Optical microresonator based on hollow sphere with porous wall for chemical sensing

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A porous-wall hollow glass microsphere (PW-HGM) was investigated as an optical resonator for chemical vapor sensing. A single mode optical fiber taper was used to interrogate the microresonator. Adsorption of chemical molecules into the nanosized pores induced a refractive index change of the thin wall and thus a shift in its resonance spectrum. The PW-HGM resonator had shown higher vapor detection sensitivity in comparison with a solid microsphere under similar test conditions. © 2011 Optical Society of America

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Spherical, circular, ring, toroid, and rectangular shaped microcavities have attracted great interest as optical microresonators [1–5]. These axially symmetric structures trap light in a small volume in the form of whispering gallery modes, resulting in optical resonances in the transmission spectrum. Among the different shapes of resonators, microsphere resonators exhibit relatively high Q-factors, good coupling efficiency, and low transmission loss when stimulated by a well-controlled coupling approach via a tapered fiber [1–3]. Microsphere resonators can potentially be used as refractive index sensors in many research areas, such as detection of biological material and changes in chemical composition or solution concentration [3–9]. Refractometers based on microsphere resonators with a sensitivity of 30 nm/RIU (refractive index unit) have been reported [5]. Gregor et al. used solid microspheres to detect gas vapors based on changes in thermal conductivity [9]. Microspheres have also been coated with a compound to minimize the influence of the external environment and improve the performance of the sensor [1,10–13]. Porous structures have been proposed for chemical sensing [11–13]. Seo et al. reported a method for enantioselective separation and catalysis using an organic porous material [11]. Dybtsev et al. showed a microporous manganese formate that exhibits permanent porosity, high thermal stability, and highly selective gas sorption properties [12]. Based on the adsorptive nature of the porous structure, microspheres coated with porous zeolite were proposed to enhance molecule adsorption for chemical sensing [13]. However, it has been observed that controlling the coating quality can be difficult.

In this Letter an optical microresonator based on a porous-wall hollow glass microsphere (PW-HGM) is reported, for the first time to the best of our knowledge. Because of the porous wall and hollow core of the PW-HGM, chemical vapor molecules can freely pass in and out of the pores and change the effective refractive index of the microsphere, which in turn induces a shift in the resonant wavelength of the resonator. Concentration change of chemical vapor can then be measured by monitoring the wavelength shift.

PW-HGMs are composed of a chemically stable sodium borosilicate glass material constructed in the form of a hollow central cavity surrounded by a shell penetrated with a tortuous network of nanometer-scale channels [14]. The PW-HGMs employed in this study were provided by the MO-SCI Corporation. The glass is heat treated to form a distinct silica-rich and sodium borate phase with an interconnected morphology. When the glass is drawn by a leaching process, it produces interconnected pores or channels. The diameter of the PW-HGMs ranges from 10 to 100 μm. Generally, the pore sizes range from 20 to 200 nm, and the shell thickness is between 0.5 and 2 μm. The shell thicknesses and porous apertures are proportional to the size of the spheres, and the pore size can be tuned by the bead formation process. Figure 1 shows scanning electron microscope images of a PW-HGM. The small hole shown in Fig. 1(a) at the four o’clock location on the sphere is intentionally created by gently pressing the PW-HGM with a glass slide so that the detailed structure of the shell shown in Fig. 1(b) can be observed. A magnified cross-sectional image of the square area is shown at the top left corner of Fig. 1(b), in which the wormlike porous structures can be clearly seen.

The experimental setup is shown in Fig. 2. A fiber taper with a length of ~1 cm and a center diameter of ~2 μm is fabricated from a section of single mode fiber (Corning SMF-28) using a fiber stretching system. A PW-HGM is placed in contact with the taper using a micropositioning system. When light from a tunable laser passes through
the taper, part of it is coupled into the PW-HGM microresonator, where the whispering gallery mode is excited \cite{1}. If the PW-HGM is immersed in a chemical vapor, molecules are able to freely pass into the pores of the PW-HGM. A concentration change of the vapor will alter the effective index of the resonator, shift the resonant wavelength, and be detected by measuring the wavelength shift via a photo detector.

Figure 3 shows a typical normalized transmission spectrum of a PW-HGM resonator with a diameter of 75 μm in air. The diameter was measured using a measuring microscope. It was found that the amplitude of the resonance was proportional to the size of the sphere. For the 75 μm diameter PW-HGM resonator, the Q factor was calculated to be $0.249 \times 10^4$ at the resonant wavelength of 1549.27 nm. The corresponding FWHM was 0.62 nm, and the free spectrum range was 6.61 nm.

Compared with traditional microresonators based on solid glass beads, the Q factor is about $10^3$ times lower due to the higher scattering loss caused by the porous structure of a PW-HGM. However, it is this porous structure that enables the mechanism that makes a PW-HGM resonator a worthwhile chemical vapor sensor, because molecules smaller than the pores can be easily adsorbed to the resonator and therefore detected by measuring the resulting resonant wavelength shift.

To demonstrate the capability of the PW-HGM microresonator for use as a chemical vapor sensor, a series of experiments were performed by monitoring the response of the resonator to various types of vapors. During the experiments the PW-HGM microresonator was placed in a chemical vapor chamber, which was connected to the output of a bubbler placed inside an ice bath. The input end of the ice-immersed bubbler was linked to a nitrogen gas tank. The chemical–water solution sample was filled in the bubbler and nitrogen gas served as a carrying gas that, under the control of a flow meter, brought the volatized chemical from the chemical sample into the test chamber. The vapor concentration was varied by changing the concentration of the solution. In all the experiments the flow rate of the nitrogen was held constant. The resonator was interrogated by a broadband light source, and the transmission spectrum was recorded by an optical spectrum analyzer.

Vapors containing different concentrations of ethanol were measured. The results are shown in Fig. 4, from which it can be seen that an increase in the vapor concentration results in a corresponding shift in the resonant wavelength toward a longer wavelength. The inset shows the wavelength shift as a function of the solution concentration. Measurements were performed five times at each concentration with the error bars shown in the figure. Curve fitting of the resonant peaks was performed to...
eliminate the random intensity noise. The standard deviations based on the five-time measurement data at 5%, 10%, 25%, 50%, and 100% concentrations were 0.03, 0.03, 0.03, 0.04, and 0.04 nm, respectively.

The response of the PW-HGM microresonator sensor to different chemical vapors has also been tested. The spectrum change and resonant wavelength shift of the sensor in response to vapors from deionized (DI) water, pure ethanol, and pure acetone, all mixed in a nitrogen carrier gas, are shown in Fig. 5. To show the sensitivity improvement of PW-HGM microresonators compared with that of traditional solid microsphere resonators, the responses to acetone and ethanol vapors from different concentration solutions were measured. Figure 6 shows the wavelength shift as a function of the solution concentration for both kinds of resonators. For better visualization, the wavelength shifts of the solid microsphere were magnified 10× in Fig. 6. The resonant wavelength of the resonator increased rapidly when the vapor concentration was low. The wavelength shift became slow at high vapor concentrations. The nonlinear relationship between the wavelength shift and the concentration agrees qualitatively with the Langmuir adsorption model. The response curves suggest that the PW-HGM microresonator sensor has higher sensitivity at lower vapor concentrations. The PW-HGM has shown different sensitivities to different types of chemical vapors. Adsorption of chemical vapors of different refractive indices may result in different amounts of change in the effective index of the glass–vapor mixture. Therefore, it is expected that the sensitivity of the PW-HGM will depend on the size and polarity of the molecule, as well as the adsorption strength toward a specific molecule.

From Fig. 6 it can be seen that when compared with the traditional solid microsphere resonator under the same experimental conditions, the vapor detection sensitivity of the PW-HGM microresonator is significantly higher. The wavelength shifts of the PW-HGM at 100%, 25%, and 5% acetone–water vapor were measured to be 3.46, 2.74, and 1.69 nm, respectively. In contrast, the wavelength shifts of the solid microsphere at 100%, 25%, and 5% acetone–water vapor were measured to be 0.15, 0.14, and 0.07 nm, respectively. The sensitivity of a solid microsphere is apparently lower due to the non-porous surface, which lacks the capability of adsorbing molecules.

In summary, a PW-HGM was investigated as an optical microresonator for chemical vapor detection. Adsorption of chemical vapor molecules into the nanosized pores in the wall of the PW-HGMs changes the effective refractive index of the material, causing a shift in the resonance spectrum toward longer wavelengths. The amount of wavelength shift increased as the vapor concentration increased. It is expected that the sensitivity of the PW-HGM will depend on the porosity and thus the average pore size. After calibration, this deterministic relation can be used for chemical vapor sensing. The Q-factor of the PW-HGM is significantly smaller than that of a solid microsphere. However, because of the porous structure, it showed a higher sensitivity compared with a solid microsphere when used for chemical vapor detection.

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References