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LSPR based fiber optic sensor for fluoride impurity sensing in potable water

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Abstract. We have designed localised surface plasmon resonance (LSPR) based fiber optic sensor. Silver nanoparticles are deposited on a few centimetre length of bare core at the middle part of plastic clad silica fiber by means of a simple and low cost laser induced nanoparticle deposition technique. The nanoparticle deposition was confirmed by TEM analysis. The nanoparticle coated fiber is used to design the sensor and the response of sensor was studied to sense fluoride impurity in water.

1. Introduction

Potable water is one of the most valuable natural resource that our planet has. Water is essential to sustain life and a safe, adequate and accessible supply must be available to all. Improving access to safe drinking-water can result in tangible benefits to health. Fluoride has beneficial effects on teeth at low concentrations (below 1 ppm) in drinking-water, but excessive exposure to fluoride in drinking-water give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. Fluoride levels between 0.3 and 6.9 mg l^{-1} was found in four villages in the Jind district of Haryana, India [1]. Choubisa et al. examined the prevalence of skeletal fluorosis in Rajasthan in adults exposed to fluoride levels of 1.4 & 6 mg l^{-1} [2] The recommended level of fluoride in drinking water is 1-1.5mg/l as directed by World Health Organization (WHO) [3]. There are various chemical as well as optical techniques used for determination of fluoride impurity in water [4] such as ion selective electrode, colorimetric method [5], atomic absorption spectroscopic method [6], ion chromatography [7] etc. These techniques in general require expensive and standard laboratory equipment and sample pre-treatment apart from the trained staff. Consequently for quick analysis of fluoride in potable water there is a need to develop a simple sensitive and convenient method.

In recent years, localised surface plasmon resonance (LSPR) based fiber optic sensors have fascinated many researchers for various applications in physical chemical and biochemical field [8-9] due to their simplicity in design, low cost, high sensitivity, accuracy, on line monitoring, remote sensing etc. LSPR based fiber optic sensor probe was fabricated by using simple and low cost laser induced nanoparticle deposition technique [10]

2. Theory

Localised surface plasmons (LSPs) are quanta of charge density oscillation in metal nanoparticles. Surface plasmons are excited when the frequency of incident light becomes equal to that of the oscillation frequency of conduction electrons of metal nanoparticles. This results in the absorbance of incident light and is called localised surface plasmon resonance (LSPR). The LSP resonance wavelength is highly dependent on the shape, size, material and surrounding medium of the nanoparticles [11] which can be utilised for sensing applications. In our case the unclad portion of a multimode PCS fiber is coated with silver nanoparticles. The nanoparticles are surrounded by sensing medium. Light is launched from one end of the fiber. If P_0 is the power transmitted by the fiber in the absence of a sensing medium, then the power transmitted along the fiber in the presence of a sensing medium is given by [12].

$$P = P_0 e^{-\gamma L} \quad (1)$$

Here γ is the evanescent absorption coefficient of the sensing medium, L is the length of sensing medium. The evanescent field interact with the nanoparticles resulting in wavelength dependent absorption. The evanescent absorption coefficient of a ray making angle θ with the normal to the interface is given by [13].

$$\gamma = \frac{NE\lambda n_2 \cos\theta \cot\theta}{2\pi\rho L n_1^2 \cos\alpha cos^2\theta_c (sin^2\theta - sin^2\theta_c)^{1/2}} \quad (2)$$

Here E is the extinction coefficient of a single metal nanoparticle, ρ is the radius of core of the fiber, N is the total number of nanoparticles that can be attached to the bare core of the fiber, n_2 is the refractive index of the metal nanoparticle, n_1 is the refractive index of core of the fiber, $\theta_c = Sin^{-1}(n_2/n_1)$ is the critical angle for sensing region and α is the skewness parameter. The extinction coefficient of metal nanoparticle is derived using Mie theory and is given by [11].

$$E = \frac{24\pi R \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2(\lambda,R)}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2(\lambda,R)} \quad (3)$$

ε_1,ε_2 being the real and imaginary part of metal dielectric constant, respectively. ε_m is the dielectric constant of surrounding medium and R is the radius of nanoparticle. A sharp absorption peak will be observed in the absorption spectrum when ε_1= -2ε_m , called as the resonance condition. For different values of the dielectric constant of sensing medium (ε_m), the resonance condition will be satisfied for different values of the wavelength and this is the principle of the working of a sensor.

3. Experimental

To fabricate the sensor, cladding of known length (2-3cm) is removed from the middle portion of multimode plastic clad silica (PCS) fiber having diameter 125µm. The bare core of the fiber is dipped in solution of silver nitrate and trisodium citrate for the deposition of silver nanoparticles on the core.
A water cell of length 5cm and diameter 1.5cm with inlet and outlet provisions is designed, holes are provided at the two ends through which fiber is inserted in the water cell such that the bare core should be inside the water cell and remain straight.(as shown in photograph)

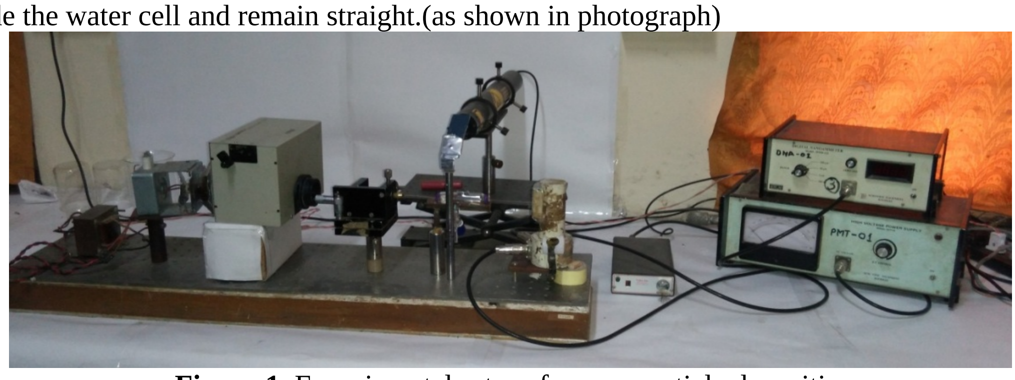
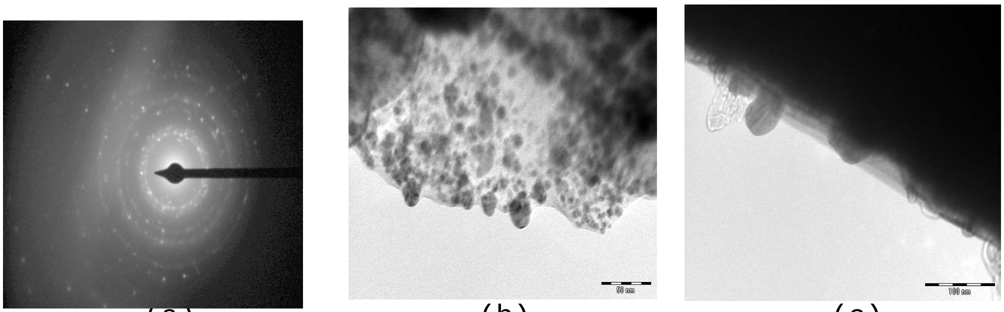


Figure 1. Experimental set-up for nanoparticle deposition



(a) (b) (c)

Figure 2. TEM Image of deposited silver nanoparticles.

Light beam from He-Ne laser wavelength 633nm was focussed on bare core immersed in the solution of silver nitrate and sodium citrate. Photochemical reaction causes the formation of silver nanoparticles which deposit on the core of unclad fiber. To exploit LSPR phenomena light from tungsten halogen lamp (THL) of 50watt power was coupled at one end of the fiber through microscope objective (MO) having same numerical aperture. The output intensity is detected by using a photomultiplier tube (PMT).The preliminary test of nanoparticle deposition is confirmed by the reduction in the output intensity. Continuous measurement of intensity vs wavelength at the output end was taken via spectrum analyser and the dip at the surface plasmon resonance in the output spectrum was observed. The deposition of nanoparticles was finally confirmed via transmission electron microscopy (TEM) as shown in figure 2. Designed sensor was tested for the detection of fluoride impurity in water. Standard water samples having fluoride concentrations 30ppm, 50ppm, and 100ppm were prepared by dissolving sodium

Fluoride (NaF) in distil water and the output current is measured for different wavelength. The output spectrum shows the red shift in resonance wavelength with increase in fluoride concentration.

4. Result

Figure 2(a) shows the diffraction image of deposited nanoparticles which confirms the deposition of silver particles. We note that silver nanoparticles grow and deposit on the fiber core after laser illumination. During the process of laser induction, silver particles are reduced in the solution under illumination. The illumination time was 6 minute. The deposited nanoparticles are of irregular shape having diameter up to 50nm.

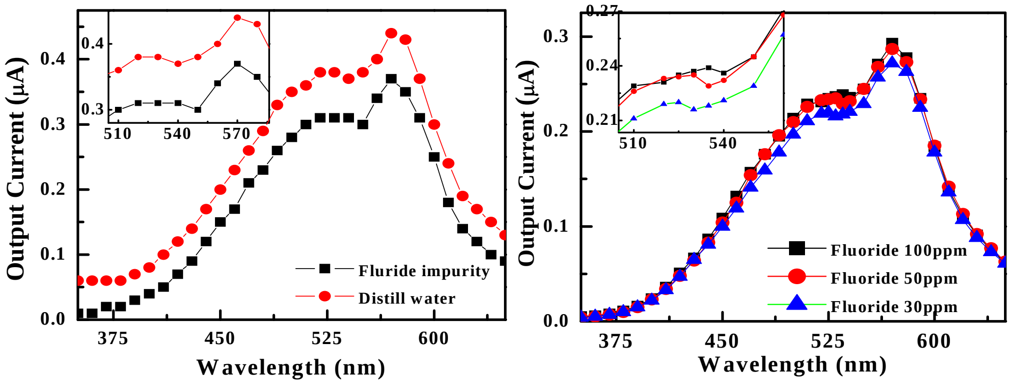


Figure 3. Output intensity for distil water and fluoride solution

The output spectrum with distil water shows dip at 541nm wavelength. We observed a shift in the dip position in presence of known concentration of fluoride solution.The output intensity was plotted for different known concentrations (30ppm, 50ppm, 100ppm) of fluoride in distil water. We observed that the surface Plasmon resonance dip shifted to longer wavelength with increasing fluoride impurity.

5. Conclusion

We have proposed design of fiber optic sensor based on localised surface Plasmon resonance (LSPR) to detect fluoride impurity in water. Silver nanoparticles were deposited by simple and low cost laser induced nanoparticle deposition technique. The experimental results exhibit the usefulness of the technique for detection of impurities in water.

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