Whispering Gallery Modes in Highly Hexagonal Symmetric Structures of SBA-1 Mesoporous Silica

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An interesting optical resonant mode, called whispering gallery mode (WGM), has been discovered inside highly hexagonal three dimensional symmetry of SBA-1 mesoporous silica. The hexagonal structure provides a suitable environment for the light wave to circulate around due to multiple total internal reflection at the resonator’s boundary and generates the resonant states. Based on the hexagonal total internal reflecting model, the observed eigenmodes can be explained quite well. We also discovered that under the condition of WGMs, the absorption of CO$_2$ and H$_2$O molecules can be greatly enhanced.

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The concept of resonators has been utilized in every kind of wave, and their eigenmodes play an important role in many technical applications, such as musical instruments and in various kinds of lasers. Many different optical resonators have been designed to improve the efficiency of optoelectronic devices. One of them, an interesting type of resonator, shaped as a microcylinder or a microsphere is called dielectric whispering gallery resonator. Inside the resonator, multiple total internal reflections (TIR) at the resonator’s boundaries confine the light wave to circulate around the resonator, which is able to enhance the lasing behavior. Recently, in the course of analyzing and employing microporous zeolites or wurtzite structured material, such as ZnO, a lot of attention have been focused on the hexagonally shaped resonators of whispering gallery modes (WGM) lasing.

Mesoporous silica ranging from millimeter to nanometer sized spheres, films, hollow tubulars, and fibers have been synthesized under basic or acidic conditions. Among the mesoporous silicas, SBA-1 is the most interesting one due to its highly symmetric three dimensional structure. Compared to microporous zeolites, the formation of single crystal of mesoporous silica is average more difficult because of the low energy cost in the formation of defects. The periodic mesoporous materials showing crystal-like regularity over very large areas would offer unusual functions and perceived utility in a wide range of applications.

In this paper, we present the investigation of WGMs in highly hexagonally symmetric three dimensional structure of SBA-1 mesoporous silica. The observed fine structures in the Fourier transfer infrared spectra (FTIR) can be explained quite well in terms of the theoretical calculation based on TIR mode. In addition, we showed that the absorption of gas molecules, such as CO₂ and H₂O can be greatly enhanced due to the existence of WGM in highly hexagonally symmetric three dimensional structures. This finding provides an excellent opportunity for creating
highly sensitive gas sensors and optoelectronic devices by the implementation of WGMs.

In order to prepare single crystalline of SBA-1, we synthesize mesoporous silica from the C_{18}TMACl-sodium silicate-H_{2}O components at PH value at 1.5 around the isoelectric point (IEP) of silica. The slow growth rate is a significant requirement for formatting well-defined morphology crystals. In contrast for normal method using TEOS as silica source in standard acid synthesis, a very dilute acidified sodium silicate solution (PH = 1.5) was used as the silica source. The x-ray powder diffraction (XRD) patterns of the synthesized samples were collected on a Scintag X1 diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) was performed on Hitachi S-800 operated at an accelerating voltage of 20 KeV.

Figure 1(a) shows the X-ray diffraction (XRD) patterns of the calcined SBA-1 mesoporous silica synthesized from C_{18}TMACl system by using the delayed-neutralization process, which possess sharp XRD peaks characteristic of the three dimensional decaoctahedron \( Pm\overline{3}m \) mesostructure of SBA-1 mesoporous silica. To observe the appearance of SBA-1 mesoporous silica, we recorded the scanning electron micrographs (SEM). Figure 1(b) shows the SEM image of SBA-1 mesoporous silica spread on ITO glass. The estimated size variation is about ± 25%. The inset in Fig. 1(b) reveals the single crystal morphology of decaoctahedron mesostructure, which is quite homogenous.

To characterize the optical properties, the reflectance spectra were measured by a Nicolet Continuum Infrared Microscope. In the measurement, the objective serves to focus light on the surface, and also collects the light signal from the sample. For a typical Nicolet Continuum, a 15 time objective with the standard 10 time ocular provides a total light magnification of 150 times. The working distance and numerical aperture of the objective are 11 mm and 0.58 mm, respectively. All the spectra were
taken under the premise that the incident light wave is always perpendicular to the sample surface. The mesoporous silica of SBA-1 was spread on Indium-Tin-Oxide (ITO) glass coated with an Au film of 100 nm. The coated Au film can serve as an excellent reflector for the incident light wave.

As the SEM image shown in the inset of Fig. 1(b), the highly symmetric three dimensional structure of SBA-1 mesoporous silica provides an excellent environment for the light wave to resonate. The decaoctahedron mesostructure of SBA-1 has three cross sections of hexagonal cavities. A light wave interferes with itself when having one full circulation within the resonator. When the total phase shift of the light wave along the path happens to be an integer multiple of $2\pi$, the constructive interference will be enforced. Therefore, it is necessary to find out the phase shift of the light wave propagating one full circulation inside the cavity. The calculation of the WGM phase shift of hexagonal cavity can be obtained from the Fresnel formula as follow.\textsuperscript{10}

The reflectance of the TE polarization is given by

$$
    r_{TE} = \frac{n \cos \theta_i - i \sqrt{n^2 \sin^2 \theta_i - 1}}{n \cos \theta_i + i \sqrt{n^2 \sin^2 \theta_i - 1}},
$$

and for the TM polarization

$$
    r_{TM} = \frac{-1}{n} \frac{\cos \theta_i + i \sqrt{n^2 \sin^2 \theta_i - 1}}{\cos \theta_i + i \sqrt{n^2 \sin^2 \theta_i - 1}}.
$$

Let

$$
    \alpha_{TE} = \frac{\sqrt{n^2 \sin \theta_i - 1}}{n \cos \theta_i},
$$

and

$$
    \alpha_{TM} = -\frac{\sqrt{n^2 \sin \theta_i - 1}}{n \cos \theta_i}.
$$
then we can simplify the formula in the form

\[ r = \frac{1 - i\alpha}{1 + i\alpha}. \] (5)

Let us consider the resonance condition that

\[ e^{i\text{Re}(k)l} r^6 = 1, \] (6)

After some algebraic manipulations, we arrive at the total boundary phase \( \varphi \) given by

\[ \tan\left(\frac{\pi}{6}\varphi\right) = \alpha. \] (7)

Then, we obtain the following equation:\textsuperscript{11,12}

\[ L = \lambda\left[ N + \frac{6}{\pi} \tan^{-1}\left(\frac{\beta\sqrt{3n^2 - 4}}{\pi}\right)\right], \] (8)

The left side of the equation (8) is the distance of light wave propagating a full circulation in the hexagonal cavity. The factor \( \beta \) depends on the polarization of light wave, i.e., for the TM polarization \( \beta_{\text{TM}} = n^{-1} \) has to be used and for the TE polarization \( \beta_{\text{TE}} = n \). The leading term in the right hand side of the equation corresponds to the wavelength in cavity. The integer \( N \) characterizes the interference order of the resonance, which is identical with the respective WGM number. And the last term in the right hand side is the total phase shift after reflecting a full circulation in the hexagonal structure of the SBA-1 mesoporous silica.

To calculate the WGM positions of the SBA-1, the refraction index \( n = 1.46 \) and the light path \( L = 22.0 \mu\text{m} \) are used. Table I lists the calculated values of the low-order WGMs for \( N \leq 5 \). We can clearly see that the WGMs of the TE and TM polarization locate in the range from 8500 nm to 3000 nm.

Typical Fourier transfer infrared reflectance spectra with different sample concentrations are shown in Fig.2. In order to confirm the effect of the WGMs, the spectrum of ITO glass doped gold is also recorded for comparison. Figure 2 represents the spectra for the decaoctahedrons spread onto the ITO glass from sparse
to dense, and the guided arrows are the WGMs of the theoretical calculated positions. The FTIR spectra cover a range between 2.5 \( \mu \text{m} \) and 9.0 \( \mu \text{m} \). We can clearly see that the sharp structures in the FTIR spectra can be correlated with the calculated WGMs quite well. It confirms the fact that the WGMs do exist in SBA-1 mesoporous silica with highly hexagonal symmetric structure. The local maximum reflectances represent the theoretical WGM positions as one should expect. However, quite interestingly, there are several pronounced absorption features at 4.5 \( \mu \text{m} \), 6.67 \( \mu \text{m} \), and for wavelength larger than 8000 nm. All of them are consistent with the position of the WGMs. Besides, the features at around 4.5 \( \mu \text{m} \) and 6.67 \( \mu \text{m} \) are consistent with the absorption of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) molecules, respectively.\(^{13}\) It indicates that the increase in the absorption of the gas molecules is due to the existence of the WGMs in SBA-1 mesoporous silica. This behavior can be easily understood by the fact that when the condition of WGMs is satisfied, the light wave is trapped in the cavities. As the light wave keeps traveling inside the cavities filled with gas molecules, the absorption due to the gas molecules becomes stronger and stronger. It is worth nothing that the light wave can be completely absorbed at some particular wavelength, such as at 6.2 \( \mu \text{m} \) and 8.5\( \mu \text{m} \). To further confirm our interpretation shown here, we have measured the FTIR spectra with a constant concentration of SBA-1 sample at \( 1.0 \times 10^{-4} \) \( 1/\mu \text{m}^2 \) but variable \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) molecules concentration. The change of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) molecules concentration was achieved by varying nitrogen purging flow rates with 750 and 1500 SCCM (SCCM denotes cubic centimeter per minute at STP) on SBA-1 mesoporous silica. We can clearly see that the absorption intensities of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) molecules decrease with increasing nitrogen purging flow rate. Our result therefore indicates that the absorption strength of gas molecules can be greatly enhanced by the WGMs of mesoporous structure. This is a very important finding because it provides an excellent opportunity for creating highly efficient gas sensors and optoelectronic
devices.

In conclusion, we have reported an investigation of the optical whispering gallery modes in highly hexagonally three dimensional symmetric SBA-1 mesoporous silica. By using the hexagonal cavity model, the theoretical WGM positions can be obtained, which were confirmed by our experimental results. Quite interestingly, it is found that the absorption strength of CO₂ and H₂O molecules can be greatly enhanced when the absorption frequencies of gas molecules match with the WGMs in SBA-1 mesoporous structure. The light wave can even be completely absorbed. This finding provides an excellent opportunity for creating highly efficient optoelectronic devices and gas sensors.

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References


Table:
Table I. The calculation of whispering gallery mode of SBA-1 mesoporous silica.

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Figure Captions:

Fig. 1 (a) X-ray diffraction pattern of SBA-1 mesoporous silica. (b) The top view scanning electron microscope image of the mesoporous silica SBA-1 material. The inset figure shows a single SBA-1 sample.

Fig. 2 Typical infrared reflectance spectra of SBA-1 mesoporous silica. The density of SBA-1 samples range from $1.0 \times 10^{-4} \, \mu \text{m}^2$ to $2.5 \times 10^{-2} \, \mu \text{m}^2$.

Fig. 3 (Color online) Infrared reflectance spectra with a fixed density of SBA-1 mesoporous silica at $1.0 \times 10^{-4} \, \mu \text{m}^2$ and variable gas concentration. To change the gas concentration, the sample was purged with different flow rates of nitrogen at 750 and 1500 SCCM.
(a) X-ray intensity (a.u.)

2θ/degree

(100)

(110)

(b) SEM images with scales 1.5 μm and 4 μm.