

Refractometric Sensing Using Gradient Plasmonic Nanostructures: Mapping Spectral Information to Spatial Patterns

Wen-Di Li^{1*}, Siyi Min¹, Shijie Li¹, Zhouyang Zhu¹, Chuwei Liang¹, Jingxuan Cai¹

¹Department of Mechanical Engineering, The University of Hong Kong, Pokfulam, Hong Kong, China

*corresponding author, E-mail: liwd@hku.hk

Abstract

We report a spectrometer-free, pattern-based refractometric sensing scheme. This new detection scheme uses gradient plasmonic nanostructures to map spectral information to spatial locations and then use commercial imaging sensors, rather than spectrometers, to detect pattern change induced by local refractive index change due to adsorbed analyte molecules. Our preliminary results show the sensitivity performance of this new method can be comparable to conventional spectrometer-based methods, but with much more compact and cost-effective setup.

1. Introduction

Detection and identification of small amount of gas molecules, biomarkers, bacteria, and other chemicals is of great importance in our daily life for environmental monitoring, early disease detection, food safety inspection, just to name a few. Many detection schemes have been developed towards these applications. Thanks to the fast development of nanofabrication techniques in the past decade, plasmonic nanostructures with well-defined dimensions and geometries have received intensive attention for this purpose. Collective resonance of electrons in plasmonic nanostructures selectively scatters incident light at fingerprint wavelengths and such scattering behavior highly depends on the dimensions, geometries, and local refractive index. Therefore, if the target substance to be detected is locally adsorbed or attached to the plasmonic nanostructure, spectral change in the reflected or transmitted light will be induced and can be used as an indicator for detection and identification of the target substances.

Conventional substance detection scheme based on spectral change on plasmonic nanostructures relies on direct spectroscopy measurement of the reflected and transmitted light using spectrometers and collection optics. Although great effort has been devoted in developing low-cost and portable spectrometers for consumer applications, there is still no mature and affordable consumer-level spectrometers available in the market, keeping the plasmonic refractometric sensing based chemical detection tools out of reach for daily applications.

Our work aims to explore a novel scheme for detecting the refractive index induced spectral change in light scattered from plasmonic nanostructures using image acquisition and

recognition method instead of direct spectroscopy characterization. We will map spectral information to spatial patterns by using gradient plasmonic nanostructures deterministically fabricated over centimeter-scale area. The gradient plasmonic nanostructures have key dimensions, such as the diameter of pillars or holes, continuously varying with spatial position. Instead of using a spectrometer to obtain scattered spectra, we use a low-cost camera to take images of light transmitted through the sample. When the environmental refractive index is slightly changed, the image of the reflected light will exhibit changed patterns. We will develop corresponding image processing algorithm to extract useful information from the obtained image and detect substances adsorbed or attached on the sensing structures. Our approach provides a low-cost and high-sensitivity alternative method for refractometric sensing based substance detection and has great potential to be implemented in consumer applications.

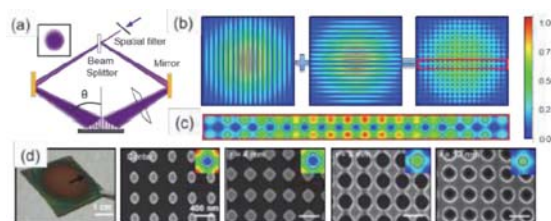


Fig. 1. Interference lithography fabrication process for spatially varying gradient nanostructures. (a) Schematic representation; (b) numerical simulation of double exposure for two-dimensional dots and holes with gradient sizes; (c) zoomed-in view of the numerical simulation of the red box region in (b); and (d) preliminary fabrication results showing the gradient feature sizes on 370-nm-period two-dimensional structures.

2. Fabrication of Gradient Plasmonic Structures

Gradient plasmonic nanostructures in our work are fabricated using interference lithography (IL). Conventional IL emphasizes pattern uniformity; therefore, uniform exposure intensity over the patterning area is desired. To fabricate spatially varying structures, we intentionally utilize the non-uniform Gaussian-shaped intensity distribution of the two coherent beams to realize spatially varying patterns (Fig. 1).

As shown in Fig. 1d, we successfully fabricated spatially varying two-dimensional nanostructures with circular symmetry. Exposed patterns on the positive-tone photoresist show pillars at the center, where the Gaussian beam has the maximum intensity. The diameter of pillars increases with the distance from the center. Nearby pillars start to merge and the overall pattern evolves into a hole array with the diameter of holes reducing when the distance from the center is further increased. We also use the IL system to make nanoimprint templates with the gradient structures and then, use NIL and other nanofabrication processing, including reactive ion etching and e-beam evaporation, to fabricate different types of gradient plasmonic structures for various sensing demonstrations.

3. Experimental Results

We carry out a series of experimental demonstrations and compare the performance of our new sensing scheme with existing spectrometer-based refractometric sensing methods. A schematic of our sensing setup is illustrated in Fig. 2a. A camera is used to record the transmitted intensity pattern on the gradient plasmonic sensing chip. Before and after exposing the sensing chip to analyte substances, two transmitted images are taken and compared. An image processing algorithm is developed to retrieve the change in the patterns to detect the existence of analyte substances.

We have performed preliminary experiment on hydrogen gas sensing by using a silver gradient plasmonic structure

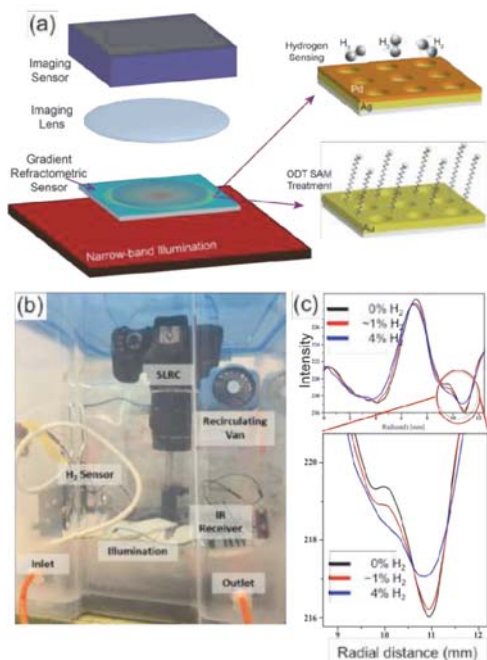


Fig. 2. (a) Schematic of the sensing setup for hydrogen sensing and a self-assembled monolayer, with future potential for biosensing applications; (b) hydrogen sensing setup; and (c) preliminary result showing that less than 1% hydrogen can be detected using the proposed pattern-based sensing.

with 20-nm-thick palladium deposited as the hydrogen-responsive layer [1-3]. The sensing platform is shown in Fig. 2b, which uses an LED source with a center wavelength of 635 nm and a bandwidth of 20 nm, and a Canon EOS 550D camera as the image sensor. A plastic enclosure is used as the gas sensing chamber with the inlet connected to a H₂/N₂ forming gas cylinder. A commercial hydrogen gas sensor is installed in the chamber to monitor the real-time hydrogen concentration. Our preliminary testing result (Fig. 2c) shows that hydrogen gas with 1% and 4% concentrations can induce a clearly resolvable intensity pattern change, which is comparable to many published plasmonic refractometric hydrogen sensing results [3-5]. We believe that there is considerable room for improvement of the sensing performance of our gradient plasmonic sensors and will explore its ultimate limitations in the subsequent investigation.

4. Conclusions

We report an innovative spectrometer-free, pattern-based refractometric sensing scheme. Our research covers novel fabrication methods, numerical modeling and image processing algorithm, and experimental prototype demonstration of gradient plasmonic structures for refractometric sensing. Our preliminary results show the sensitivity performance of this new method can be comparable or even superior to conventional spectrometer-based plasmonic refractometric sensing methods, but with much more compact and cost-effective setup. This work will potentially open a new avenue towards the development of consumer-level sensing solutions in biomedical and other areas.

Acknowledgements

Research Grants Council of Hong Kong (Grant No. 27205515 and 17246116) and the University of Hong Kong (Grant No. 201611160057 and 201511159175).

References

1. B. Sutapun, M. Tabib-Azar, and A. Kazemi, Pd-coated elastooptic fiber optic Bragg grating sensors for multiplexed hydrogen sensing, *Sensors and Actuators B-Chemical* **60**: 27-34, 1999.
2. Y. G. Sun and H.H. Wang, High-performance, flexible hydrogen sensors that use carbon nanotubes decorated with palladium nanoparticles, *Advanced Materials* **19**: 2818, 2007.
3. N. Liu et al., Nanoantenna-enhanced gas sensing in a single tailored nanofocus, *Nature Materials* **10**: 631-636, 2011.
4. A. Tittl et al., Palladium-Based Plasmonic Perfect Absorber in the Visible Wavelength Range and Its Application to Hydrogen Sensing, *Nano Letters* **11**: 4366-4369, 2011.
5. C. Wadell, S. Syrenova, and C. Langhammer, Plasmonic Hydrogen Sensing with Nanostructured Metal Hydrides, *ACS Nano* **8**: 11925-11940, 2014.