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# Fiber optic hydrogen sulfide gas sensors utilizing ZnO thin film/ZnO nanoparticles: A comparison of surface plasmon resonance and lossy mode resonance

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ABSTRACT

Fabrication and characterization of fiber optic sensors employing surface plasmon resonance (SPR) and lossy mode resonance (LMR) for the detection of hydrogen sulfide gas have been carried out. Three kinds of probes, two utilizing LMR technique and the one utilizing SPR technique, have been fabricated over unclad core of the fiber using zinc oxide (ZnO). The first LMR probe, named as LMR 1, has been fabricated by coating ZnO thin film with an over layer of ZnO nanoparticles while the second LMR probe, named as LMR 2, has a layer of ZnO nanoparticles over the unclad core of the fiber. The third probe, named as SPR probe, has been fabricated by coating silver film and a thin over layer of ZnO over unclad core of the fiber. The variation of peak absorbance/resonance wavelength with the concentration of the hydrogen sulfide gas has been used to calibrate all the three sensors having different platforms. The results show the maximum sensitivity to $H_2S$ gas for LMR 1 probe while the minimum for the SPR probe. In addition, the LMR 1 probe is highly selective to hydrogen sulfide gas in comparison to other two probes. This has been confirmed by performing experiments using different gases. The LMR 1 sensor probe has number of advantages, in addition to high sensitivity and selectivity, such as low cost, miniaturized probe, fast response, reusability of the probe, capability of online monitoring and remote sensing.



## 1. Introduction

Hydrogen sulfide ($H_2S$) is a colourless, incendiary gas with a foul smell of rotten eggs. It is usually released into the atmosphere as a decomposition product or as a toxic industrial by-product in petroleum and oil refineries, waste water treatment and kraft paper mills. It is a highly inflammable gas which reacts with oxygen to give sulphur dioxide, another toxic gas. Studies show that people can get the smell of rotten egg in concentration less than 1 ppm and it will start showing its toxicity for concentration greater than 20 ppm. Hydrogen sulfide can be sensed at low concentration by its foul order, but it will cause irritation to eyes, lungs, etc. As the concentration increases there would be breathing difficulties and at high concentration it is extremely hazardous as it causes olfactory fatigue, which is a condition in which the person can lose his ability to realize even the presence of gas. This kind of exposing to higher concentrations of hydrogen sulfide poses serious health risks and threatens to life. Moreover, using hydrogen sulfide odour as a forewarning is not well grounded hence the use of sensors are important [1,2].

Nanotechnology has established its application in various fields of science and technology which deals with materials and particles size in the range of 10–100 nm. Since last few decades, nanoparticles have made its role clear in different applications including sensors due to their optical, electrical, electronic and magnetic properties. Now days, metal oxide nanoparticles are having increasing applications due to their unique structural properties, physical properties, chemical properties, electronic-electrical properties, nano size and nanostructures. For example, zinc oxide (ZnO) based nanoparticles have got applications in rubber manufacturing, sunscreen lotions, food additives and gas sensing [3]. It is a direct band gap p-n junction semiconductor with a wide band gap range which makes it useful for different optoelectronic applications in the mid infrared range [4]. In addition, it is surface conductive thereby making its role clear in sensor applications. A characteristic property of such conductometric metal oxide is reversible interaction of its surface with the gas [5–16].

Surface plasmon resonance (SPR) is one of the most propitious techniques that have unfolded so many challenging possibilities in the world of plasmonics, especially sensors, over the last few decades. To bring out SPR technique we need a metal-dielectric

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interface which handles charge density oscillations. The propagation of charge density oscillations at this interface is known as surface plasmons [17–21]. The physics of SPR starts from total internal reflection of a p-polarized light incidence at an interface to give evanescent wave propagation. The decaying evanescent field away from the interface and propagating along the metal-dielectric interface excites the surface plasmons when it possesses the same wave vector as that of surface plasmons [22–30]. Tremendous amount of work has been carried out on the SPR based fiber optic sensors for the detection of various analytes due to large number of advantages like high sensitivity, low cost, miniaturized probe, real time monitoring and capability of remote sensing [22–24,27–29]. In the case of SPR, it is necessary for the thin film coated over the substrate to have its real part of permittivity to be negative and it needs TM polarized light for its generation [31]. But it is also possible to design an optical fiber sensor by using a different type of resonance mode supported by the fiber and is called lossy mode resonance (LMR) which can be obtained by both TE and TM polarized lights. LMR based devices for sensing applications have been reported in the literature using various metal oxides [31–35]. The similarity between SPR and LMR is that, in both the cases the real part of the dielectric constant of the layer used is greater than the dielectric constant of the surrounding medium [31–33]. In the literature both the high reflectance and low reflectance region of transparent conducting metal oxides have been reported [32,33]. In the high reflectance region, the imaginary part of the dielectric constant of such metal oxides is in the range of metals and hence supports SPR. But in the case of low reflectance region, the imaginary part is lower and suitable for LMR. Utilizing LMR in metal oxides for sensing applications has the advantage of sensitivity enhancement in the low reflectance wavelength region (visible region) [34]. Recently, the field of sensors has introduced refinement of surface bailiwick with the use of nanoparticles which has brought up a new revolution by improving its features and results. The use of nanoparticles of conductometric materials such as zinc oxide has enhanced the effect of resonances (SPR and LMR) when compared to the thin films because of its higher surface area to volume ratio [33].

In the present study, a comparison of the fiber optic sensing features of SPR and LMR based sensors fabricated by using different contours of ZnO for the detection of hydrogen sulfide gas is carried out. The purpose of using ZnO for the sensing of hydrogen sulfide is that hydrogen sulfide reacts with the ZnO and changes its dielectric constant. Two kinds of LMR sensor probes are considered. One, having coating of ZnO film over unclad core of the fiber with an over layer of ZnO nanoparticles, giving the effects of both thin film and nanoparticle (LMR 1). The other LMR probe has coating of ZnO nanoparticles over the unclad core of the fiber (LMR 2). To bring about the SPR nature or to fabricate a SPR based probe a metal layer is introduced between the fiber core and the ZnO layer. The fabrication of SPR and LMR sensor probes has been discussed in the experimental section. To characterize these probes the spectra of the transmitted light for different concentrations of the gas around the probe are recorded and the corresponding peak absorbance/resonance wavelengths are determined. The performance of all the three probes is compared in terms of their calibration curves and sensitivities.

## 2. Experiments

### 2.1. Preparation of ZnO nanoparticles

For the preparation of ZnO nanoparticles Pacholski method was used. The materials used were zinc acetate dihydrate ($(C_2H_3O_2)_2 Zn{\cdot}2H_2O$), methanol ($CH_3OH$) and sodium hydroxide (NaOH). The 0.01 M of zinc acetate dihydrate was prepared by mixing the required quantity of it in 100 ml of methanol and was used as the first solution. Second solution was prepared by mixing 100 ml of sodium hydroxide into 100 ml of methanol. The second solution was then added drop by drop in to the first solution at a particular temperature and rotations per minute under persistent stirring. The mixing of two solutions gave nanoparticles of ZnO. The resulting nanoparticles were found to be hexagonal in shape as confirmed in results and discussion section. The mixture was then allowed to cool at room temperature. The size and shape of nanoparticles can be varied by varying the growth temperature and the concentration of integrants.

### 2.2. Fabrication of sensor probes

For the fabrication of probes, plastic clad silica fiber of numerical aperture 0.40 and core diameter 600 μm was used. Three kinds of probes as mentioned in introduction were fabricated for studying hydrogen sulfide gas sensing. For each probe, 1 cm length of the fiber was unclad from the centre of about 22 cm total length. It was then cleaned with Millipore water followed by acetone. For SPR probe, silver film of 40 nm thickness was uniformly coated over unclad core of the fiber using thermal evaporation vacuum coating unit. It was followed by a ZnO coating to give a thin film of 12 nm thickness again using thermal evaporation coating unit that works in high vacuum. The coating unit has a thin film thickness monitor which has the ability to control and measure the thickness while the film is being deposited using quartz crystal as the sensing element having an accuracy of 0.1 nm. The coated thickness was confirmed by using ellipsometry. For the second type of probe named as LMR 1, 1 cm unclad central portion of the fiber was first coated with a 12 nm thick film of ZnO by using thermal evaporation technique and then ZnO nanoparticles were coated over it by dipping the fabricated probe in ZnO nanoparticle solution at a temperature of 60 °C. For the third type of the probe, named as LMR 2, 1 cm unclad central portion of the fiber was coated with the prepared zinc oxide nanoparticles by dip coating method at a temperature of 60 °C. The sensor probe models of SPR (Ag/ZnO thin films), LMR 1 (ZnO thin film/ZnO nanoparticles) and LMR 2 (ZnO nanoparticles) are shown in Fig. 1.

### 2.3. Experimental setup

For all the three probes the same experimental setup, shown in Fig. 2, was used. The setup was consisted of a cylindrical metal chamber with provisions for inserting fiber optic probe, passing of gas and making the chamber air tight. A rotary pump was connected to the chamber to remove gas from the chamber and to maintain the vacuum inside whenever required. There was provision for connecting two gas cylinders to the chamber at the same time. For the sensing of hydrogen sulfide gas, its gas cylinder was connected to one port and the nitrogen gas cylinder was connected to another port for purging. There were knobs for adjusting the concentration of gas inside the chamber. The experiments were performed for the concentration range of hydrogen sulfide gas from 10 ppm to 100 ppm or 10 μL $H_2S$/l to 100 μl $H_2S$/l. The concentration of hydrogen sulfide gas in ppm (or μl $H_2S$/l) was measured using a calibrated vacuum gauge attached with the gas chamber. Since the conventionally used unit to measure the concentration of a particular gas in air is ppm and in the current work the gas concentration is in vacuum therefore the units μl $H_2S$/l has also been used for the concentration of $H_2S$ gas where 1 ppm = 1 μl $H_2S$/l. Light from the tungsten halogen lamp (AvaLight-HAL) was launched into the fiber probe from one end and the spectrum of the transmitted power received at the other end of the fiber was recorded by a spectrometer (AvaSpec-3648) interfaced with a computer. The spectra were recorded for different concentrations of the gas inside the chamber