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Potential Applicability of Ag/PVA Nanocomposites as Sensing Material in Fiber Optic pH Sensor

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Abstract: In this study, the potential applicability of Ag/PVA nanocomposites as pH sensing material based on shift of LSPR is reported. A pH sensor is fabricated from low cost fiber optic and optoelectronic components including a Diode LASER (LD) source 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 U-bent fiber having coating of bulk Ag/PVA material. The material characterization and sensor performance results reveal the potential applicability of Ag/PVA nanocomposites as pH sensing material.

Keywords: pH; Sensor; Nano

1. Introduction

In recent years, great efforts have been directed towards the development of fiber optic pH sensor [1-3]. Fiber optic pH sensors have numerous advantages over conventional sensors including small and compact in size, immune to electromagnetic interference, remote sensing capability, ability to be multiplexed and the most important of which is they don’t require a reference electrode for the pH measurement [4]. In Fiber Optic pH sensor, the presence of pH environment can modulate optical or spectroscopic properties of light such as absorbance, reflectance, fluorescence, energy transfer etc. and these can be detected at the fiber output. [5,6]. For this type of sensors, generally, special materials that can reversibly change their optical characteristics with external environmental changes should be affixed or coated at the sensing portion of the optical fiber to detect physical and chemical changes.[7,8]. In this context, the metal polymer nanocomposites are expected to be potential candidate because of their unique physical and chemical properties [9]. The metal nanoparticles such as silver, gold exhibit a unique optical property called localized surface plasmon resonance (LSPR) which arises 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 [10-12]. There are several reports on the application of metal polymer nanocomposites as sensing material in various chemical and electronic sensors [13-16]. But limited works are reported for the applications of Ag/PVA nanocomposites as sensing material. ***Power et al.*** [17] developed a humidity sensor by casting Ag/PVA nanocomposites on an interdigital electrode array and the principle used in their work is the change of mobility of Ag nanoparticles in presence of water vapour. On the other hand ***Martinez-Pastor et al.***[18] designed a chemical sensor with this nanocomposites in the form of thin film which is based on the shift of LSPR position in interaction with chemical species.

In this study, we outline the feasibility of developing a fiber optic pH sensor with Ag/PVA nanocomposites as sensing material and its performance. The fabrication techniques of Ag/PVA nanocomposites as well as the sensor are important ingredients in this report. The basic principle of the present work is shift in the localized surface plasmon resonance (LSPR) extinction maximum (λmax.) of Ag nanoparticles in Ag/PVA nanocomposites in presence of pH of the liquid environment.

2. Experimental

2.1 Preparation of Ag/PVA nanocomposites

In the present work, the silver nanoparticles are generated in the PVA matrix by thermal annealing process. The synthesis process of the present work of Ag/PVA nanocomposite by thermal annealing process is the modified form of the process used by ***S. Porel. et al***.[19]. In their work thermal treatment is used after casting the reaction mixture on the substrate i.e. on the thin films. But in our work, heat treatment is used in the solution stage of the reaction mixture. The main advantage of the nanocomposites in solution form is its flexible applications. This type of nanocomposites can be used as coating on any symmetrical objects and surfaces where direct heat treatment is not possible.

In the present work, $AgNO_3$ and PVA of analytical grade purity are used without further purification. The general procedure involves the following steps-

(i) $AgNO_3$ solutions of concentration 40 mmol/L is prepared by dissolving $AgNO_3$ powder in distilled water. The mixture is stirred at room temperature in magnetic stirrer.

(ii) PVA solutions of 4wt.% is prepared in distilled water. The mixture is stirred at 60 ^{0}C for 3 hrs. in magnetic stirrer.

(iii) $AgNO_3$ solution and PVA solution is mixed in 1:1 ratio and thermal treatment of the solution is done at 130 ^{0}C for 25 minutes in digital oven to generate the Ag nano particles within PVA matrix.

(iv) The nanocomposite material is dip coated to form thin film on chemically cleaned glass substrate. The films are dried for several days at room temperature.

During sample preparation, the morphology of the films and the particle size can be varied by controlling the temperature of the reaction, time of reaction and the molecular ratio of reactants to matrix. The details fabrication chemistry and the results are reported in our earlier work [20].

2.2 Sensor fabrication

The present fiber optic pH sensor is prepared by using a PMMA (polymethyl methyl acrelyte) multimode fiber [Core diameter 980/1000 micron, numerical aperture (NA) 0.5, refractive indices of the core and the cladding are 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 ^{0}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 ^{0}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.2.1) fibers are cleaned with acetone and then dried in air for few minutes. The sensing regions of the two fibers are coated with the fabricated Ag-PVA nanocomposite. 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.

2.3 Experimental Set up

Figure 2.2 shows the experimental setup for measuring pH values using the fabricated fiber-optic pH probe. The light emitted from the intensity stabilized 4 mW diode laser (LD) source of wavelength 670 nm is guided to the sensing region of the probe via a 50:50 beam splitter to avoid any fluctuation in the LD . The photograph of the experimental set up is shown in figure 2.3.

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). The LD 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. The detector output is recoded in a digital multimeter. In this experiment, water (liquid) with different pH (from 4.0 to 9.4) 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.

Fig. 2.1: Photograph of the the tapered U-bent fiber probe.

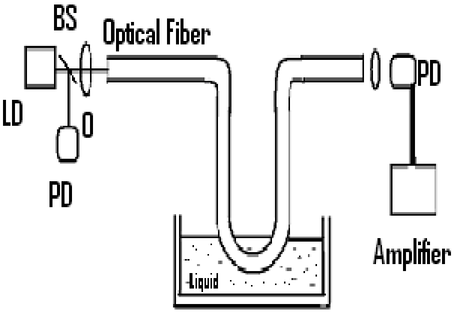

Fig. 2.2: Block diagram of the experimental set up

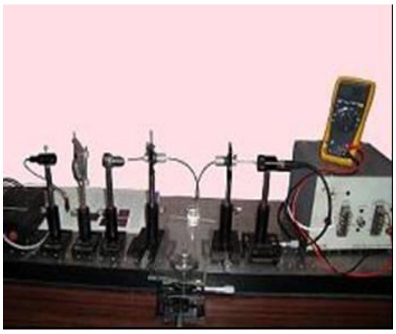

Fig. 2.3: Photograph of experimental set up

2.4 Analysis techniques

The generation of Ag/PVA nanocomposite and the size and shape of Ag nanoparticles in PVA matrix are confirmed by characterizing the prepared nanocomposite by Perkin- Elmer spectrophotometer, Scanning Electron Microscopy (SEM) and Atomic Force Microscope (AFM) (Molecular Imaging PICOSCAN TM 2500 USA).

3. Results And Discussions

3.1 UV-VIS Absorption, SEM and AFM Characterization

The UV-VIS spectrum for the fabricated film is shown in fig.3.1. The recorded spectrum shows an intense single peak at 414.4 nm. The corresponding particle size (diameter) estimated from Evanoff and Chumnov [21] relation D = 0.715λmax – 258 based on Mie Scattering Theory is 38.3 nm
[Where D = particle diameter (nm), and λmax is the SPR peak position in UV-Vis absorbance spectrum]. The singular peak in the spectrum reveals spherical shape of the Ag nanoparticles [22]. This spherical nature of the particles is further confirmed by AFM characterization. Fig. 3.2 reveals the effect of pH on λmax of Ag/PVA nanocomposites. The properties of the spectra are listed in table 1. From the table, it is found that there is red shift of λmax with increase of pH which is the key advantage of our proposed pH sensor.

Table 1: Properties of the fabricated films

Sample No.	pH	λmax (nm)	D (nm)
A	4	414.4	38.3
B	6.2	419.6	42
C	7.6	427.6	47.7

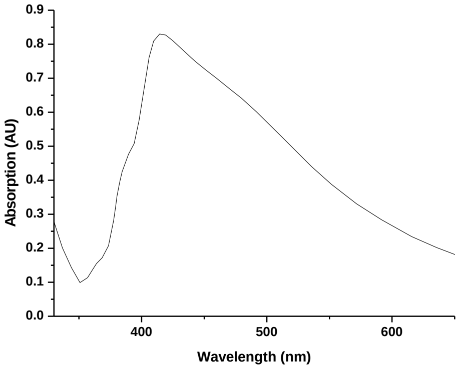

Fig. 3.1.: UV-VIS Spectrum of the fabricated nanocomposite films.

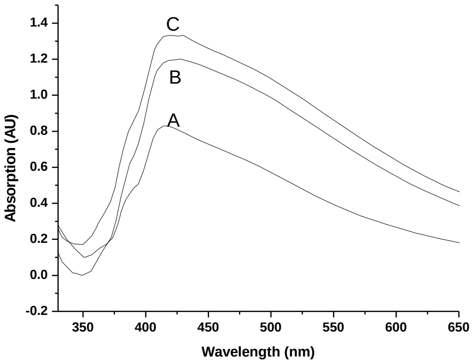

Fig. 3.2: Effect of pH on λmax of the fabricated nanocomposite film [A-=pH4, B=pH6.2, C=pH7.6]

The surface morphology and the finer details of the particles of the fabricated Ag/PVA nanocomposite thin film are investigated through SEM [fig. 3.3] and AFM characterization [fig. 3.4(a) and 3.4(b)].

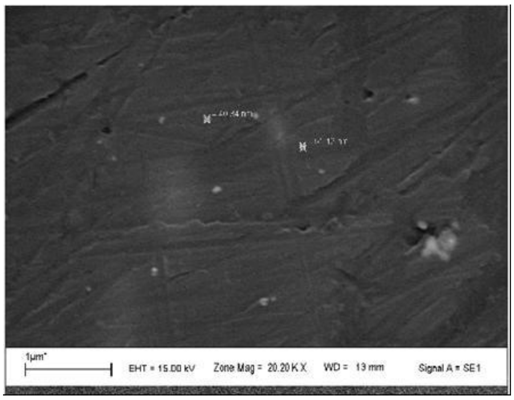

Fig. 3.3: SEM picture of the film

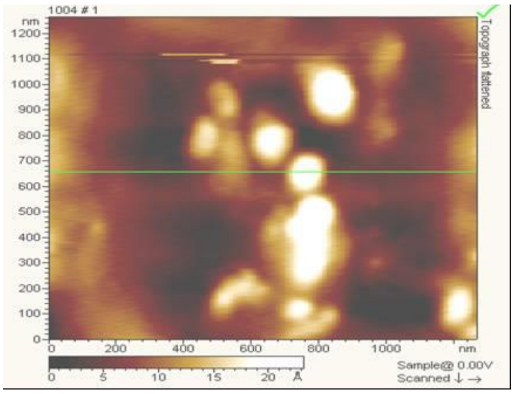

Fig. 3.4(a): AFM picture of the film

(Particle Shape)

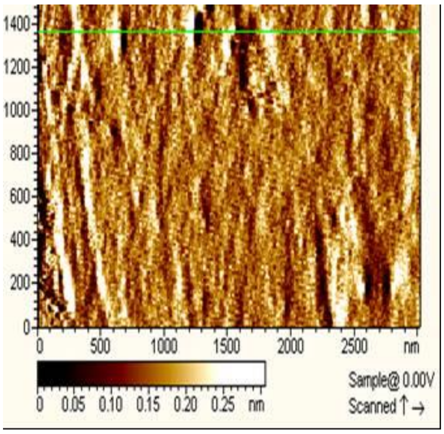

Fig. 3.4(b): AFM picture of the film

(Morphology)

3.2 Sensor Performance

To study the sensor performance, experimental investigations are carried out with U-bent and tapered U-bent fiber of same characteristics. Here the sensitivity factor is defined as the change in normalized output for a given change in pH value. In the present study, the sensitivity of the fabricate U bent fiber probe is investigated with coating of bulk Ag/PVA material and that of nanocomposite. Fig. 3.5 shows the performance of the fabricated sensors. 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 4.0 to 9.4 is 0.06 for bulk coating while it is 0.07 for nano coating. In case of tapered U-bent, the sensitivity factor in the same pH range i.e. from 4.0 to 9.4 for nano coated probe is 0.08.

The enhanced sensitivity of the nanocomposite coated U bent fiber probe in comparison to its bulk counterpart is due to the shift in LSPR extinction maximum (λmax) which is caused by change of pH at the local 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 [23].

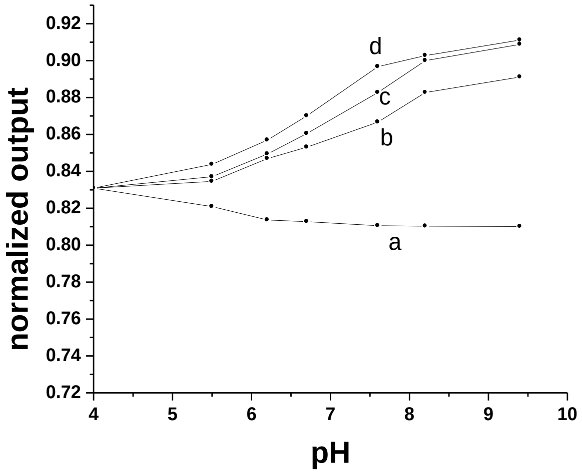

Fig. 3.5: Comparison of the sensitivity of the sensor [**a**-without Coating (U bent), **b**-Bulk Coating (U bent), **c**-Nano Coating (U bent), **d**-Nano Coating (Trapered U bent).

4. Conclusions

In the present investigation it is found that the Ag/PVA nanocomposite is sensitive to pH of the liquid environment. The theoretical expectations, material characterization results and sensor performance results are in good agreement. Hence Ag/PVA nanocomposite is a potential candidate for pH sensing material in fiber optic sensor. A significant enhancement in sensitivity (although not linear) of the sensor with Ag/PVA nanocomposite is observed in comparison to its bulk counterpart. 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. The reproducibility and optimization of the fabricated fiber probes are in progress.

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