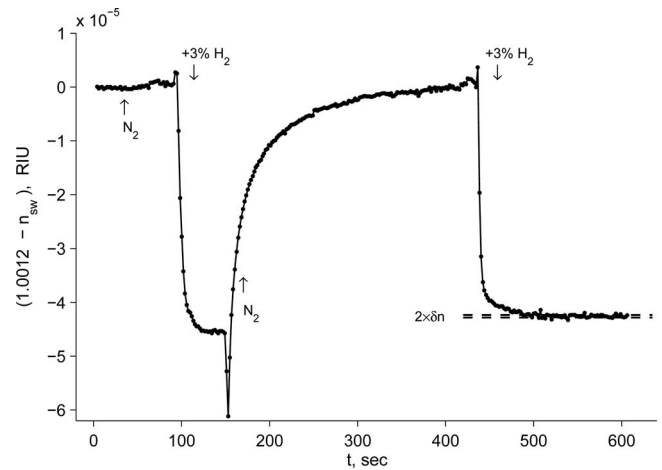


Fig. 3. Changes in the effective RI of the surface wave n_{sw} in response to hydrogen injection.

of the base line was about $\delta n = \text{std}(n_{sw}) \approx 1.4 \times 10^{-7}$ RIU/ $\sqrt{\text{Hz}}$ (where std is the standard deviation). Therefore we detected 3% hydrogen with a signal/noise ratio of ~ 300 . The signal accumulation time was about 1 s per point, and no posterior data averaging or smoothing was done.

In summary, we have demonstrated experimentally that even for lossy metals such as Pd, the LRSPP propagation length at an appropriate 1D PC structure is about 180 μm , which is 180 times greater than the propagation length in an ordinary Kretschmann configuration. We may speculate that the LRSPP propagation along such catalytically active metals as Pd, bordering with arbitrary environments (including gaseous environments), opens up new perspectives for studying (photo)chemical surface reactions. Taking into account a ~ 140 -fold increase in optical field intensity near the surface, more applications in the general area of photocatalysis and plasmon mediated chemistry are likely.

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