

COMMENTARY

Extraordinary optical transmission for surface-plasmon-resonance-based sensing

Reuven Gordon

Department of Electrical and Computer Engineering, University of Victoria, BC, Canada
rgordon@uvic.ca

In 1998, Ebbesen and co-workers demonstrated the surprising result that arrays of small holes in a metal show optical transmission resonances [1]. This result was surprising because Bethe's aperture theory predicts negligible transmission through a single small hole in a thin metal film. As a result the phenomenon was termed *extraordinary optical transmission* (EOT).

Unfortunately, the term EOT is a bit of a misnomer. Recently it has been shown that Bethe's theory, when applied to arrays of holes, predicts 100% transmission [2]. Therefore, when compared to Bethe's theory, EOT of imperfect conductors is actually a reduction in transmission!

There is also a common misconception that surface plasmons somehow enable EOT. Once again, EOT is predicted by Bethe's theory using an infinitesimally thin, perfect electric conductor [2]. As that theory does not allow for surface plasmons, surface plasmons are not required for EOT. This is an important point because we do not wish to limit the application of EOT to surface-plasmon bearing cases. EOT may be (and has been) exploited in other parts of the electromagnetic spectrum without surface plasmons, for various applications. EOT may even be demonstrated and exploited using superconductor films. (Surface plasmons are relevant to EOT for metals that support them, but they are not required for EOT.)

While it was recognized early on that EOT could be used to sense changes in bulk refractive index [3], we were the first to demonstrate monolayer sensitivity by using nanohole arrays for sensing based on surface plasmon resonance (SPR) [4]. There are considerable benefits to using nanohole arrays for SPR-based sensing, as compared with the conventional prism coupling geometry. The nanohole array approach to SPR-based sensing benefits from: (1) a collinear optical geometry for dense integration, (2) the potential for multiplexing from several nanohole arrays, (3) lower limits of detection, and (4) a reduction in the diffusion-limited adsorption time by using the nanoholes as conduits.

Up until recently, the nanohole-SPR technique has faced the challenges of reduced sensor-output sensitivity with respect to conventional SPR methods. (This is different than the analytical sensitivity, which refers to the absolute amount of analyte detected. The analytical sensitivity is large for the nanohole arrays due to the small sensing area.) Significant improvements in the sensor-output sensitivity have been achieved using crossed polarizers [5]. Thereby, the linewidth of transmission is narrowed significantly since the transmitted signal comes only from scattering between the two orthogonal polarization states by the array of holes. The interfering processes of direct transmission and co-polarization resonant transmission are suppressed. As a result, sensitivities approaching 10^{-6} refractive-index units (RIU) are possible [5].

Another limiting factor is the need for a spectrometer, an angle-scanner, or a tunable laser, which limits the portability and cost-effectiveness of the nanohole-SPR device. A recent innovation has been the removal of a spectrometer (without using a tunable laser or angle-scanner) by using biaxial arrays [6]. Biaxial arrays have two different periodicities, one along each orthogonal axis. In this configuration, lasers of two different polarization states are used

to probe the two independent resonances. Whereas one polarization state gives a reduction of laser intensity when molecules adsorb on the surface, the other polarization state gives an increase. As a result, intensity changes from surface adsorption can be separated from other types of intensity changes, for example, from optical absorption. In this method, the nanohole array itself acts as the spectrometer. By eliminating the need for an external spectrometer, significant reduction in cost and increased portability are possible.

We have recently been working to reduce the limit of detection using sensing inside the nanoholes. This has the advantage of reducing the surface area for detection. It also has the surprising benefit of providing high sensitivity, even though the sensing takes place only inside the hole. The large sensitivity arises because EOT involves two intertwined processes: (1) transmission through the holes and (2) scattering of evanescent waves by the holes. By attaching molecules inside the holes, the transmission is modified significantly and the overall transmission resonance undergoes a large shift in wavelength, even though the sensing area is reduced.

To sense only from inside the holes, we created a glass-gold-glass sandwich, where the top layer of glass was only 50 nm. We then milled the hole array through the top glass layer and the gold. The inside of the hole had exposed gold, which allowed for molecule adsorption by a thiol linkage. Large shifts in the transmission resonance wavelength were observed for adsorption of monolayers, with attomolar sensitivity.

We have also been working to achieve flow-through sensing [7]. A schematic device is shown in Fig. 1. Some exciting early results of flow-through are shown in Figs. 2 and 3. The flow-through sensing technique has the advantage of reducing the microfluidic channel to a nanofluidic channel. As a result, the diffusion time of molecules to the metal surface is greatly reduced and faster detection becomes possible. Coupled with in-hole sensing, flow-through promises unprecedented speed and limits of detection.

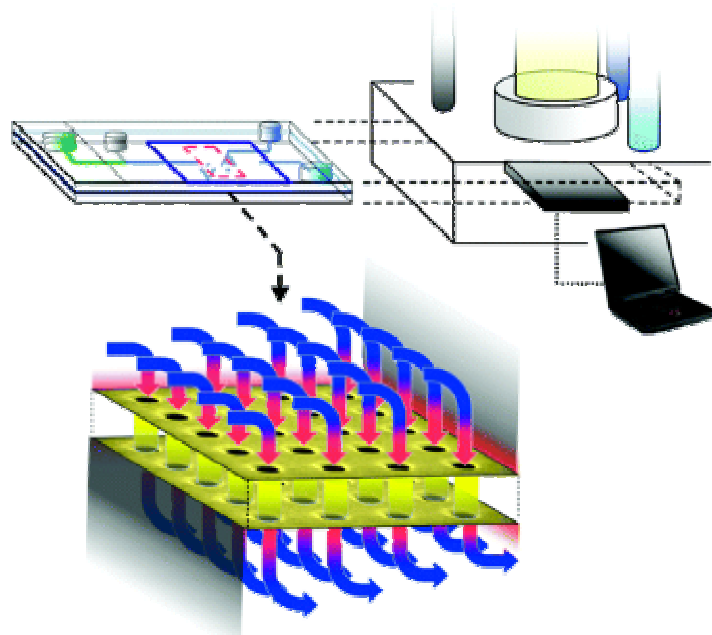


Fig. 1. Schematic of flow-through sensing using nanohole arrays. Nanohole arrays are embedded in the microfluidic chip with fluid channels on either side of the suspended array membrane. The microfluidic chip mounts in a reader device with light source and CCD array sensor, with computer interface for analysis. (Reprinted with permission from Ref. [7]. Copyright 2008 American Chemical Society.)

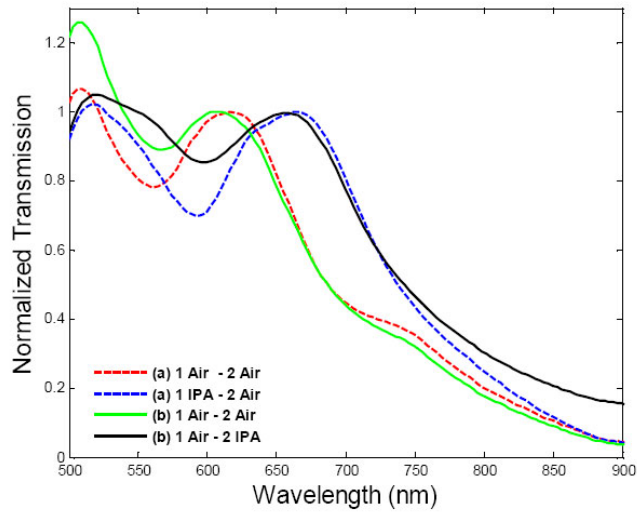


Fig. 2. Preliminary transmission resonance shift for a nanohole array from isopropyl alcohol (IPA) placed on either side of suspended gold on a 200-nm thin dielectric film. Resonance shift is the same for both sides, which shows that the IPA is flowing through the holes and being sensed on the gold side of the membrane.

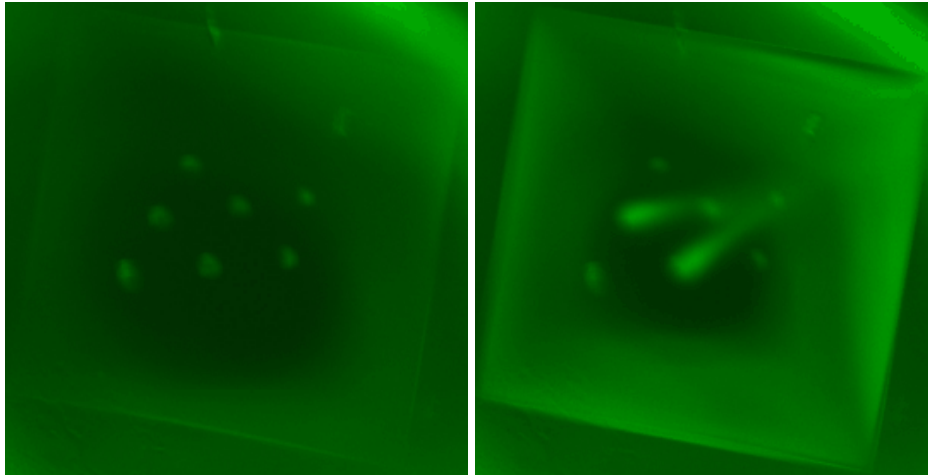


Fig. 3. Microscope images of a 300-nm thick, gold-on-dielectric membrane with nanohole arrays. The entire membrane is 0.5 mm wide (square outline). Nanohole arrays appear as specks on surface. The image on the left shows fluorescein from the other side streaming through nanoholes under pressure.

A challenge remaining for the nanohole-SPR technique is fabrication. While focused-ion beam lithography is the work-horse of many research labs, the mass production of nanohole arrays is required. Several methods, including nano-imprint lithography [8] and optical lithography [9], have been demonstrated for mass production of nanohole arrays.

Further opportunities exist in tailoring the shape of the nanohole to manipulate the electromagnetic field inside it; see, for example, Ref. 10. Since single nanoholes themselves may exhibit localized resonances, it is possible to produce sensing using a single nanohole.

In summary, sensing based on an array of nanoholes in a metal film has undergone rapid development in the past few years; the pace of research is quickening, with many opportunities for further improvement. It is expected from this trend that real-time nanohole-based sensors will be developed in the next few years that are: (1) miniaturized and stand-alone; (2) highly multiplexed; (3) highly portable; (4) highly sensitive. in terms of both output sensitivity and detection limit; and (5) inexpensive (~\$100 production cost). Nanohole arrays also hold great promise for nonlinear optics and spectroscopy [7].

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