Cavity-enhanced localized plasmon resonance sensing

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We present a method to enhance the sensing properties of a localized plasmon sensor. The concept is based on the combination of localized plasmons in nanostructures and a photonic microcavity. Metal nanorods that are placed at Bragg distance above a metal mirror form a Fabry–Pérot microcavity and constitute a coupled photonic-plasmonic system. The localized plasmon resonances of the nanorods and the phase shifts upon plasmon excitation are extremely sensitive to changes in the refractive index of the material surrounding the nanorods. Compared to the plasmonic nanorods alone, the coupled photonic-plasmonic system allows for a much more sensitive detection of small refractive index changes. © 2010 American Institute of Physics. [doi:10.1063/1.3530795]

A prominent feature of plasmonic nanostructures is their use as localized surface plasmon resonance (LSPR) sensors.¹–³ The spectrum of sensing applications implies medical demands such as the detection of biomolecules,⁴–⁷ safety-related concerns such as the measurement of gas concentrations,⁸,⁹ as well as monitoring chemical reactions.¹⁰ In all mentioned areas the detection of small quantities preferably down to single molecules is desired. Therefore, all sensors have to be evaluated with respect to their sensitivity on marginal changes in the environment. Localized plasmon resonances in plasmonic nanostructures have the potential to provide these properties.¹¹ The electric fields of the localized plasmons surround the nanostructure and associate the spectral position of the resonances to the refractive index of the environment.¹²,¹³ Furthermore, molecule-selective nanoparticles can be obtained by the functionalization of their surfaces.¹⁴,¹⁵ However, the large linewidth of plasmon resonances is a major problem because it decreases the sensitivity fundamentally. A plasmon resonance of a nanorod in the near-infrared region, for example, has a linewidth of typically a few hundred nanometers resulting in a low Q-factor. Since for practical applications a large intensity variation of the reflected or transmitted light at a certain wavelength is desired, sharp peaks with a large modulation depth are required. Our combination of plasmonic nanostructures with a Fabry–Pérot microcavity provides a way of decreasing the linewidth of the resonances and therefore improving the sensing properties of nanostructures (Fig. 1).

The reason for the large linewidth of plasmon resonances is the strong radiative damping of the metal.¹⁶ An effective way of decreasing the linewidth is to couple the plasmon to a system with a narrow resonance. This concept has already been applied successfully in the plasmonic analog of electromagnetically induced transparency,¹⁷,¹⁸ where a broad plasmonic dipole is coupled to a narrow plasmonic quadrupole resonance. The resulting structure exhibits sharp peaks and superior sensing properties. In a similar way, the plasmonic resonances can be coupled to a photonic microcavity¹⁹,²⁰ [Fig. 1(a)]. Here, the linewidth of the coupled photonic-plasmonic resonance arises from the cavity Q-factor due to the modified photonic density of states and hence the modified radiative damping rate. The sensitivity of the structure arises from a strong phase dependence of the localized plasmon excitation in the nanorod [Fig. 1(b)], which can be explained with a simple effective medium model accounting for the phase shifts. The resonance condition of an arbitrary cavity postulates that the total phase shift \[ \Delta \phi_{\text{tot}} \] accumulated during one roundtrip of the wave in the cavity has to be a multiple of \( 2\pi \). The total phase shift is the sum of the phase shifts due to the propagation of the wave through the cavity \( \Delta \phi_{\text{prop}} \) and the phase shifts upon reflection at the cavity mirrors \( \Delta \phi_{\text{refl}} \). This implies that for a cavity consisting of two mirrors at Bragg distance \( d_{\text{Bragg}} = N \lambda / 2 \) the intensity of the reflected light is 0 (perfect darkness). When one of the cavity mirrors is replaced with a plasmonic structure, in our case nanorods, the phase shift on reflection \( \Delta \phi_{\text{refl}} \) has to be replaced with the phase shift on plasmon excitation \( \Delta \phi_{\text{exc}} \), and the resonance condition reads

\[
\Delta \phi_{\text{tot}} = 2 \Delta \phi_{\text{prop}} + \Delta \phi_{\text{refl}} + \Delta \phi_{\text{exc}} = N 2 \pi,
\]

with \( N \) being an integer [Fig. 1(b)]. The phase shift upon the excitation of a localized plasmon in the nanorod \( \Delta \phi_{\text{exc}} \) can be calculated as

![Figure 1](https://example.com/fig1.png)

**FIG. 1.** (Color online) (a) Array of nanorods combined with a cavity. (b) The phase shifts occurring at one roundtrip of an electromagnetic wave in the nanorod-microcavity combination. Scanning electron microscopy pictures of the (c) bare nanorods and a focused ion beam-cut showing the (d) nanorods at Bragg distance in front of a gold mirror.

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Reflectance to the mirror merit, when the nanorods are placed at around Bragg distance is due to the finite penetration depth into the metal. Zero reflectance in simulations leads to an infinite FOM.

\[
\Delta \phi_{\text{exc}}(n) = \arctan \frac{2\beta \omega}{\omega_{\text{pl}}(n) - \omega^2},
\]

where \(\beta\) is a damping constant, \(\omega_{\text{pl}}\) is the plasmon resonance frequency, and \(\omega\) is the frequency of the incident wave. The localized plasmon excitation is modeled as a driven harmonic oscillator with the incident electromagnetic wave acting as the driving force on the conduction electrons in the metal nanorod. In this way, the phase shifts become dependent on the refractive index \(n\) of the material surrounding the nanostructure. A change in the refractive index \(\Delta n\) causes a shift of the localized plasmon resonance frequency \(\omega_{\text{pl}}\) of the nanorod. Therefore the phase shift upon plasmon excitation \(\Delta \phi_{\text{exc}}\) is changed. As a result, the total phase shift is changed and the resonance condition [Eq. (1)] for the cavity is no longer fulfilled. This causes the reflected light intensity to be substantially different from zero. Due to the small linewidth, a slight spectral shift causes a large intensity variation. This results in large values of the sensitivity \(S^*\) and the figure of merit, when the nanorods are placed at around Bragg distance to the mirror (Fig. 2).

The various definitions of the sensing capabilities of a given structure are hereby specified as follows:

\[
S = \frac{\Delta \lambda}{\Delta n}, \quad S^* = \frac{\Delta I}{\Delta n},
\]

\[
\text{FOM} = \frac{S}{\text{FWHM}}, \quad \text{FOM}^* = \frac{S^*}{I}.
\]

The sensitivity \(S\) is defined as the spectral shift \(\Delta \lambda\) caused by a certain refractive index change in the environment \(\Delta n\). Since the absolute wavelength and the linewidth of the resonance are also crucial factors for a sensor, a figure of merit (FOM) has been defined as the sensitivity \(S\) divided by the full width at half maximum (FWHM) of a Lorentz-shaped resonance. Since the detection of the spectral shift of a resonance requires a spectrometer, a more practical way of detection that will be used in biosensors is the measurement of the reflected or transmitted light intensity for one particular wavelength, using, for example, a laser diode. To take this into account, a new sensitivity usually referred to as \(S^*\) can be defined as the intensity variation \(\Delta I\) for a given refractive index change \(\Delta n\). Furthermore the absolute intensity is a substantial factor, because small intensity variations are much easier to detect when the overall intensity is already low. Therefore a new figure of merit \(\text{FOM}^*\) is defined as the sensitivity \(S^*\) divided by the absolute intensity \(I\).

We experimentally demonstrate our method of enhancing the sensitivity \(S^*\) and the figures of merit FOM and FOM* of a plasmonic sensor with water and a glucose solution on an array of nanorods. The sample was fabricated using thermal evaporation for the gold layers, spin-coating for the dielectric spacer, and electron-beam lithography for the nanostructuring. The thickness of the lower gold layer is 40 nm. The material of the dielectric spacer is a polysiloxane-based spin-on-glass (IC1-200 Intermediate Coating from Furturex, Franklin, NJ) with a refractive index of \(n_1=1.3198\) and \(n_2=1.3594\) surrounding the nanorods were used. For an accurate comparison, we used for both structures the configuration with the best FOM*, which is the detection of transmittance for the nanorods alone and reflectance for the nanorods combined with the cavity.

FIG. 2. (Color online) The (a) simulated sensitivity \(S^*\) and (b) figure of merit FOM* for different distances \(d\) of the nanorods in front of the mirror. Near Bragg distance, the enhancement is maximum. The small deviation from exact Bragg distance is due to the finite penetration depth into the metal. Zero reflectance in simulations leads to an infinite FOM*.

FIG. 3. (Color online) Comparison of the simulated (left column) and experimental (right column) spectra, sensitivities, and figures of merit for nanorods alone (curves with broad peaks) and nanorods combined with a cavity (curves with narrow peaks). Materials with two different refractive indices \((n_1=1.3198\) and \(n_2=1.3594\)) surrounding the nanorods were used. For an accurate comparison, we used for both structures the configuration with the best FOM*, which is the detection of transmittance for the nanorods alone and reflectance for the nanorods combined with the cavity.
sensitivity measurement. The small linewidth has also a large effect on the plasmonic nanostructure with a photonic cavity. In this way, the linewidth of the peak decreases drastically from 253116-2 to 600 to 90 nm in experiment to the nanorods. This is likely due to the fact that the mode localization between the nanorods, the sensing volume is increased due to the cavity. Nevertheless, since the cavity dramatically decreases the resonance volume increases due to the cavity. Nevertheless, since the linewidth of the peak decreases drastically (from 900 to 50 nm in simulation and from 600 to 90 nm in experiment), the figure of merit $FOM = S / \Delta \phi$ increases by a factor of 7.1 in simulations and a factor of 3.1 in the experimental measurement. The small linewidth has also a large effect on the sensitivity $S''$ since a small shift causes a high variation in the reflected intensity. The observed increase in the sensitivity $S''$ is 5.5 in simulation and 3.7 in experiment. At the minimum the fraction of the reflected light intensity is only 9%, resulting in an enhancement factor of 3.5 for the measured figure of merit $FOM'$. The deviations between simulated and experimental values may be due to fabrication imperfections.

The field distributions in Fig. 4 point out the concentration of the electric fields at the nanorod ends and inside the cavity at the resonance wavelength. Due to the strong field localization between the nanorods, the sensing volume is very small. A functionalization of the nanorod ends can make the localized sensor selective for only a certain kind of molecules. Additionally the field localization inside the cavity might be utilized for sensing when using porous media or placing the nanorods on pillars. Further improvements can be achieved by a combination of our structure with micro- and nanofluidic techniques.7,27

We presented a simple and powerful method to enhance the sensitivity $S''$ and the figures of merit of localized plasmonic resonances. The key lies in the combination of the plasmonic nanostructure with a photonic cavity. In this way, we make use of the strong dependence of the plasmon excitation phase shift on the plasmon resonance frequency and hence on the refractive index of the surrounding medium. In addition, the cavity dramatically decreases the resonance linewidth. Our concept can be applied to many LSPR sensor structures26,29 (e.g., colloidal systems such as nanostars) and will considerably increase their sensing potentials. Potential applications of LSPR sensing in the fields of biotechnology, medical diagnostics, or pharmacology including biomolecule detection, as well as real-time monitoring of chemical reactions or molecular kinetics, might benefit from this concept.

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FIG. 4. (Color online) Simulated time averaged electric field amplitude of a unit cell at resonance indicating the localized nature. (a) Top view and (b) side view of nanorods with a cavity.

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<th>a) Top view</th>
<th>b) Side view</th>
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2S. Link, S. Link, and N. J. Halas, Nat. Photonics 1, 641 (2007).
11N. J. Halas, Nano Lett. 10, 3816 (2010).
16J. B. Lassiter, H. Sobhani, J. A. Fan, J. Kundu, F. Capasso, P. Nordlander, and N. J. Halas, Nano Lett. 10, 3184 (2010).