CHAPTER-4
FIBER OPTIC pH SENSOR BASED ON SPR OF Ag
NANOSTRUCTURED FILM

4.1 Introduction
The pH value is one of the most commonly monitored chemical parameters of a fluid. The measurement and control of pH are required practically in all kinds of sciences including chemical, biomedical and environmental. The earliest method of pH measurement was by means of chemical indicators, e.g. litmus paper that changes itsColour in accordance to a solution’s pH. For example, when litmus is added to a basic solution it turns blue, while when added to an acidic solution the resultant colour is red. Since many chemical processes are based on pH, almost all aqua samples have their pH tested at some point. The most common systems for pH sensing are based upon either amperometric or potentiometric devices. The most popular potentiometric approach utilizes a glass electrode because of its high selectivity for hydrogen ions in a solution, reliability and straightforward operation. Ion selective membranes, ion-selective field effect transistors, two terminal microsensors, metal oxide and conductometric pH-sensing devices have also been developed [1]. However, these types of devices can often suffer from instability or drift and, therefore, require constant re-calibration. In recent years, great efforts have been directed towards the development of fiber optic pH sensor [1, 2 and 3]. Fiber optic pH sensors have many advantages over conventional sensors. They are small, immune to
electromagnetic interference and have remote sensing capability, among other desirable features. One of the key advantages is that they don’t require a reference electrode for the pH measurement. Most of the Fiber Optic pH sensors are of the intrinsic variety. Different portions of the optical fiber can be used for sensing, such as the end face or the core-cladding interface. Fiber-Optic pH sensors are based on pH induced changes in optical or spectroscopic properties such as absorbance, reflectance, fluorescence, energy transfer etc. [4, 5].

The localized surface plasmon resonance (LSPR) of plasmonic nanoparticles has been attracting great attention due to its potentiality in sensing and spectroscopic application. The plasmonic nanoparticles such as silver and gold exhibit a unique optical property by strongly absorbing and scattering light around LSPR wavelength due to the collective oscillation of the free electrons in resonance with the illuminating light field. The spectral position of LSPR is sensitive to its local environment such as refractive index (of the surrounding medium) temperature, pressure, humidity, pH etc [6, 7 and 8]. Hence pH sensor may be realized through shift in the localized surface plasmon resonance (LSPR) extinction maximum (λmax.) of Ag nanoparticles of Ag/PVA nanocomposites. In the present work, a pH sensor is constructed from low cost fiber optic and optoelectronic components including a blue light emitting diode and a photodiode. The fabricated Ag-PVA nanocomposite is coated on U-bent and tapered U-bent fiber having bent radius of 2.5 mm by dip coating method. For comparison of the sensitivity of the nanocomposite with that of the bulk material we have repeated the experiment with the two fibers having coating of bulk Ag/PVA.
4.2 Experimental

4.2.1 Preparation of Ag – nano coated pH Probe

Fig. 4.1: Photograph of the tapered U-bent fiber probe.

To prepare the pH probe, a PMMA (polymethyl methyl acrylate) fiber of core diameter 980/1000 micron and numerical aperture (NA) 0.5 are used. The refractive indices of the core and the cladding were 1.48 and 1.401 respectively. The cladding is removed from a small portion of the central region (sensing region) of the fiber by rubbing it with the help of a razor. To make the fiber U-shape, it is heated at temperature of 100 °C and then slowly bent to diameter 2.5 mm of the sensing region. This bare portion of the fiber is then converted into a taper by rubbing it with the help of a razor then by heating at 100 °C and then pulling it to one end of the fiber while the other end is fixed. The prepared U-bent and the tapered U-bent (Fig.4.1) fiber are cleaned with acetone and then dried in air for few minutes. The sensing region of the two fibers are coated with the fabricated Ag-PVA nanocomposite of minimum particle size (sample no.d4 of table no.2.4, size 47 nm). To
observe the performance of the probe with bulk material the nano coating is removed with acetone and then coated with bulk Ag-PVA composite.

### 4.2.2 Experimental Set up For pH Sensor Realization

![Image](image1.png)

**Fig. 4.2:** Photograph of the experimental set up

![Image](image2.png)

**Fig. 4.3:** Block diagram of the experimental set up.
The optical source used in this experiment is intensity stabilized 4 mW diode laser (LD) source of wavelength 670 nm (Fig. 4.3). To avoid any fluctuation in the LD, a 50:50 beam splitter is used at the input end of the optical fiber, so that a part of the light signal propagated in a direction orthogonal to the beam passing through the optical fiber can be used as reference level for the present study. Light from the beam splitter (BS) is collimated by means of microscopic objectives (O) on to the input face of the fiber. The intensity modulated beam coming out from the sensing region of the fiber is then refocused to the detector by means of another microscopic objective lens (focal length=2.5 mm). For stable light-coupling any possible relative movement between the second objective and the fiber is avoided. The diode laser source, the objectives, fiber stand and the detectors are mounted on the same bread board so that any external mechanical disturbance of the beam launcher affects the fiber as well, thereby minimizing variations in the power coupled into the fiber. The detector is a photodiode (PD) whose output is amplified by a preamplifier circuit. A digital multimeter is used for measuring the detector output. In this experiment, water (liquid) with different pH (from 3.6 to 9.3) is used which changes the intensity of the light beam from the sensitive region of the fiber probe due to shift in LSPR position of Ag nanoparticles.
4.3 Sensitivity of the Sensor

Fig. 4.4: Sensitivity of the U-bent fiber

Fig. 4.5: Sensitivity of the tapered U-bent fiber.
To study the sensitivity of the fiber-optic pH sensor based on LSPR of Ag nanstructured film, experimental investigations have been carried out with U-bent and tapered U-bent fiber of same characteristics (Fig. 4.4 and 4.5). Here the sensitivity factor is defined as the change in normalized output for a given change in pH value. For both the cases we have investigated the sensitivity of the probe for without coating, bulk coating and nanocomposite coating. For without coating U-bent probe, normalized output decreases with increase in pH. So it can’t be useful for higher pH. But the same probe with bulk and nano coating, normalized output increases with increase in pH. The sensitivity factor in the pH range from 3.6 to 9.3 is 0.06 for bulk coating while it is 0.08 for nano coating. In case of tapered U-bent, for without coating probe the sensitivity is negligible. The sensitivity factor in the same pH range i.e. from 3.6 to 9.3 for bulk coated and nano coated are 0.11 and 0.21 respectively.

For each probe the sensitivity is more for nano coating in comparison with bulk and without coating probe. It is due to the shift in LSPR extinction maximum (λmax) which is caused by local refractive index change at different pH environment.

In the present work, it is observed that pH sensor probe with tapered U-bent is more sensitive than U-bent probe. Tapering of the fiber directly influences the number of internal reflections occurring at the beam through the tapered part of the fiber and the angle of incidence of the internal reflections while maintaining the high coupling efficiency of large fiber end face. This results in an increase in penetration depth without significantly
decreasing the light transport efficiency. Consequently the sensitivity of the tapered probe sensor is enhanced by more than one order of magnitude [9].

4.4 Conclusions

In the present investigation it is found that the Ag/PVA nanocomposite is highly sensitive to pH of the liquid environment. A significant enhancement in sensitivity of the sensor with Ag/PVA nanocomposite is observed in comparison to its bulk counterpart and the matrix alone. The fiber optic sensor with tapered U-bent fiber coated with Ag/PVA nanocomposite shows higher sensitivity in comparison to the un-tapered fiber coated with the same material.
4.5 References


