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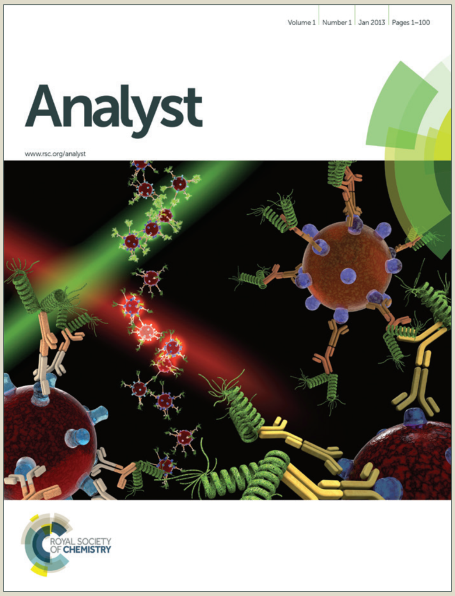

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Surface Plasmon Resonance Based Fiber Optic Detection of Chlorine Utilizing Polyvinylpyrollidone Supported Zinc Oxide Thin Films

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ABSTRACT:

Highly sensitive chlorine sensor for aqueous medium is fabricated using optical fiber surface plasmon resonance (OFSPR) system.OFSPR based chlorine sensor is designed with the multilayer type platform by zinc oxide (ZnO) and polyvinylpyrollidone (PVP) films morphology manipulations. Among all the methodologies of transduction which are reported in the field of solid state chemical and biochemical sensing, our attention is focused onto the Kretschmann configuration optical fiber sensing technique using the mechanism of surface plasmon resonance. The optical fiber surface plasmon resonance (SPR) chlorine sensor is developed using multimode optical fiber with the deposited PVP supported ZnO film over silver coated unclad core of the fiber. The spectral interrogation mode of operation is used to characterize the sensor. In Ag/ZnO/PVP multilayer system, the absorption of chlorine in the vicinity of the sensing region is performed by the PVP layer and the zinc oxide layer enhances the shift in resonance wavelength. It is, experimentally, demonstrated that the SPR wavelength shifts nonlinearly towards the red side of the visible region with the increase in the chlorine concentration in aqueous medium while the sensitivity of the sensor decreases linearly with the increase in the chlorine concentration. As the proposed sensor utilizes optical fiber it possesses the additional advantages of fiber such as less signal degradation, less susceptible to electromagnetic interference, possibility of remote sensing, probe miniaturization, probe re-usability, online monitoring, small size, light weightand low cost.

KEYWORDS: Surface plasmon resonance, optical fiber, sensor, zinc oxide, polyvinylpyrollidone, chlorine.

1. INTRODUCTION

Chlorine is present in water as a disinfectant and is added into the water to destroy harmful bacteria, virus etc. but if its quantity is above the prescribed limit then it causes water borne diseases to the human body. Further, if chlorine is inhaled by the humans above a certain quantity it causes cholera and several types of cancer. The reason behind these is the chlorinated by-products such as "chlorinated hydrocarbons" or trihalomethanes (THM's) which are harmful for human body. Most of the THM's are formed in water when chlorine reacts with naturally occurring substances such as decomposing plant and animal materials. Risk for several types of cancer and cholera are now being correlated to the consumption of chlorinated drinking water or being in touch with the chlorinated swimming pool water.[1] Therefore, it is important to maintain the quantity of free residual chlorine in the drinking or the swimming pool water which is adequate enough to disinfect bacteria and virus that may be brought into pool by swimmer himself, rain, dust particles etc. Hence, chlorine sensors with high reliability, high sensitivity, good stability and rapid response are required for the early and local detection of chlorine. Although several types of chlorine sensors are available and an immense research is going on for the detection of chlorine content in water by microelectrode methodbut these sensors have a number of drawbacks. In microelectrode based chlorine sensors, the sensing layers are in micro level[2-4] having no additional advantage which the nano size structures generally have such as 'increased surface to volume ratio'. For easy sensing of an analyte, surface to volume ratio should be more.

Nowadays, concept of surface plasmon resonance (SPR) along with optical fiber has led to a fruitful technology in sensing of several parameters. This technology has emerged as a powerful tool for sensing of various physical, chemical, biochemical parameters and has found applications in environment monitoring, microbiology, medical technology etc. Among the various other sensing techniques, viz interferometers, waveguide methods and grating coupler, the SPR technique has edge over conventional optical sensor techniques because it possesses several important and improved features like high sensitivity, easy to operate, no requirement of electrical signal, reliability, safety etc.[5-11] Surface plasmon resonance is also a fascinating technique for gas sensing and is useful in sensing of several flammable, explosive and toxic gases. The technique is based on the excitation of surface plasmons at the metal-dielectric interface. Surface plasmons can be considered as the 'electromagnetic excitations' or 'charge density oscillations of conduction electrons' propagating along the boundary between metal and dielectric.[12-15] Instead of metal, other lossy media with sufficiently high free electrons density can also be considered. Such surface plasmon (SP) wave can be excited only by p-polarized incident light wave. In nature, SP wave is TM polarized and their electromagnetic fields decay exponentially in metal as well as in dielectric.[16-19] When a specific resonance condition is reached i.e. the condition where the propagation constant of the excitation light becomes equal to the propagation constant of the SP wave, the maximum power of the incident electromagnetic wave can be coupled with the surface plasmons as a result the power carried with the reflected wave drops down remarkably. The resonance condition is sensitive to the value of the refractive index or the dielectric function of the surrounding medium (analyte). [20-24] This mechanism of the change in refractive index (or dielectric function) which appears in the form of the shift of the power reflectance minimum can be used to sense the properties of the surrounding medium such as concentration of gas or other chemical substances.

In this paper, we report the fabrication and characterization of a fiber optic chlorine sensor in which the experimental measurements of SPR spectra are carried out on optical fiber core modified by depositing several materials viz. silver (Ag), ZnO (zinc oxide) and polyvinylpyrollidone (PVP) for different concentrations of chlorine present in aqueous sample. Silverin place of other metals is usedfor the fabrication of the probe because in the case of silver the ratio of the real and imaginary parts of the dielectric constant is highest soit exhibits a very sharp SPR curve.[25-27] The absorption of chlorine takes place by a sensitive thin layer of PVP supported on zinc oxide. The presence of chlorine in water around PVP layer modifies the effective refractive index of the PVP film which results in the shift in SPR spectrum on changing the concentration of chlorine in water. It is observed that the addition of chlorine in water leads to the change in the pH of the water. To confirm whether the shift in SPR spectrum is solely due to chlorine or pH, the experiments carried out on the probe with water of different pH values show no shift in SPR spectrum which implies that the PVP layer is sensitive towards chlorine only. The additional advantage of proposed sensor, in comparison to microelectrode based sensor, is that the thicknesses of Ag, ZnO and PVP films are in nano range thus have large surface to volume ratio so the gas molecules get more access to sensing surface and get easily sensed.

2. EXPERIMENTAL

2.1Fabrication of the probe

For the fabrication of the fiber optic probe for chlorine sensing, plastic clad silica fiber of core diameter 600 micrometer and numerical aperture 0.37 (Fiberguide Industries) was used. First of all, cladding was removed from approximately 1 cm length, in the middle, of the 15 cm long fiber. After removing cladding, the unclad portion of the fiber was cleaned by acetone and subsequently by methanol in the ultrasonic bath. Thin film of silver of typically 40 nm thickness was deposited over unclad core of the fiber using high tension plasma bombardment in a vacuum chamber with chamber pressure typically $5x10^{-6}$ mbar by thermal evaporation coating unit (Hind High Vacuum Co., Model: 12A4D). To achieve such a low pressure, two types of vacuum pumps were provided in the coating unit. One was rotary pump and the other was diffusion pump. The vacuum chamber was connected to both these pumps. The high vacuum was achieved step by step. First, the rotary pump was started to increase the vacuum level in the chamber up to 10^{-3} mbar which was termed as 'roughing the chamber'. As the pressure inside the chamber reached to 10^{-3} mbar, the diffusion pump was started to increase the vacuum level further, this time the vacuum level reached to the orders of $5x10^{-6}$ mbar which is called as 'baking the chamber'. At this level of vacuum, the heating of the material was initiated by passing the current so the word 'baking' was used for the material to be coated. The amount of current used depends on the melting point of the material to be coated which ranges from 0-100 amperes. The substrate fiber was fitted just above the material to be coated on it in the vacuum chamber. The roughing of the system takes about 20 min, followed by baking for further 20 min. The increase in the temperature of the chamber was avoided by continuously running water. For coating, gradually the current was increased to evaporate silver for the deposition on the unclad portion of the optical fiber kept in the chamber. As the surface plasmon resonance highly depends on the thickness of the metal layer, the rate of deposition and the thickness of the silver film were monitored by quartz digital thickness monitor attached with the chamber of the unit. For achieving uniform thickness of the silver film over core of the fiber, the fiber was repeatedly rotated during coating. After this, the system was allowed to cool and the fibers were taken out of the vacuum chamber. As the coating was carried out in high vacuum environment the chances of oxidation of silver are very less. Films of zinc oxide (10 nm) and then PVP of different thickness were deposited over silver coated fibers using same method as used for silver coating.

In the fabricated probe, silver plays the role of an SPR active metal, ZnO is responsible for shifting the resonance wavelength to the longer range and PVP acts as a chlorine sensing layer as it is highly sensitive tochlorine. By coating the unclad portion (core) of the optical fiber with a thin layer of silver, an SPR optical arrangement based on Kretschmann configuration is realized. It may be noted that PVP is hygroscopic in nature.[28] Therefore, the coated probe was annealed at high temperature in vacuum to make the probe reusable. Further it reduced the permeability of the film towards the liquid sample.[29]

Figure 1 shows the lateral cross-sectional view of the SPR based fiber optic chlorine sensor probe fabricated by using multi-layers of Ag/ZnO/PVP thin films. Because of the difference of refractive indices between the core and the cladding material an evanescent wave is induced at the interface of the core and silver layer. After propagating through the sensing region, the light would partially re-coupled into the core of the downstream multimode fiber. In this way, by coating the unclad portion of the optical fiber by Ag/ZnO/PVP layers, an SPR optical arrangement is realized in the similar way as in the case of prism based Kretschmann configuration sensor. The basic reason to use thepolymer PVP over the ZnO layer is to combine the properties of ZnO and PVP so as to improve the sensing behavior. ZnO is found to be such that it has large number of defects or oxygen vacancy on its surface and PVP is proved to be such that its dielectric function is influenced in the presence of chlorine.

2.2. Experimental set up

The schematic diagram of the experimental set up of the chlorine sensor based on optical fiber is depicted in Figure 2. The setup is consisted of the glass flow cell where the fabricated fiber optic probe was fixed and its one end was connected to the polychromatic light source while the other end was connected to the spectrometer that was interfaced to the personal computer to record the SPR spectrum. The boat shape glass flow cell was designed in such a way thata proper sealing arrangement at all its openings could be achieved to prevent the leakage. The glass flow cell was evacuated time to time manually so as to remove the residual and undesirable gases or liquids from it. The water samples of varying chlorine concentration were prepared separately. The precautions were taken in filling the flow cell with the prepared sample so that chlorine released within the water and reaction between water and chlorine resulted in the formation of hypochlorous and hydrochloric acids as products which accordingly changed the pH of the solution. The SPR spectra were recorded for different concentrations of chlorine present in the water at room temperature and pressure. The resonance wavelengths and sensitivity corresponding to different concentrations of chlorine were determined from these SPR spectra.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the mechanism of sensing of chlorine by the fabricated probe having multilayer of Ag/ZnO/PVP. At room temperature and pressure, the addition of chlorine in water initiates the reaction between chlorine and water resulting in the formation of two acids as intermediate products which change the pH of the aqueous solution from neutral (pH 7.0) to acidic (less than pH 7.0). In this way, the absorption of chlorine changes the pH of the solution. These acids contain chloride ions which change the complex dielectric function of PVP and ZnO thin films where PVP acts as chlorine sensing layer and its dielectric function gets influenced by the chloride ions. The physical reason of the change in the dielectric function of PVP supported ZnO film can be better understood by the reactions involved during the whole process. As soon as the chlorine is dissolved in water it gets disproportionate into hydrochloric acid (HCl) and hypochlorous acid (HClO). The hydrochloric acid, a strong acid, contains hydrogen ions (H^+) and chloride ions (Cl^-) whereas hypochlorous acid is a weak acid and partially dissociates into chloride ions (H^+) and hypochlorous ions (OCl^-); the presence of these two acids changes the neutral (without adding chlorine to water) behavior of solution into acidic. When chloride ions enriched solution comes in contact with the fabricated probe (fiber core/Ag/ZnO/PVP) it changes the dielectric function of PVP which in turn shifts the resonance wavelength. The reaction involved is given below.

$$H_2O_{(l)} + Cl_{2\,(g)} \rightleftharpoons HClO_{(l)} + HCl_{(l)}$$

The two acids get disproportionate into hydride ions, chloride ions and hypochlorous ions according to the following reactions

$$HClO \rightleftharpoons H^+ + OCl^-$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

The hypochlorous acid is the principal water disinfectant and gets disproportionate into H^+ and OCl^- ions. The OCl^- ion is a strong oxidizing agent and is an effective biocide widely used to kill bacteria and algae. The hypochlorous acid remnant within the water solution is free residual chlorine. Thus, chlorine in the form of HClO is needed for sanitation whereas the chlorine in the form of ClO^- is needed for oxidization.

Figure 4 shows the SPR spectra of fiber optic SPR probe having layers of silver (Ag), zinc oxide (ZnO) and polyvinylpyrollidone (PVP) with respective thicknesses of 40 nm, 10 nm and 5 nm for chlorine concentration values varying from 0 ppm to 5 ppm at room temperature. It may be noted that as the concentration of chlorine increases, the SPR curve shifts towards red which implies that with the increase in the concentration of the chlorine the SPR resonance wavelength increases. Figure 5 shows the variation of the resonance wavelength of the SPR spectrum with the concentration of the chlorine. It is clear from the figure that the resonance wavelength increases with the increase in the concentration of the chlorine but the rate of increase in resonance wavelength decreases as the concentration of chlorine increases. It appears that the resonance wavelength saturates beyond 5 ppm concentration which implies that the sensor has a fixed range of operation. Since the concentration of chlorine in water beyond 5 ppm is harmful for the human body, therefore, it is required to sense the chlorine up to 5 ppm.[30]As mentioned above, the shift in the resonance wavelength is because of the interaction of the chlorine with the PVP molecules and their adsorption in the pores of ZnO film. For the lower concentration of chlorine, the available PVP molecules per chloride ions is large so the change in the resonance wavelength is more but if we increase the concentration of the chlorine molecules beyond a certain value the number of PVP molecules per chloride ions decreases. Hence, at higher concentration of the chlorine no further shift in the resonance wavelength is observed. In terms of optical properties, the refractive index of PVP increases with the increase in the concentration of chlorine and it becomes constant after nearly 5 ppm concentration of the chlorine.

Figure 6 shows the variation of the sensitivity with the concentration of the chlorine for the probe having Ag/ZnO/PVP multi-layers coatings over unclad core of the fiber. The sensitivity has been defined as the shift in resonance wavelength per unit change in the concentration of the chlorine in water. With the increase in the concentration of the chlorine, the sensitivity linearly decreases. It becomes negligible at higher concentrations of the chlorine and becomes nearly zero for the concentrations greater than 5 ppm. The physical reason behind this is that at higher concentrations of chlorine, the chloride ions got reacted completely with the molecules of the PVP and a small repulsion force roles in and due to this the sensitivity decreases.

It may be noted that the experiments carried out above were on the probe having 5 nm thickness of PVP layer. The thicknesses of silver and zinc oxide layers used have already been optimized and reported in the literature. Therefore, to obtain the optimum thickness of the polyvinylpyrollidone thin film the experiments were carried out on fiber optic probe with different thicknesses of PVP layer keeping the same thicknesses of silver and zinc oxide layers. The optimum thickness corresponds to the maximum shift in the resonance wavelength for a given change in the concentration of chlorine in water and hence to the maximum sensitivity of the sensor. Figure 7 shows the shift in the resonance wavelength as a function of the PVP layer thickness for the chlorine concentration range 0-5 ppm. According to the plot, as the thickness of the PVP layer increases the total shift in the resonance wavelength for 0 to 5ppm concentration change of the chlorine increases up to a particular value of the thickness after which if the thickness of the PVP film is increased the total shift in the resonance wavelength decreases. The maximum shift and hence the maximum sensitivity occurs around 5 nm thickness of the PVP layer. To confirm this the SEM images of the deposited PVP layer of varying thicknesses were recorded to see the morphology of the top PVP layer. Figures 8(a) to 8(c) show such SEM images of 3 nm, 5 nm and 7 nm thick PVP film over ZnO and silver coated fiber optic SPR probe, respectively. It can be seen that the film in all the three cases is not continuous and formed from islands. This is due to the intermixing of the PVP in the ZnO matrix which has strong influence on the dielectric function of the composite. It can be seen from the SEM images that the formation of islands is maximum in the case of 5 nm thick PVP film than in 3 or 7 nm thick films. In addition, the sputtered PVP layer occupies the position of some defects level of the ZnO similar to phenomenon like the substitutional defects in which a foreign atom occupies a position in the parent atom resulting in the intermixing of the two materials.[31] On interaction of PVP supported ZnO films with the chlorine molecules, the dielectric function of the film gets highly influenced due to which a red shift in the SPR spectrum is obtained. But the intermixing of the PVP with the ZnO particles can occur only up to a certain limit beyond which the intermixing or the possession of PVP particles in the ZnO matrix is not allowed due to the roles of some repulsion forces among the PVP particles. This is the reason of the optimum thickness of PVP layer which means that beyond a certain limit, the PVP molecules in ZnO matrix become constant and on further increasing the thickness of the PVP layer the intermixing decreases and the PVP remains stick on the surface of ZnO. Since the PVP and ZnO intermixed matrix is responsible for the chlorine sensing the depositing of the PVP beyond a certain limit introduces a repulsion force among them which reduces the shift. There are various other material in which the mixing of the material is useful. The intermixing of the material and accordingly formation of alloys can also be understood by metal-metal interaction which occurs in Au-Ag, Au-Cu, and Au-Pd.[32]

In order to justify the best combination of the fabricated layers for chlorine sensing, shift in resonance wavelength versus concentration of the chlorine were determined for probes fabricated with different combinations of the layers. Figure 9 shows the shift in resonance wavelength for chlorine concentration range from 0 ppm to 5 ppm for probes fabricated with different combinations of layers. It is clear from the figure that the amount of shift is highest for the multilayer Ag/ZnO/PVP; the basic reason for highest sensitivity of this combination is that in this combination Ag plays the role of an SPR active metal, ZnO is responsible for shifting the resonance wavelength to the longer range and PVP acts as the chlorine sensing layer as it is highly sensitive for chlorine. Beside this probe the other probes tested were having following combinations of layers: ZnO/PVP, Ag/PVP, and Ag/ZnO. In ZnO/PVP probe, Ag is absent which is SPR active material and therefore reduces the shift in SPR curve, similarly in Ag/PVP in which ZnO is not sandwiched between Ag and PVP, the absence of oxygen vacancy available in ZnO decreases the attachment of chlorine molecules and hence the extra shift in SPR curve. In the case of Ag/ZnO, no PVP layer, least amount of shift is observed which may be due to those molecules which reside over the surface of ZnO due to its oxygen vacancy and get sensed.

As mentioned above, increase in chlorine concentration decreases the pH of the water, the pH of the water samples were measured for different concentrations of the chlorine present in the water. Figure 10 shows the variation of the pH with the concentration of the chlorine. With the increase in the concentration of the chlorine, the pH of the solution continuously decreases and enters in acidic value from the neutral value. It becomes nearly 6.3 for 5 ppm concentration of chlorine and is in accordance with the reported values[33].The reason behind decrement in pH has already been discussed above in detail. Therefore, to verify whether the shift in resonance wavelength is due to chloride ions or pH the experiments on Ag/ZnO/PVP coated probe were carried out for water samples of different pH values and resonance wavelength from their SPR spectra were determined. Figure 11 shows the variation of resonance wavelength with the pH of the solution for the fabricated probe having layers of Ag (40nm)/ZnO (10nm)/PVP (5nm). From the figure it is noted that no shift in resonance wavelength is observed on changing the pH of the solution. It is therefore clear that the fabricated probe cannot sense the pH of the solution and it is only be used to sense the chlorine concentration in aqueous solution. Hence the use of fabricated multilayer probe for chlorine sensing is justified.

It may be noted that the proposed sensor is capable of sensing only admissible limit of chlorine in drinking and swimming pool waters. In other words, the concentration of chlorine which can be sensed by the probe in the present study is the optimum level of chlorine which will be safe if consumed by the human being and beyond this limit, it will be harmful no matter how much quantity it exceeds from the optimum limit.[33]Any concentration of chlorine greater than 5 ppm in aqueous medium will give the maximum sensor response. Therefore, the aim of the present study is to detect the chlorine content before it causes harm to the human body.

In the present study, the sensing of chlorine in aqueous medium has been carried out using Ag/ZnO/PVP multilayer coated fiber optic sensor. To check the specificity/selectivity of the sensor towards chlorine in aqueous medium, one has to study the response of the sensor to various other gases independently. However, there are many gases which cannot be dissolved in water or their content in water is so small that it cannot be comparable to the content of chlorine. Further, their solubility depends on the temperature of the water. But there are few other gases (like CO_2, SO_2 and NH_3) which can be dissolved in large quantity in water but these cannot be sensed by PVP layer coated probe only. Some modifications may be required for the sensing of some of these gases.[34-36] Due to this reason, experiments, to confirm the selectivity/specificity of the sensor towards chlorine, have not been carried out for other gases which can be dissolved in water. The results reported in the literature can be taken as the proof of selectivity of the sensor. However, the experiments carried out and the predictions made in the present study are new to the researchers working in this area.

4. CONCLUSIONS

In summary, fabrication and characterization of the surface plasmon resonance based fiber optic chlorine sensor have been carried out. The probe is fabricated by depositing thin films of silver, zinc oxide and polyvinylpyrollidone over the unclad portion of the fiber by thermal evaporation technique. The sensor works on the principle of the change in the refractive index of the polyvinylpyrollidone supported zinc oxide film when the molecules of the sensing layer come in contact with the chlorine. Spectral interrogation method is used for the characterization of the sensor. The sensitivity of the sensor linearly decreases with the increase in the concentration of the chlorine. The performance of the sensor is compared with those having different combinations of the same multilayers. The maximum amount of shift in resonance wavelength is obtained in the case of Ag/ZnO/PVP layers fabricated sensor. The sensor possesses maximum sensitivity for 5 nm thickness of the PVP film.

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Figure captions

Figure 1: The lateral cross-sectional view of the SPR based fiber optic chlorine sensor probe utilizingAg/ZnO/PVP thin films.

Figure 2: Schematic of the experimental set-up for the detection of chlorine.

Figure 3: Mechanism of sensing of chlorine by the fiber optic probe having multilayer of Ag/ZnO/PVP.

Figure 4: Surface plasmon resonance spectra of fiber optic SPR probe for different concentrations of the chlorine. The probe has multilayer of silver (40nm) and zinc oxide (10 nm) and PVP (5nm).

Figure 5: Variation of resonance wavelength with the concentration of the chlorinefor the fabricated probe having layers of Ag (40nm)/ZnO (10nm)/PVP (5nm).

Figure 6: Variation of sensitivity of the sensor with the concentration of the chlorine for the SPR probe having multilayer of Ag (40nm)/ZnO (10nm)/PVP (5nm).

Figure 7: Variation of the total shift in the resonance wavelength (for 0 to 5 ppm concentration of chlorine) with the thickness of the PVP layer. The thickness of the silver layer was 40 nm and that of zinc oxide was 10 nm.

Figure 8: SEM images of the Ag (40nm)/ZnO (10nm)/PVP deposited films for (a) 3 nm, (b) 5 nm, and (c) 7 nm thick PVP film.

Figure 9: Shift in resonance wavelength for chlorine concentration range from 0 ppm to 5 ppm for different fabricated sensing probes.

Figure 10: Variation of pH of the chlorinated water as a function of concentration of chlorine.

Figure 11: Variation of resonance wavelength with the pH of the solution for the fabricated probe having layers of Ag (40nm)/ZnO (10nm)/PVP (5nm).

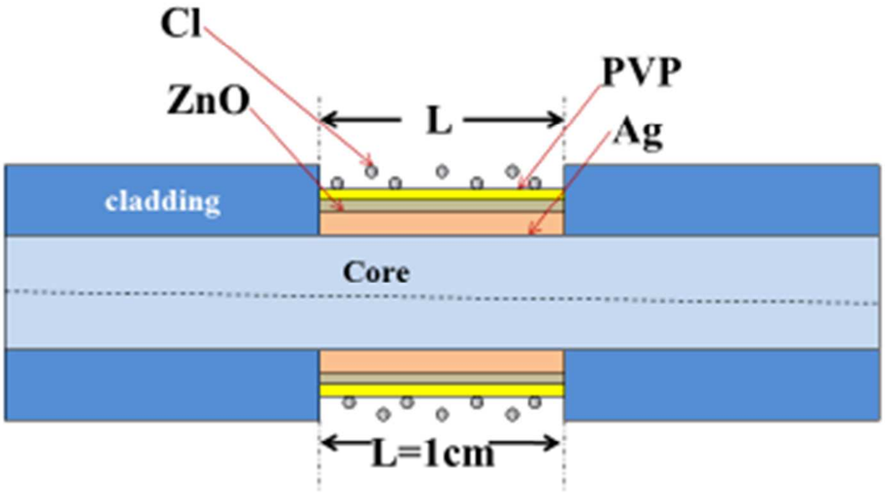

Figure 1

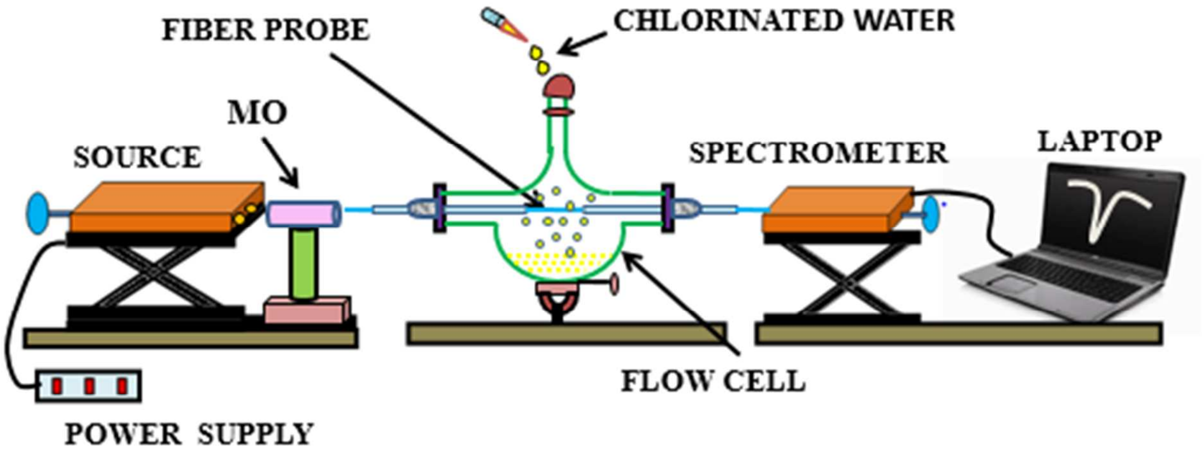
FIBER PROBE
CHLORINATED WATER
MO
SOURCE
SPECTROMETER
LAPTOP
FLOW CELL
POWER SUPPLY

Figure 2

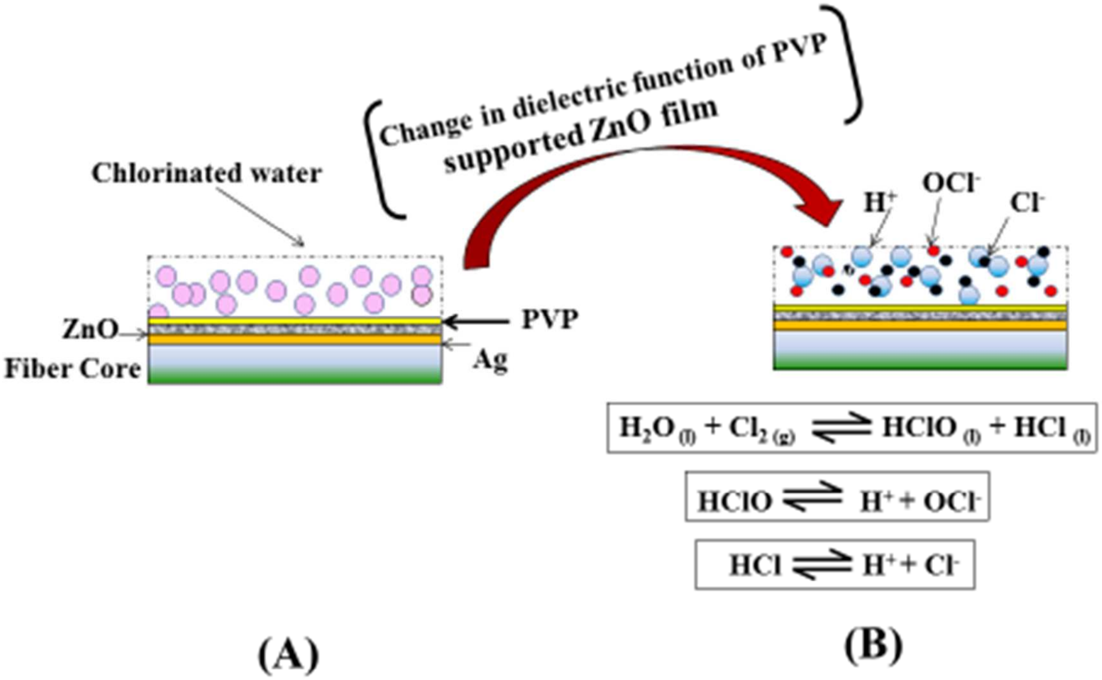
Change in dielectric function of PVP supported ZnO film
Chlorinated water
ZnO
PVP
Fiber Core
Ag
H+
OCl-
Cl-
$H_2O_{(l)} + Cl_{2\,(g)} \rightleftharpoons HClO_{(l)} + HCl_{(l)}$
$HClO \rightleftharpoons H^+ + OCl^-$
$HCl \rightleftharpoons H^+ + Cl^-$
(A)
(B)

Figure 3

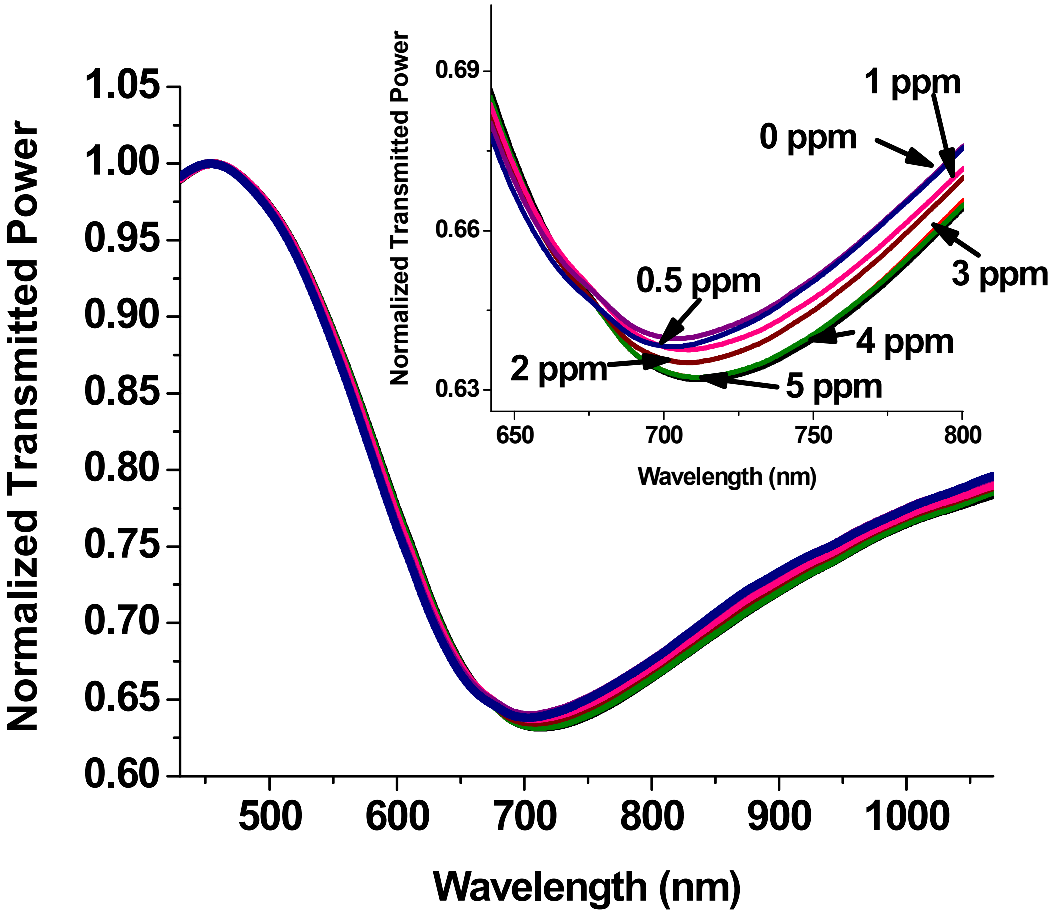
Normalized Transmitted Power
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
500
600
700
800
900
1000
Wavelength (nm)
Normalized Transmitted Power
0.69
0.66
0.63
650
700
750
800
Wavelength (nm)
1 ppm
0 ppm
0.5 ppm
3 ppm
4 ppm
2 ppm
5 ppm

Figure 4

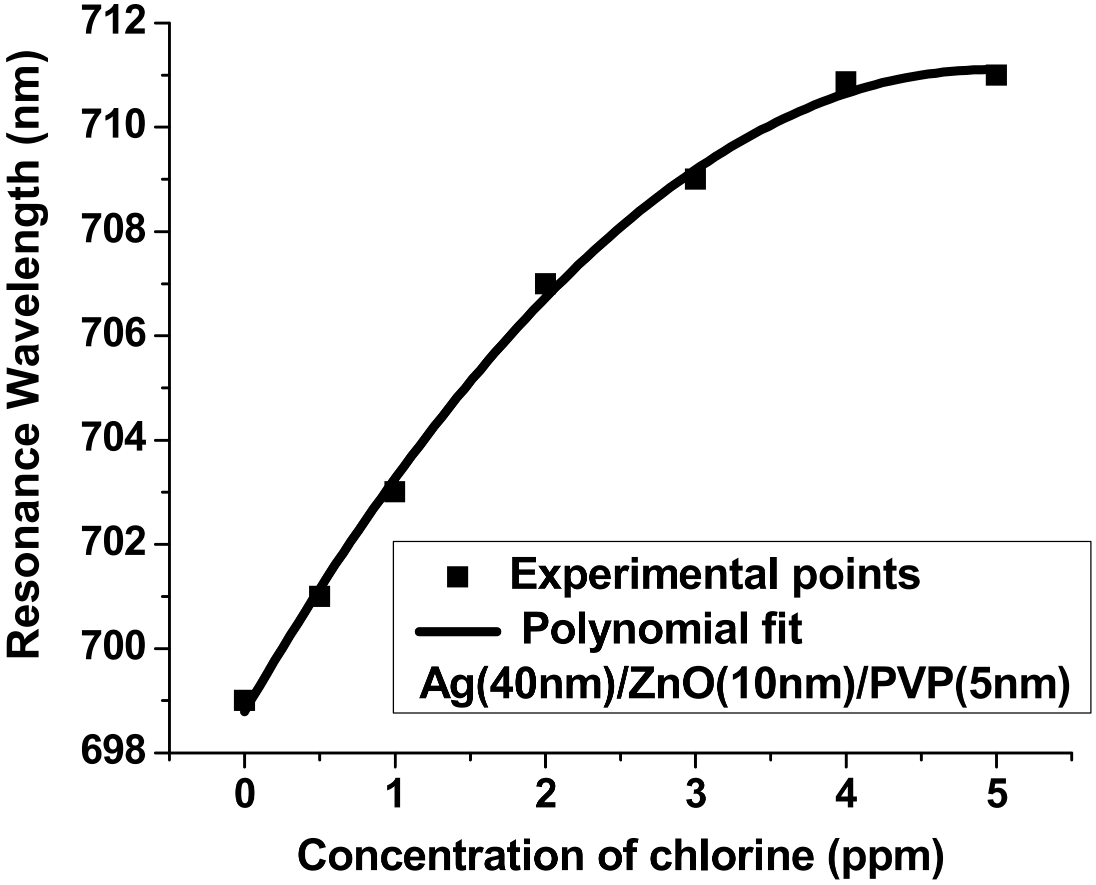
Resonance Wavelength (nm)
712
710
708
706
704
702
700
698
0
1
2
3
4
5
Concentration of chlorine (ppm)
■ Experimental points
Polynomial fit
Ag(40nm)/ZnO(10nm)/PVP(5nm)

Figure 5

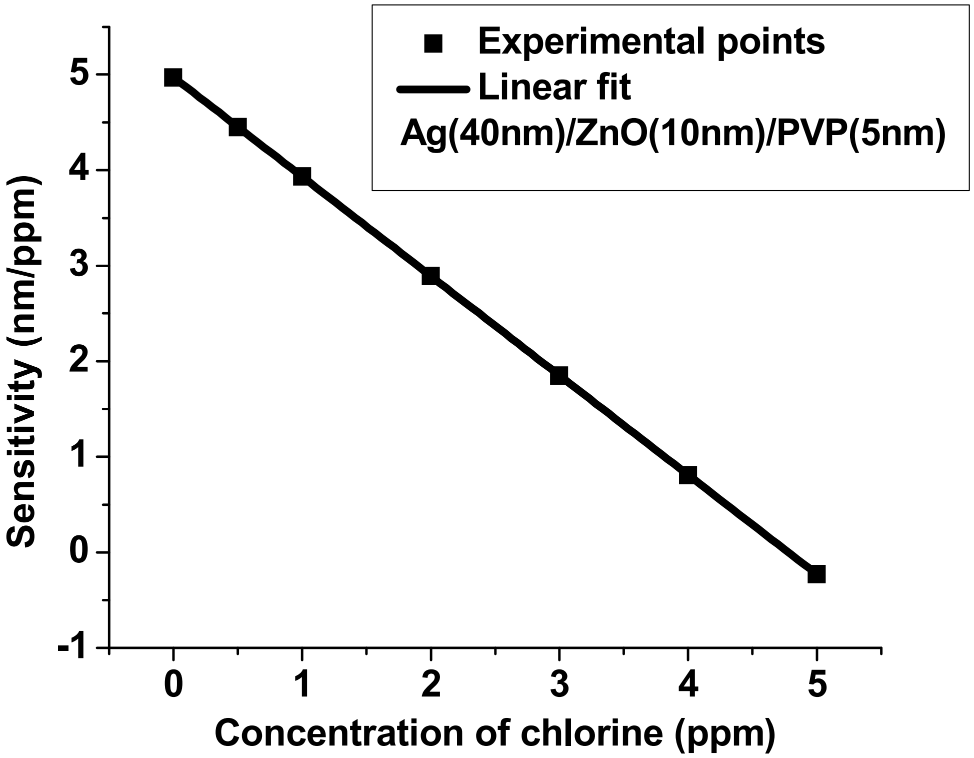
■ Experimental points
Linear fit
Ag(40nm)/ZnO(10nm)/PVP(5nm)
Sensitivity (nm/ppm)
5
4
3
2
1
0
-1
0
1
2
3
4
5
Concentration of chlorine (ppm)

Figure 6

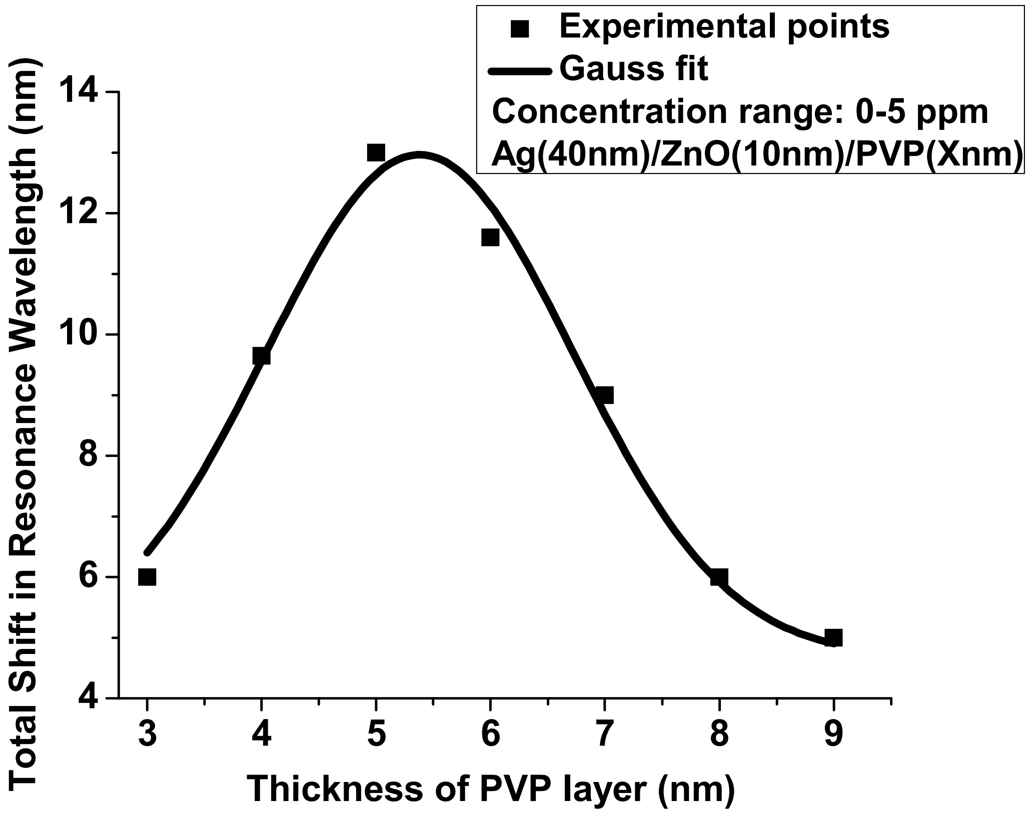
■ Experimental points
Gauss fit
Concentration range: 0-5 ppm
Ag(40nm)/ZnO(10nm)/PVP(Xnm)
Total Shift in Resonance Wavelength (nm)
4
6
8
10
12
14
3
4
5
6
7
8
9
Thickness of PVP layer (nm)

Figure 7

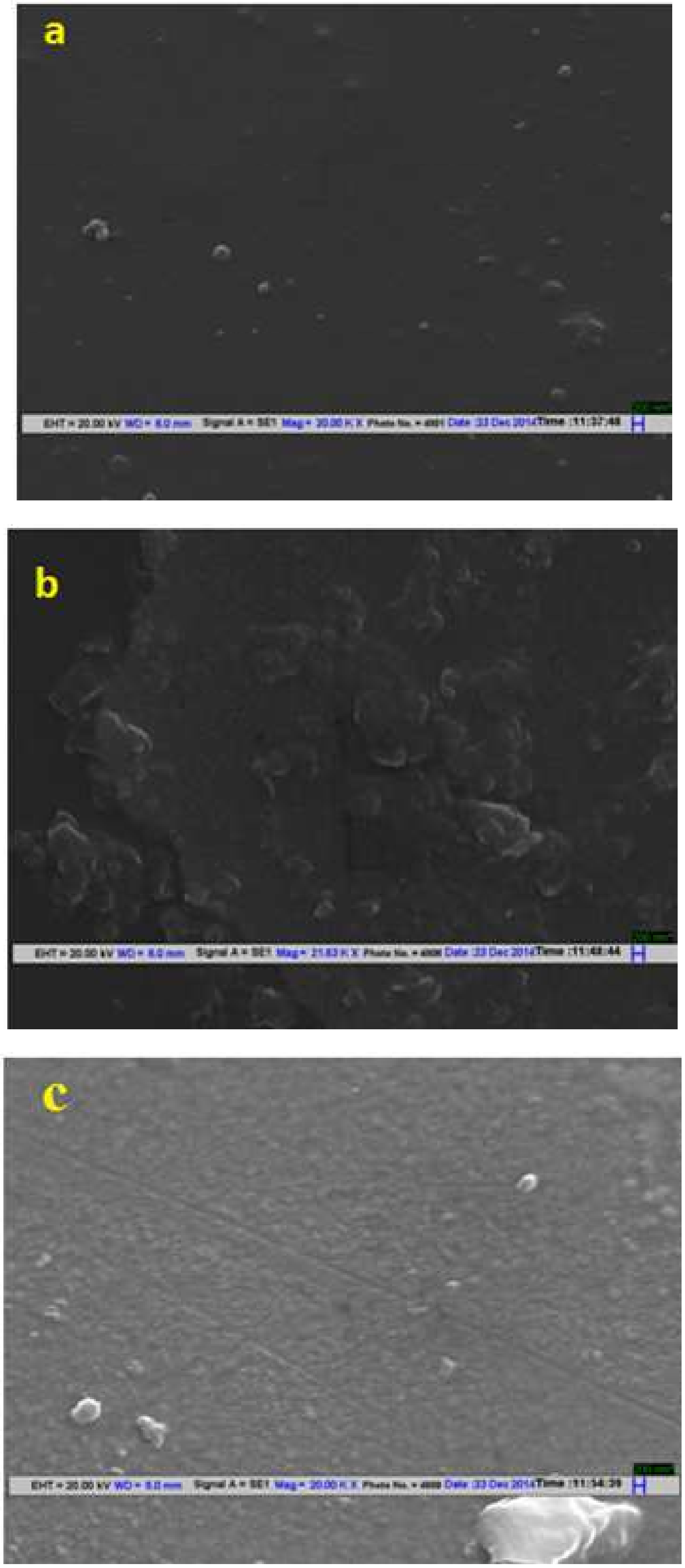
a
EHT = 20.00 kV WD = 8.0 mm Signal A = SE1 Mag = 20.00 K X Date :23 Dec 2014 Time :11:37:48
b
EHT = 20.00 kV WD = 8.0 mm Signal A = SE1 Mag = 21.83 K X Date :23 Dec 2014 Time :11:43:44
c
EHT = 20.00 kV WD = 8.0 mm Signal A = SE1 Mag = 20.00 K X Date :23 Dec 2014 Time :11:54:39

Figure 8

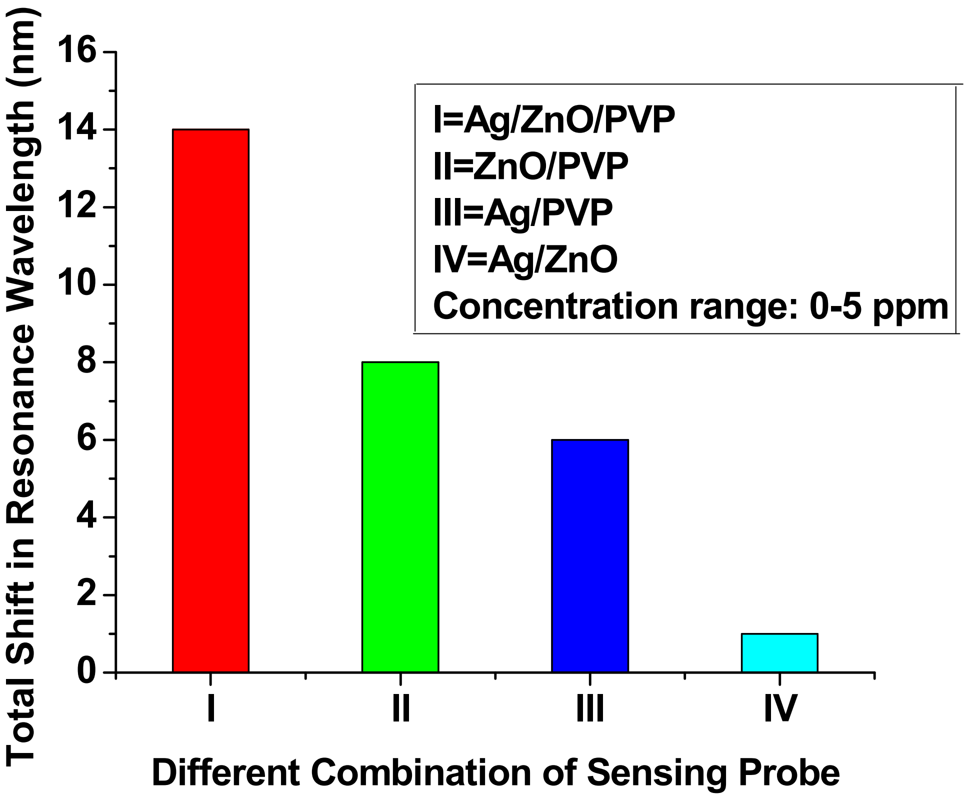
Total Shift in Resonance Wavelength (nm)
0
2
4
6
8
10
12
14
16
I=Ag/ZnO/PVP
II=ZnO/PVP
III=Ag/PVP
IV=Ag/ZnO
Concentration range: 0-5 ppm
I
II
III
IV
Different Combination of Sensing Probe

Figure 9

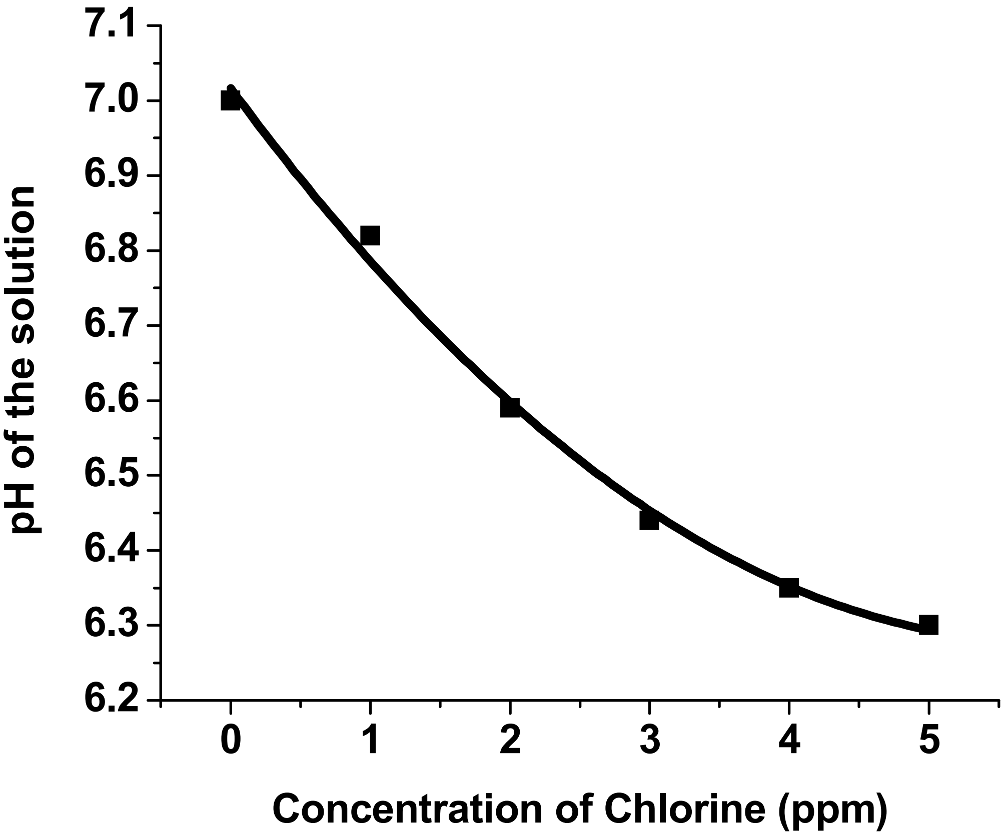
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
pH of the solution
0
1
2
3
4
5
Concentration of Chlorine (ppm)

Figure 10

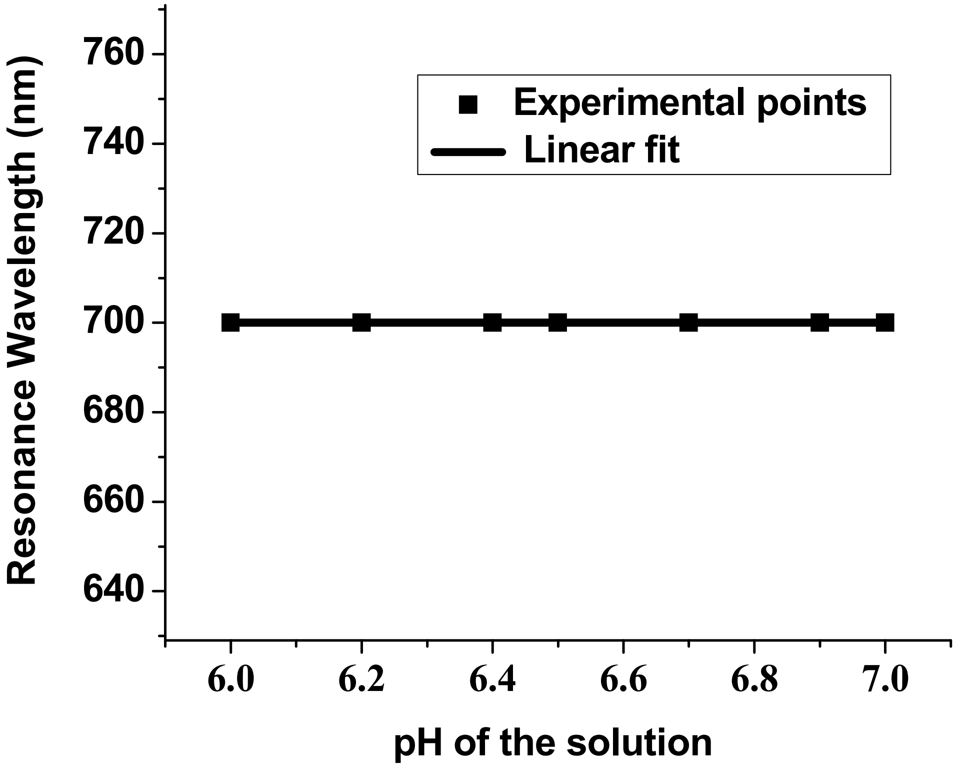
Resonance Wavelength (nm)
760
740
720
700
680
660
640
Experimental points
Linear fit
6.0
6.2
6.4
6.6
6.8
7.0
pH of the solution

Figure 11