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Gas Sensing with High-Resolution Localized Surface Plasmon Resonance Spectroscopy

Julia M. Bingham, Jeffrey N. Anker,[†] Lauren E. Kreno, and Richard P. Van Duyne*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

Received August 17, 2010; E-mail: vanduyne@northwestern.edu

Abstract: We report the first inert gas sensing and characterization studies based on high-resolution localized surface plasmon resonance (HR-LSPR) spectroscopy. HR-LSPR was used to detect the extremely small changes ($<3 \times 10^{-4}$) in bulk refractive index when the gas was switched between He(g) and Ar(g) or He(g) and N_2(g). We also demonstrate submonolayer sensitivity to adsorbed water from exposure of the sensor to air (40% humidity) versus dry N_2(g). These measurements significantly expand the applications space and characterization tools for plasmonic nanosensors.

The development of high-resolution localized surface plasmon resonance (HR-LSPR) spectroscopy has demonstrated the possibility of measuring extremely small wavelength shifts in noble-metal nanoparticle extinction spectra.[1,2] The wavelength shift ($\Delta\lambda_{\max}$) can be approximated as:

$$\Delta\lambda_{\max} = m(n_2 - n_1)(1 - e^{-2d/l_d}) \qquad (1)$$

where m is the refractive index (RI) sensitivity [in nm/RI unit (RIU)], n_2 and n_1 are the RIs of different surrounding media, d is the effective thickness (in nm) of medium 2 (n_2), and l_d is the electromagnetic field decay length (in nm).[3] The demonstrated ability to measure wavelength shifts on the order of 10^{-3} nm led us to ask what would be the smallest change in RI that could be measured by HR-LSPR. The use of inert gases has proven to be an excellent approach to answer this question. Sensitive and selective detection of gas-phase analytes is a significant challenge across many disciplines, from chemical warfare agents[4,5] to biomarker[6] detection. Therefore, it is advantageous to expand traditional solution-phase detection schemes to gaseous media. Plasmonic sensors have begun to expand into gas-phase applications because of their high sensitivity to the surrounding environment. In order for plasmonic gas sensors to be functional for any of the applications mentioned above, the sensitivity of the sensor must be carefully characterized. Herein, the high sensitivity of a plasmonic sensor is demonstrated through the detection of inert gases solely using changes in bulk RI.

The field of plasmonics is based on the LSPR spectroscopy of noble-metal nanoparticles. A significant consequence of the LSPR is the wavelength-dependent extinction (absorption and scattering) that depends on the nanoparticle size, shape, and surrounding RI.[7] LSPR nanosensors utilize changes in the local nanoparticle environment, which are manifested as a red shift in the extinction spectrum.

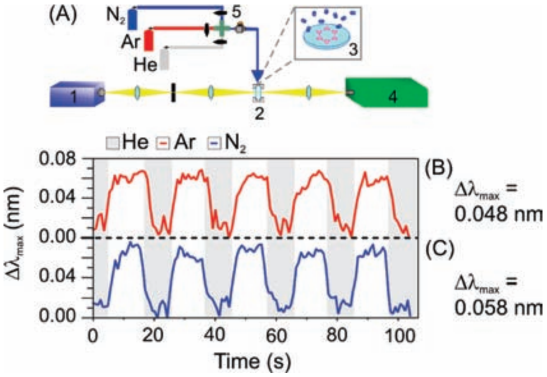

Figure 1. (A) HR-LSPR gas detection apparatus: (1) lamp, (2) flow cell, (3) nanoparticle substrate, (4) HR-LSPR spectrometer, (5) gas-dosing system. (B, C) Plots of LSPR extinction maximum of Ag nanoparticles vs time as the gas was switched between (B) He(g) (shaded areas) and Ar(g) and (C) He(g) and N_2(g).

Propagating SPR spectroscopy has also been used for gas sensing because of its high sensitivity to bulk RI changes[8,9] and has demonstrated imaging capabilities sufficient to distinguish He from Ar in a N_2 atmosphere.[10] Other RI-based detection methods include photonic microring resonators[11] and optical microcavities.[12] Luchansky et al.[11] reported a refractive index sensitivity of $\sim 2 \times 10^{-6}$ RIU with a sensing decay length of 63 nm for a silicon photonic microring resonator. LSPR sensors have a smaller sensing volume than propagating SPR sensors[13] and photonic sensors.[11,12] Typically, this results in higher sensitivity per unit volume for the local environment but lower sensitivity to bulk RI changes. Therefore, previous studies of LSPR nanosensor response have utilized changes between two liquid environments with relatively large RI differences. LSPR gas sensing has been demonstrated for chemical changes occurring at the nanoparticle surface but not for small changes of bulk RI. For example, Hu et al.[14] demonstrated gas sensing with Ag nanoparticles by measuring the disappearance and reappearance of the LSPR when the Ag was exposed to O_2(g) and H_2(g), respectively. Lu and co-workers[15,16] demonstrated vapor sensing by LSPR spectroscopy through detection of volatile organic compounds and showed enhanced vapor selectivity using self-assembled monolayers.[15] Here we report inert gas detection utilizing HR-LSPR spectroscopy based on bulk RI changes alone. Furthermore, we demonstrate the vapor-sensing capability of our sensor utilizing humid air and dry N_2 gas.

To demonstrate the gas-sensing capabilities of the HR-LSPR nanosensor, the inert gases He, N_2, and Ar were used to modulate the environment surrounding Ag and Au nanoparticles fabricated by nanosphere lithography.[17] The RIs of He, Ar, and N_2 are 1.000036, 1.000281, and 1.000298 RIU, respectively. The gas environment was switched between He and either Ar or N_2 every 10 s (Figure 1) or 5 s (Figure S1 in the Supporting Information). The HR-LSPR apparatus was interfaced with a gas-dosing system to manually modulate among the three gases while measuring the LSPR (Figure 1A). The gas temperature was the same as the room temperature. The cylinders were held at room temperature, and there was minimal adiabatic cooling at the low flow rates employed; also, there was sufficient time to equilibrate in the two-stage pressure regulator and the flow tubes.

[†] Current address: Department of Chemistry and Center for Optical Materials, Research and Technology (COMSET), Clemson University, Clemson, SC 29634.

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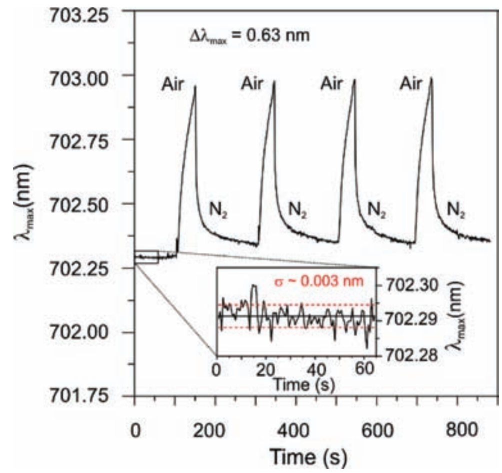

Figure 2. Plot of LSPR extinction maximum vs time for switching between 40% humid air and dry N_2 gas. A reproducible $\Delta\lambda_{max}$ value of 0.63 nm was observed. The inset depicts the low level of noise ($\sigma \approx 0.003$ nm) observed for the HR-LSPR experiment.

Extinction spectra were acquired every 600 ms, and the λ_{max} values of the spectra were plotted as a function of time. The plot of LSPR λ_{max} versus time for bare Ag nanoparticles using 10 s switching times is shown for He/Ar (Figure 1B) and He/N_2 (Figure 1C), where the shaded regions represent He gas flow. The $\Delta\lambda_{max}$-versus-time plots exhibit mass-transport-limited rise and fall times, indicating the observation of bulk RI changes rather than adsorption on the nanoparticle surface. Average $\Delta\lambda_{max}$ values of 0.048 and 0.058 nm for He/Ar and He/N_2 switching, respectively, were observed, which are consistent with the predicted shifts obtained from eq 1 using $m = 200$ nm/RIU.[18] Therefore, changes in the bulk environment corresponding to RI differences of only 2.45×10^{-4} and 2.62×10^{-4} RIU, respectively, were observed. We expect that the signal-to-noise ratio can be improved by using automated mass flow controllers, lock-in detection, and improvements in lamp stability. Experiments performed using octanethiol-functionalized Ag nanoparticles (data not shown) demonstrated an RI sensitivity ~20% less than that for bare nanoparticles, consistent with previous work.[19] This result was expected, as the octanethiol layer occupies ~1.5 nm of the electromagnetic field decay length.[20] These results confirm that LSPR RI-based gas detection is possible when an adsorbate layer is present.

To further demonstrate the sensitivity of HR-LSPR spectroscopy, the response of Au nanoparticles to water vapor was examined. Au nanoparticles were selected instead of Ag to avoid any potential interference from silver oxidation. The bulk environment was modulated between dry N_2 and 40% humid air by turning on/off the N_2 gas flow. When the N_2 flow was off, the N_2 in the cell gradually escaped and exchanged with the ambient room air for 60 s, followed by 140 s N_2 purges. The λ_{max} response is plotted as a function of time in Figure 2. The RI of water vapor is 1.000261 RIU, which is slightly less than that of N_2. Therefore, switching from N_2 to water vapor would be expected to cause a small blue shift if only the bulk RI change is considered. Instead, a large red shift was observed, and the shape of the response indicates that liquid water from the humid air adsorbs on the nanoparticle surface and then desorbs when N_2 is added. The response was highly reproducible for multiple samples with an average $\Delta\lambda_{max}$ of 0.63 nm for the humid air exposure time (60 s). These shifts correspond to an effective adsorbate layer thickness of 0.024 nm, assuming a decay length (l_d) of 5 nm. The striking conclusion drawn from this estimate is that HR-LSPR spectroscopy has submonolayer (~10% coverage) sensitivity to liquid water!

Detecting gases on the basis of small RI changes not only demonstrates subtle bulk RI changes but also provides a reliable method for characterizing the RI sensitivity of plasmonic materials and calibrating plasmonic sensors using gas-phase modulation. Liquids have been used for such characterization in the past, but solvent annealing, the ability to wash away weakly bound nanoparticles under strong flow, and potential interactions between the liquid and adsorbed molecules limit the applicability of liquid-based RI sensitivity characterization. Gas-phase detection provides a benign characterization tool. Although the gas sensor has displayed excellent sensitivity, LSPR sensors are not inherently selective. The integration of reversible partition layers will solve this problem and is being addressed in continuing studies. In addition, volatile organic molecules that adsorb onto plasmonic surfaces can be detected and identified using surface-enhanced Raman spectroscopy (SERS).[4]

In conclusion, the first LSPR RI-based sensing experiment utilizing inert gases has now been demonstrated. Changes in RI as low as 2.45×10^{-4} RIU could be observed reliably and reproducibly because of the low noise level in the HR-LSPR spectrometer. Additionally, the HR-LSPR gas sensor exhibited changes in the nanoparticle extinction spectrum λ_{max} consistent with typical RI sensitivities of Ag nanoparticles. The gas sensor demonstrated rapid switching capabilities of 5 or 10 s, which is a significant characteristic of gas detection. We have also shown submonolayer sensitivity to water adsorbed on nanoparticles from exposure to 40% humid air. Use of the HR-LSPR nanosensor has proven to be a sensitive method for detection of gaseous analytes.

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Supporting Information Available: Gas-switching data using 5 s intervals. This material is available free of charge via the Internet at http://pubs.acs.org.

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