

Simultaneous Chemical and Refractive Index Sensing in the 1–2.5 μ m Near-Infrared Wavelength Range on Nanoporous Gold Disks

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Supporting Information

ABSTRACT: Near-infrared (NIR) absorption spectroscopy provides molecular and chemical information based on overtones and combination bands of the fundamental vibrational modes in the infrared wavelengths. However, the sensitivity of NIR absorption measurement is limited by the generally weak absorption and the relatively poor detector performance compared to other wavelength ranges. To overcome these barriers, we have developed a novel technique to simultaneously obtain chemical and refractive index sensing in 1–2.5 μ m NIR wavelength range on nanoporous gold (NPG) disks, which feature high-density plasmonic hot-spots of localized electric field enhancement. For the first time, surface-enhanced near-infrared absorption (SENIRA) spectroscopy has been demonstrated for high sensitivity chemical detection. With a self-assembled monolayer (SAM) of octadecanethiol (ODT), an enhancement factor (EF) of up to ~10⁴ has been demonstrated for the first C–H combination band at 2400 nm using NPG disk with 600 nm diameter.



Together with localized surface plasmon resonance (LSPR) extinction spectroscopy, simultaneous sensing of sample refractive index has been achieved for the first time. The performance of this technique has been evaluated using various hydrocarbon compounds and crude oil samples.

KEYWORDS: Nanoporous gold disks/nanoparticles, surface-enhanced near-infrared absorption spectroscopy, hydrocarbon sensing and identification, vibrational molecular overtones and combination bands, plasmonics, near-infrared molecular fingerprinting

ear-infrared (NIR) absorption spectroscopy in the 1–2.5 N μ m wavelength range can provide chemical information based on the overtones and combination bands of fundamental vibrational modes in the infrared (IR) wavelength range. NIR absorption features are significantly broader and weaker due to the fact that the underlying processes are quantum mechanically forbidden. However, substantially lower water absorption allows NIR spectroscopy to be performed on samples with high water content, e.g., biological specimen and other in situ measurements, which otherwise restricts the use of IR light.^{1,2} Due to the shorter wavelength, NIR imaging has better spatial resolution than IR imaging. Since common optical materials such as glass and silica are optically transparent within the NIR range, instrument development is relatively easier than in the IR range. Furthermore, the choice of light source such as lamps and lasers is broader for the NIR range. However, small NIR absorption cross-section results in less sensitivity compared to measuring the IR fundamentals. In addition, NIR measurements are more challenging compared to those in other spectral regions because of the lack of high-sensitivity detectors. To overcome these barriers, we propose the use of plasmonic nanostructures.

Plasmonic sensing techniques have gained significant interest due to high sensitivity. By material design and geometrical engineering, a variety of plasmonic nanostructures and nanoparticles have been investigated and demonstrated as potential candidates for practical applications. Surface plasmon resonance (SPR) technique utilizes propagating plasmons to detect bulk refractive index changes or local index changes due to surface adsorbates. Localized surface plasmon resonance (LSPR) technique, in contrast, derives its sensitivity from nonpropagating plasmons and typically involves extinction spectroscopy. To date, most LSPR techniques rely on nanoparticles with LSPR peak well within 1 μ m for two major reasons: (1) the most commonly used materials, gold and silver nanoparticles, feature LSPR in the visible wavelength

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Figure 1. (A–D) Schematic representation of the nanosphere-mask fabrication of the NPG disk substrate. (E–F) Scanning electron microscopy (SEM) images of random arrays of NPG disks and (G) normal-incidence extinction spectra of NPG disks arrays on glass in air with diameters: 350 nm (red) and 600 nm (blue) nm, respectively. Scale bar is 500 nm.

range, and (2) the convenience of using silicon detectors with high sensitivity and relatively low cost. Since both SPR and LSPR are sensitive to refractive index changes, molecular specificity is achieved by the use of "functionalized" surfaces. For example, by previously immobilized antibodies on the surface, SPR/LSPR can detect the binding of specific antigens. Surface functionalization, however, restricts sensing to specific targets and thus has limitation in sensing a broad range of species simultaneously, which is known as multiplexing.

In addition to index sensing, the most well-known plasmonenhanced spectroscopic techniques include surface-enhanced Raman spectroscopy (SERS),^{3,4} metal- or surface-enhanced fluorescence $(M/SEF)^{5-7}$ and surface-enhanced infrared absorption spectroscopy (SEIRA).^{8,9} Unlike SPR/LSPR, these spectroscopic techniques can provide various degrees of molecular information without relying on surface functionalization. For example, Raman scattering and infrared absorption are often called "fingerprinting" techniques because they provide key information to the underlying molecular structures. Wang et al. demonstrated simultaneous SERS and SEIRA for sensitive molecular detection using periodic arrays of plasmonic gold nanoshells.⁹ In a study by Brown et al., a further increase in the SEIRA enhancement factor in the mid-infrared range can be achieved by combining fan-shaped plasmonic antenna arrays with reflective gold planes.⁸ Although SERS and SEIRA are both vibrational techniques, they are different in the following aspects. First, in contrast to SERS, there are relatively fewer choices of plasmonic substrates that provide significant enhancements in the infrared wavelengths. In addition, the demonstrated per molecule enhancement factor for SEIRA has been less than that for SERS, partly due to the reduced dependence on the electric field. SERS is known to depend on E-field to the fourth power, whereas SEIRA depends on the second.9,10 SEIRA studies were mostly demonstrated for the absorption enhancement of the fundamental vibrational modes in the mid-IR region (\sim 3–8 μ m).^{9,11–13} Therefore, a significant gap exists for the NIR wavelength range, where highly effective plasmonic nanomaterials are lacking.

Surface-enhance near-infrared absorption (SENIRA) spectroscopy can provide a novel sensing mechanism for molecular compounds with overtones and combination modes of carbon-hydrogen (C-H) bonds and hydroxyl (O-H) groups.¹⁴ The first overtones of the C-H vibration in the 1600-1800 nm window differ largely for liquid hydrocarbons.^{14,15} SENIRA measurements are particularly useful in distinguishing crude oils rich in asphaltenes. Hence, this spectral region is highly informational for chemical composition analysis of crude oil samples. A prominent example is downhole optical fluid analyzer utilized in oil and gas exploration for in situ compositional analysis of reservoir fluids.^{2,16} As mentioned earlier, the inherent problem of NIR measurements is the weaker absorption of these modes compared to the corresponding fundamental modes in the mid-IR region, as well as the inferior detector sensitivity. Hence, SENIRA has the potential in mitigating such limitations. The ability to improve signal strength in the NIR range from relevant hydrocarbon molecules through the use of new nanomaterials with suitable optical properties will significantly improve detection limits for NIR sensors.

Recently, we have demonstrated that disk-shaped nanoporous gold (NPG) nanoparticles are a unique class of plasmonic nanomaterials with tunable LSPR, 3-dimensional near-field hot-spot distribution, large surface area, excellent SERS and SEF enhancement factors, and high sensitivity to local index changes.^{17–21} By taking advantage of the abundant hot-spots and tunable plasmonic peak in NPG disks,²² we have developed several applications such as single-molecule DNA hybridization monitoring,²³ label-free molecular sensing and imaging by stamping NPG disk substrate onto a surface with target analytes,²⁴ integrated microfluidic SERS sensor for labelfree biomolecular sensing,²⁵ photothermal conversion for lightgated molecular delivery, and inactivation of heat-resistant pathogens.^{26,27} NPG disks are shown to absorb strongly in the NIR region with size-tunable resonance.¹⁸

LSPR Shift Due to Refractive Index Changes. The NPG disks (diameters: 350 and 600 nm) were fabricated according

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Figure 2. (A) Schematic diagram of the sample configuration. (B) Normal-incidence extinction spectra of water on NPG disks of two diameters: 350 and 600 nm with the O-H combination peak at 1920 nm. (C) Normal-incidence extinction spectra of disks (350 nm diameter) in various solvents of known refractive indices varying from 1.33 to 1.49: water (n = 1.33), 5% w/w NaCl in water (n = 1.34), ethanol (n = 1.36), hexane (n = 1.37), iso-octane (n = 1.39), hexadecane (n = 1.43), and toluene (n = 1.49); inset: The LSPR shift with respect to air for the corresponding refractive indices for each solvent are shown.

to schematic representation shown in Figure 1A-D. The fabrication of NPG disks involve(s) the advantage of using topdown lithographic nanosphere patterning and bottom-up atomic dealloying resulting in the unique plasmonic properties of NPG disks. In Figure 1A, an Au-Ag alloy film (~80 nm thick) was first sputtered onto a glass substrate. A single layer of polystyrene (PS) beads was then deposited on the alloy film. To shrink the PS beads, the substrate was subjected to oxygen plasma treatment. The process continues with sputter-etching in Ar plasma resulting in the transfer of the bead pattern onto the alloy film (Figure 1B). After the nanosphere patterning, the residue of PS beads were removed by sonicated in chloroform (Figure 1C). The alloy disks were then dealloyed with concentrated nitric acid resulting in the nanoporous disks in a random array format (Figure 1D). During dealloying, a 10% volume reduction of the disks was observed, consistent with previous reports.¹⁸ The scanning electron microscopy (SEM) images show the surface morphology and monolayer distribution of the patterned NPG disks on a glass coverslip (Figure 1E-F). The average pore size is $\sim 10-15$ nm. The NPG disks are well-separated with a monolayer surface coverage of $\sim 50\%$.

The extinction spectra in Figure 1G provide information for the wavelength range where the in-plane plasmonic resonance is identified in air medium.¹⁸ The in-plane LSPR resonance of 350 nm NPG disks locates at 890 nm. As the diameter increases, it red-shifts to 1415 nm for the 600 nm diameter disks. Here we evaluate the index sensitivity of the NPG disk substrate. The LSPR peak shifts of NPG disks due to the change in refractive index in the surrounding media have been demonstrated previously.¹⁸ Herein, the index sensitivity of the LSPR shift of 350 nm NPG disk is evaluated by the use of various liquid samples of known refractive indices. The organic thin films, estimated to be $\sim 10 \ \mu m$ in thickness using a Fabry– Perot free spectral range calculation, were sandwiched between a blank glass coverslip and a NPG disk coated glass coverslip (Figure 2A).²⁸ The NIR extinction spectra were acquired at normal incidence. In Figure 2B, the LSPR of NPG disks of two diameters both red-shifted when the samples were immersed in water: from 890 to 1070 nm for 350 nm NPG disks; from 1415 to 1700 nm for 600 nm disks. It is interesting to see that the O-H combination peak at 1920 nm has been more significantly enhanced by the 600 nm disks compared to the 350 nm disks because the LSPR of 600 nm disks aligned better with the O-H peak. In Figure 2C, a progressive red-shift of the in-plane LSPR is observed on 350 nm disks with respect to further increase of the sample index. The index sensitivity, $d\lambda/$ dn, was calculated to be 525.7 nm per refractive index unit (RIU) via the plot of peak shift vs n in different media in the inset of Figure 2C.

The NIR spectral region of LSPR coincides with a number of molecular vibrational modes for different functional groups, e.g., methyl (C–H), hydroxyl (O–H), etc. Hence, this allows us to consider the enhancement effects due to the spectral overlap of LSPR and the molecular vibrational modes. As mentioned previously, significant enhancement of the O–H combination mode of water was observed in Figure 2B. The O–H combination peak at 1920 nm can be clearly identified as a relatively narrow vibrational band compared to the broader LSPR band of 350 nm (at 1070 nm) and 600 nm (at 1540 nm) NPG disks. The O–H combination peak intensity is considerably larger in intensity (20 times stronger in intensity, see Table S2 in Supporting Information) on 600 nm NPG disk (Figure 2B) than on glass substrate, while the intensity is less



Figure 3. (A) SENIRA of octadecanethiol (ODT) SAM on NPG disks with two different diameters: 350 (red) and 600 (blue) nm compared against the absorption of bulk ODT solution (black). The peak represents the first C–H overtone and combination band at ~1725 and ~2400 nm, respectively. (B and C) Extinction spectra showing redshift of LSPR band of 350 and 600 nm NPG disks upon addition of ODT SAM.



Figure 4. SENIRA spectra of (A) hexadecane, (B) dodecane, and (C) siloxane on 350 (blue) and 600 (red) nm NPG disk-glass substrate. The first CH and second CH overtone at \sim 1700 and \sim 1200 nm are the major vibrational modes strongly affected by the LSPR enhancement of the NPG disks.

enhanced on the 350 nm NPG disks. The higher absorption intensity of the O–H mode can be correlated to the closer spectral overlap of the corresponding LSPR band of the 600 nm disks in the water medium. Recent studies showed that near-field effects enhance plasmonic far-field response more effectively when paired well within the LSPR range.^{9,29}

SENIRA Enhancement Factor and Index Sensing of Octadecanethiol Self-Assembled Monolayer. The surface enhancement factor (EF) of SERS and SEIRA substrates are most rigorously determined using self-assembled monolayer (SAM) of thiols because of their reliable packing mechanism and better quantification accuracy.^{8,11,29} Hence, we first examine the SENIRA on NPG disk arrays using octadecanethiol (ODT) SAM. For these experiments, sensitivity is correlated to the relative intensity obtained for an equivalent number of molecules. Figure 3 shows the NIR spectra for 350 and 600 nm NPG disk arrays functionalized with the ODT SAM and a control experiment acquired from ODT in methanol solution. Here the ODT signals originate from the C-H combination (~2400 nm) and the first C-H overtone (\sim 1700 nm). The amount of molecules are estimated for a monolayer film on each disk multiplied by the disk monolayer density within the irradiated spot. Therefore, the large surface area of NPG has already been considered in our calculation. For example, each NPG disk has an estimated surface area about 6 times of that of a nonporous disk. Thus, the enhancement factor here has no contribution from the increased surface area.¹⁷ Furthermore, the surface area variation between the 350 and 600 nm diameter NPG disks has been accounted for by considering the differences in their size and monolayer

coverage. The EF values are computed for the NIR absorption bands of the ODT molecules using the following equation:

$$EF = \frac{I_{\rm NPGD}}{I_{\rm o}} \times \frac{N_{\rm o}}{N_{\rm NPGD}}$$
(1)

where the N_0 is the number of ODT molecules in methanol solution contributing to the normal absorption, $N_{\rm NPGD}$ is the number of ODT molecules from the monolayer contributing to the enhanced absorption on NPG disks, and $I_{\rm NPGD}$ and $I_{\rm o}$ are the intensities of the absorption band from NGP disks and ODT solution, respectively. EFs of $>10^4$ are estimated (see Table S1 of Supporting Information) for the C-H combination peaks at ~2400 nm on both the 600 and 350 nm NPG disks. On the other hand, an EF value of nearly 10⁴ is determined for the first C-H overtone at ~1700 nm for 600 nm NPG disks. To the author's knowledge, this is the first time SENIRA enhancement factors have ever been reported. The estimated EF values for the ODT SAM are relatively high considering the fact that these NIR vibrational modes (overtones and combination bands) have lower absorption coefficients compared to mid-IR modes.^{9,11} NIR detection of hydrocarbons are mostly performed in bulk quantities due to its weaker vibrational absorption coefficients in the NIR wavelengths (i.e., C-H overtone and combination bands). The LSPR tunability of NPG disks allows optimization for enhancing C-H and O-H vibrational bands in sensing and identification of hydrocarbons.

Figure 3B and C shows the index sensing capability of ODT SAM on the NPG disks indicated by LSPR redshifts. Similar to the index change-induced redshift in Figure 2C, ODT SAM



Figure 5. (A) LSPR shift of NPG disks of diameters 350 and 600 nm in different PMMA film thicknesses. (B) SENIRA spectra of the PMMA film (100 nm thickness) at first overtone combination band at 1398 nm. (C) SENIRA intensity at 1398 nm for the PMMA film at different thicknesses (50–150 nm).

results in redshifts of \sim 55 and \sim 140 nm for 350 and 600 nm disks, respectively. The combination of index sensitivity of the NPG disk array and the SENIRA of ODT SAM demonstrates the dual-modality approach in a single measurement.

SENIRA of Nonthiol Model Compounds. In order to evaluate the general performance of nonthiol hydrocarbon sensing by SENIRA, extinction measurements from liquid hydrocarbon thin films on NPG disk arrays are compared. The same sampling apparatus and configuration shown in Figure 2A were used: (1) experimental sample (NPG disk on glass), and (2) reference sample (glass without NPG disk). The extinction spectra of the hydrocarbon films sandwiched between two coverslips were measured. The measured spectra consist of three components: a broad and slowly varying background owning to LSPR, a high-frequency fluctuation owning to a Fabry-Perot like cavity formed by the top and bottom glass/ solution interfaces, and C-H overtone and combination bands. The LSPR component was approximated by low-order polynomial and subtracted. The high-frequency fluctuations were removed by Fourier filtering. The residuals were taken as the C-H overtone and combination bands. The fringes were also fit by a standard Fabry-Perot model to estimate the cavity length to be ~10 μ m. After these steps, the SENIRA spectra of hexadecane, dodecane, and siloxane on 350 and 600 nm NPG disk were obtained by subtracting the corresponding spectra on glass. This subtraction step removes the contribution from the bulk sample and accentuates the SENIRA contribution. In other words, I_{SENIRA} is defined as $I_{\text{enhanced}} - I_{\text{bulk}}$ where I_{enhanced} and Ibulk are the spectra obtained from the NPG disk sample and that without NPG disks, respectively.

The processed SENIRA spectra are shown in Figure 4A-C, where the second and first overtone of the C-H vibrational mode of the hydrocarbons are consistently present at ~1200 and 1725 nm, respectively. The first overtone of C-H combination peaks at ~1400 nm are significantly weaker in peak intensity compared to the first and second C-H overtones as expected from vibrational selection rules.³⁰ Higher enhancement is observed in the second overtone (~1200 nm) compared to the first overtone (~1725 nm) on 350 nm NPG disk, which can be explained by the better alignment of the second overtone with the LSPR band of the 350 nm NPG disk array. On the other hand, the same effect is observed for the 600 nm NPG disk where the first overtone is enhanced more than the second overtone due to better spectral overlap of the plasmon peak for the first C-H overtone. For the 350 nm NPG disk, the in-plane LSPR maximum at ~1100 nm for hexadecane medium particularly enhances the second C-H overtone at ~1200 nm. In contrast, the absorption intensity of the first C-H overtone at 1725 nm is less enhanced in the

presence of 350 nm NPG disk because the first C–H overtone is further away from the in-plane resonance band of the 350 nm NPG disk.

In Table S2 (in Supporting Information), the bulk intensity (I_{bulk}) , enhanced intensity (I_{enhanced}) , and the processed SENIRA intensity (I_{SENIRA}) for various peaks are documented in Columns 4–7. It is noted that the effective sensing distance or "pathlength" of SENIRA is an order of magnitude smaller than that of the bulk, as further discussed in the next section.

Effective Distance of Plasmonic Enhancement of Nonthiol Hydrocarbon Thin Films. To further characterize the SENIRA and LSPR effects on nonthiol molecules, we have performed a series of experiments using thickness-controlled thin films. Herein, poly(methyl methacrylate) (PMMA) films with varying thicknesses (50-150 nm) were deposited on the NPG disk substrate by spin-coating. The protocol used is based on the study of coating PMMA film of uniform thickness on glass substrates.³¹ Thickness of the various PMMA thin films was confirmed using ellipsometric measurements. The LSPR peak of the NPG disk substrate with different PMMA film thickness are summarized in Figure 5A, where a significant redshifting trend is observed for both 350 and 600 nm diameter NPG disk substrates. The 600 nm NPG disks show a larger overall shift due to its higher sensitivity to index changes. The LSPR shift appears to plateau when the film thickness reaches ~110 nm, representing the experimentally verified LSPR sensing range in good agreement with the literature.^{5,6} Figure 5B displays the SENIRA spectra of the combination overtone peak at 1398 nm of the PMMA film. Higher intensity is observed from the 600 nm NPG disk, indicating higher enhancement due to the more overlap of the PMMA overtone peak to the LSPR band.

To accentuate the sole contribution due to plasmonic enhancement, previously defined I_{SENIRA} (= $I_{\text{enhanced}} - I_{\text{bulk}}$) is plotted versus the PMMA film thickness. An incremental increase in I_{SENIRA} is observed when the PMMA film thickness varied from 50 to 100 nm and plateaued near 110 nm. The changes in I_{SENIRA} can be linked to z-direction localization of plasmon enhancement of the NPG disks. The plasmon decay length of the NPG disks can be estimated to coincide with a threshold thickness (~110 nm) where enhancement ceases to exist. It is noted that this particular plasmon decay length is specific for PMMA at its specific NIR modes and results are expected to vary slightly for other hydrocarbon films. The determination of the plasmon decay length has been previously reported for application in LSPR-based sensing.32-34 For the results in Figure 4 from the previous section, the ratio of I_{SENIRA} over *I*_{bulk} is provided in Table S2 (in Supporting Information) where we emphasize again that the I_{SENIRA} is from a ~110 nm

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thin film and I_{bulk} is from a 10 μ m thick film. We further calculated the intensity per nanometer for I_{bulk} and I_{SENIRA} in Table S2. These results are also listed for the SENIRA of PMMA at different thickness in Table S3 in Supporting Information.

SENIRA Sensing of Petroleum Hydrocarbons. Next, we study SENIRA using pyrene, a polycyclic aromatic hydrocarbon (PAH) carcinogen, and crude oil samples. Following the same sample preparation, the SENIRA spectra obtained from pyrene and crude oil (Louisiana sweet grade) are shown in Figure 6A–



Figure 6. SENIRA spectrum of (A) pyrene and (B) crude oil (Louisiana sweet grade) on 350 (blue) and 600 (red) nm NPG disk substrates.

B. For example, the pyrene sample has two major peaks at 1590 and 1720 nm due to the presence of double-bonded carbon atoms in its chemical structure. Using 600 nm NPG disk, these two major peaks are enhanced considerably more compared to those on 350 nm NPG disk. The SENIRA spectrum of the crude oil closely resembles a hydrocarbon mixture with high alkane content (first and second C-H overtone) with trace polycyclic modes at 1600 nm. A higher intensity for the first C-H overtone for crude oil is also observed for the 600 nm NPG disks than on 350 nm NPG disks. The higher enhancement when the overtone band is better aligned with the NPG disk LSPR resulted to stronger SENIRA signal useful for sensitive detection. These results show that SENIRA on NPG disk substrates can be potentially employed for chemical sensing for PAH and other hydrocarbon components in petroleum products.

In conclusion, we have demonstrated the first-time observation of surface-enhanced near-infrared absorption of overtone and combination bands on NPG disk substrates. In addition, sensing of local refractive index has been achieved simultaneously using a single measurement. From bulk-quantity amounts of hydrocarbons (path length = $10 \ \mu m$) down to selfassembled molecular monolayers, we have demonstrated effective dual-modality sensing (index and SENIRA) at different molecular pathlengths. With self-assembled monolayers of ODT, a SENIRA enhancement factor of up to $\sim 10^4$ has been shown. By monitoring the incremental response of the LSPR shift and SENIRA intensity to the thickness of deposited PMMA film, the z-direction plasmon decay length has been experimentally obtained at ~110 nm for the NPG disk substrate. SENIRA sensing is strongly affected by the spectral overlap of the molecular overtones with the LSPR band defined largely by the disk diameter. Typically, the NIR peak intensity receives more enhancement when it is better aligned with the LSPR band. We have further tested this technique over a highly carcinogenic pollutant and crude oil samples demonstrating the potential industrial applications. A critical advantage of this new technique is its high sensitivity. These results have laid the

groundwork for better molecular detection and identification in the $1-2.5 \ \mu m$ NIR wavelength range.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.6b01959.

Fabrication method of NPG disks, infrared absorption measurements, and tables of calculated SENIRA parameters (PDF)

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Notes

The authors declare no competing financial interest.

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