Toward molecular identification

Siyka Shopova

Plasmonic enhancement of whispering gallery mode sensors can increase their sensitivity by more than two orders of magnitude.

Scientific research in areas as diverse as healthcare and defense could benefit from improvements to sensor technologies. In particular, there is a need for devices that are both highly sensitive and do not require the targeted pathogens or molecules to be tagged with fluorescent markers or other forms of label. To achieve high sensitivity, scientists have looked into resonance phenomena. Over the past decade, optical whispering gallery mode (WGM) resonance within glass or other dielectric materials fashioned into microspheres, disks, or toroids have been investigated as one sensitive label-free platform. At the same time, progress has also been made with another type of label-free platform involving plasmonic, or electron, resonances within thin metal layers or nanoparticles. The idea is that even a small change in the environment around these structures, caused by nearby target particles, results in a measurable change in the resonance condition. Recently, colleagues and I have developed a hybrid whispering gallery mode-nanoplasmonic (WGM-NP) sensor that relies on an optical WGM resonance within the plasmonic resonance. The design essentially involves attaching a plasmonic nanoparticle (a gold nanoshell) to the surface of a WGM glass microsphere (see Figure 1). This sensor is over two orders of magnitude more sensitive than conventional WGM sensors, and potentially allows for the molecular identification of a specimen. Indeed, recently the hybrid WGM-NP sensor was used to detect and establish the size of the smallest known virus.

The WGM-NP sensor achieves its high sensitivity due to the extremely narrow resonance lines within the glass microsphere at frequencies that match the plasmonic resonance within the metallic nanoparticle. This ‘resonance within the resonance’ generates a strong local electric field near the metallic nanoparticle, which is necessary for sensitive detection. The field falls off rapidly from the metal surface, thus creating strong gradient forces that pull the target particles toward these electric field hot spots. Rather like the conventional WGM sensor, the resonance of the hybrid sensor shifts toward a lower frequency in response to the presence of a target particle in the vicinity of the hot spots. We have experimentally proven the sensitivity enhancement over the conventional resonator by comparing the response of the hot spots and the glass surface to the same target nanoparticles. The hybrid WGM-NP sensor shows the highest enhancement for small particles (<3nm) totally immersed in the strong electric field near the plasmonic nanoparticle. However, the potential of the WGM-NP goes further. We have also proposed a new self-referencing detection mechanism that will eliminate the effects of temperature changes around the hybrid sensor. When the resonance lines of the bare glass microsphere are sufficiently narrow, the resonant mode splits upon the adsorption of the plasmonic nanoparticle on the surface of the glass microsphere (see the inset of Figure 1). The two branches of the split mode correspond to the symmetric and anti-symmetric standing wave states. The plasmonic particle sits at the intensity peak of the symmetric branch. Whenever a target particle binds to the plasmonic particle, a sudden change in the dip depth and position of this branch is observed, but there is, in comparison, very little change to the antisymmetric branch (see Figure 2).
Figure 2. Detection of polystyrene particles (radius 40nm) with a hybrid WGM-NP sensor. (Upper) The resonant mode is split (Δx) by a gold nanoparticle on the equator of the glass microsphere. The resonance lines change further (dip depths y₁ and y₂) upon adsorption of polystyrene particles. (Lower) The split (on the right) and the ratio of the dip depths (on the left) are monitored simultaneously. Each step in the graph corresponds to the arrival of a new polystyrene particle. λ: Wavelength.

For a microsphere resonator with only one plasmonic nanoparticle on its surface, the changes in dip depths correspond to the amount of adsorbed target particles. For a conventional WGM sensor, analyzing the mode split has already been reported as a sensitive self-referencing method. For the hybrid sensor there is an advantage in measuring the dip depth ratio, because it leads to a much better signal-to-noise ratio (compare the two step-like curves in Figure 2) and a lower overall detection limit.

Although the sensitivity of WGM-NP sensor is extremely high and the detector is self-referencing, the split mode changes alone cannot distinguish between the capturing of target molecules and the capturing of other molecules without chemical modification of the plasmonic nanoparticle’s surface. In the future, we want to exploit the potential for monitoring the surface Raman scattering, which will mean a target molecule can be identified by its Raman footprint.

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Siyka Shopova is an adjunct professor of physics.

References