

A Coupling Wave Optical Waveguide Chemical Sensor Constructed by Combining the Ion-exchange and the Sol-gel Methods

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A coupling wave optical waveguide sensor was proposed, and realized by combining the ion-exchange and the sol-gel methods. The new optical waveguide (OWG) sensor is based on a stacked slab optical waveguide codirectional coupler, and proved to be advantageous over conventional OWG sensors. A gas sensor fabricated as an example easily detected 5 ppm H₂S.

In the last decade, optical waveguide (OWG) techniques have drawn considerable attentions from the viewpoint of developing integrated optical chemical or biological sensors for monitoring environmental pollution and industrial processes.¹⁻³ OWG sensors are classified into two types, i.e. evanescent wave sensors and guided wave sensors, depending on whether a measurand interacts with evanescent wave (waves extending to cladding) or guided wave (waves confined in guiding films).² We have recently demonstrated a large improvement in sensitivity of a evanescent wave sensor.³ Moreover, we have theoretically proved that guided wave sensors will have larger sensitivities because of their highly efficient sensing interaction.⁴ To fabricate a guided wave sensor, sensing materials are incorporated into a permeable guiding film of an OWG by for example the sol-gel method. However, these guiding films usually suffer from large scattering due to the non-uniformity in micro-structure, and therefore cannot carry light for a long distance. This particularly causes difficulties, for example no enough space for placing test-cells, when light is introduced in and drawn out of the guiding film by the prism coupling method.

In this letter, we propose a new type of guided wave sensor, i.e. coupling wave optical waveguide (CWOWG) sensor based on codirectional coupling theory, in order to solve the difficulty stated above. The structure of the CWOWG sensors is schematically shown in Figure 1. In this structure, waveguide 2 acts as the sensing part of the sensor by incorporating sensing-materials in guiding film 2, and hence serves as a sensing waveguide. Waveguide 1 serves as a carrying waveguide by inputting and outputting the light. Cladding 1 usually has the same refractive index as that of the substrate. When light is introduced into the carrying waveguide, the guided mode of thereof will excite the guided mode of the sensing waveguide via evanescent-coupling, and thus a coupling wave will form in the sensing waveguide. According to codirectional coupling theory,⁵ the power of two waveguides will interact with each other and vary periodically in their propagating direction. In this way, part of the light power will be coupled into the sensing waveguide.

The feature of the CWOWG sensors is that the roles of light-power carrying and sensing are separately played by two waveguides (unlike the case of conventional guided wave sensors, where the two roles are played by a same waveguide). This permits us to use a low-loss waveguide for introducing and carrying light power, and a permeable film located on any desired place of the carrying waveguide for sensing.

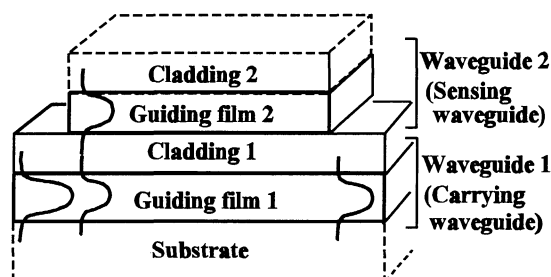


Figure 1. Schematic structure of coupling wave optical waveguide sensors.

According to our theoretical analyses,⁶ the average absorption coefficient of the sensing-material in CWOWG sensors can reach about 50 % the absorption coefficient of the same material in the conventional Lambert-Beer law. Even though this value is not as large as that in conventional guided wave sensors (generally above 90 %⁴), it is significantly better in comparison with that in evanescent wave sensors (generally several percent⁴).

To construct actual CWOWG structures, we employed the ion-exchange method to fabricate the carrying waveguide, and the sol-gel method to fabricate the sensing waveguide. Because the ion-exchange in glass can give a fiber compatible, low loss waveguide (< 1dB/cm) with low cost,^{7,8} and the sol-gel method makes it easy to incorporate sensing materials into guiding film 2.

Guiding film 1 was fabricated by K⁺-Na⁺ ion-exchange in a sodalime glass slide at 400 °C for 2 h in a KNO₃ melt. Cladding 1 was a sol-gel film coated by dip-coating method. γ -glycidylpropyltrimethoxy silane (GLYMO) (Tokyo Kasei Kogyo Co., Ltd.) and titanium tetraisopropoxide (Wako Pure Chemical Industries Ltd.) were used as precursors of the sol-gel process,⁹ and refractive index and thickness of the film were measured by an ellipsometer. The refractive index was adjusted to 1.510 which was close to the refractive index of the substrate slide glass by setting Si:Ti=0.65:0.35 (in mole fraction). The thickness of the film was about 0.20 μ m at withdrawal speed of 20 cm/min. There are two important points in the sol-gel procedure employed here: 1) the organic groups of GLYMO make it possible to get dense sol-gel film without baking; 2) the hydrolysis is performed by homogeneous generation of water, instead of adding water directly, and thus a transparent, homogeneous film is obtained.⁹ Guiding film 2 was formed on the top of waveguide 1 by sol-gel method in the same manner mentioned above. In this case, the refractive index of the thin film was adjusted to 1.530 by setting Si:Ti=0.6:0.4 (in mole fraction), and the thickness of the film was about 0.50 μ m at withdrawal speed of 60 cm/min. The film was

doped with thionine dye by dissolving the dye into the original sol-gel solution at a concentration of about $2.5 \times 10^{-5} \text{ mol dm}^{-3}$. We chose thionine dye because the fluorescence of this dye is reportedly quenched by H_2S without any response to SO_2 , HCl and NH_3 ,^{10,11} and thus, fluorescence-based OWG sensors can be constructed.

The CWOWGs fabricated above were arranged in an experimental setup shown in Figure 2(a). A He-Ne laser ($\lambda=543.5 \text{ nm}$) was used as a light source. Figure 2(b) is a photograph of the fluorescence streak of thionine dye excited by the coupling waves. The fluorescence intensity varied periodically along the propagating direction. Such a periodic pattern gives good evidence of the periodicity shown in Ref. 5. The fluorescence of thionine dye was effectively excited, and then was very easily detected. The fluorescence spectrum is shown in Figure 3. We tested the responses of the fluorescence intensity at the wavelength of 625 nm to 5 ppm H_2S , and the result is also shown in Figure 3. The fluorescence was indeed reversibly quenched by H_2S likely because of its reversible reduction of the excited state thionine although the detailed mechanism is not clear yet.¹⁰ The response to the concentration still needs to be investigated more in detail, but the CWOWG structure proved to be effective in developing the guided wave type OWG sensors.

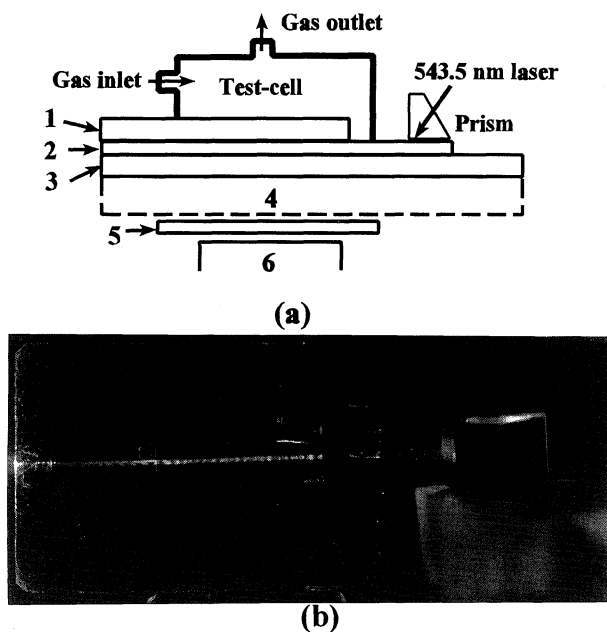


Figure 2. (a) Schematic diagram of the experimental setup. (1: thionine-doped sol-gel film, 2: sol-gel film, 3: ion-exchanged thin film, 4: sodalime slide glass, 5: interference filter (center wavelength: 625 nm), 6: photomultiplier.), and (b) Photograph of the fluorescence streak of thionine dye.

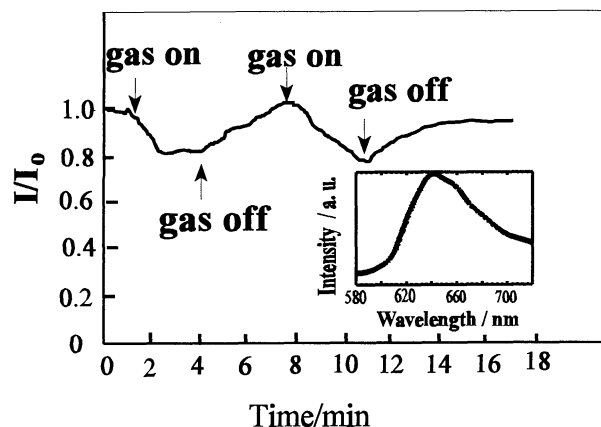


Figure 3. Responses of the fluorescence intensity at 625 nm to 5 ppm N_2 -diluted H_2S gas. The inset shows a fluorescence spectrum of thionine doped in the sol-gel film.

In conclusion, we have successfully realized CWOWGs by combining the ion-exchange and the sol-gel methods, and have experimentally demonstrated that CWOWG structure has a great potential in developing chemical and biological integrated optical sensors.

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References and Notes

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