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Harald Ian D.I. Muri[a], Andon Bano[a], and Dag Roar Hjelme[a]

[a]Norwegian University of Science and Technology, Gunnerus gate 1, Trondheim, Norway

ABSTRACT

We present a first demonstration of a novel multi-parameter fiber optic (FO) sensor concept based on gold nanoparticles (GNP) embedded in a stimuli-responsive hydrogel material. A hemispherical hydrogel immobilized on the optical fiber end-face forms a low-finesse Fabry-Perot (FP) interferometer. The GNPs exhibit local surface plasmon resonance (LSPR) that is sensitive towards the refractive index of the surrounding environment, while the stimuli-responsive hydrogel is sensitive towards specific chemical compounds. We evaluate the quality of the interferometric and LSPR signal as a function GNP concentration and of hydrogel swelling degree stimulated by ethanol solutions. The GNPs shows to have little influence on the visibility of the FP etalon, while LSPR of GNP shows to be sensitive towards the surface refractive index rather than bulk refractive index. This demonstration shows that the sensor concept has the potential to be used in applications such as an intravenous two-parametric real-time sensor for medical purpose.

Keywords: Fiber optic sensors, smart hydrogel, hydrogel, LSPR, nanoplasmonics, multiparametric sensor

1. INTRODUCTION

Multiplexed fiber optic sensors utilize often the attenuation of light, Fiber Bragg Gratings (FBG), or interferometric cavities to sense one single point with one parameter and another single point with another parameter. For medical applications, there is a great need for many sensing parameters in one single point only with other important features like small dimensions, label-free sensing, real-time monitoring and high sensitivity. Localized surface plasmon resonance (LSPR) that noble metal nanoparticles (NMNO) exhibit have shown to have promising optical properties for label-free sensing. Single point fiber optic (FO) LSPR based sensors proposed over the last decade applies often LSPR interacting with evanescent field around the fiber core or with the light at the fiber end-face.[1,2] In this paper, a combined interferometric and LSPR based FO sensor is proposed as a first step demonstration evaluating the quality of interferometric and LSPR attributes of gold nanoparticles (GNP) immobilized in an acrylamide hydrogel of the fiber end-face. The half-sphere of the hydrogel on the fiber end face represents a low-finesse Fabry-Perot (FP) etalon where the optical length is read out as a measure of the stimuli responsive hydrogel volume. Similar to previous work, free spectral range (FSR) or change in phase is read out of the reflected interferometric signal and subsequently the optical length.[3] The change in optical length is related to a change in physical length of the gel or simultaneously the change of refractive index of the gel. Since the reflection at gel-solution interface is low, multiple reflections can be neglected leading to FSR that is inverse proportional to optical length. The reflection from GNP immobilized in acrylamide have a spectrum representing LSPR with properties similar to a damped lorentzian. The LSPR peak position dependence on refractive index of medium (n_m) can be expressed by following solutions from Mie theory or Drude model.[4] From Mie theory scattering and extinction are dependent on light frequency, n_m, size, shape, and material composition. For small range of n_m Drude model express the LSPR peak position with corresponding wavelength as a function of n_m. As LSPR depends on n_m label free sensing is possible by surface functionalizing the GNP with receptors that can selectively bind to specific biomolecules where a recombination of receptor-biomolecule is red shifting the LSPR peak position. However, in this paper, as a first step towards two parametric label free sensing, the LSPR

Further author information: (Send correspondence to Harald Ian Muri)
Harald Ian Muri: E-mail: harald.muri@ntnu.no, Telephone: +4773412688
Dag Roar Hjelme: E-mail: dag.hjelme@iet.ntnu.no, Telephone: +4773559604
Andon Bano: E-mail: andonb@stud.ntnu.no, Telephone: +393209450050

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peak position of GNP is evaluated as a function being immobilized in the acrylamide gel and as a function of the hydrogel swelling degree stimulated by ethanol solutions. The visibility of the interferometric signal is also evaluated as a function of GNP density inside the hydrogel that should introduce a loss factor (absorption, scattering, mode-mismatch) inside FP etalon. The fiber optic setup made in this paper can be combined with applications such as real-time monitoring of specific markers for critical ill patients under or after surgery.[3]

2. MATERIALS AND METHODS

The fiber optic sensor have been fabricated as described from previous work.[5] In this paper 100nm citrate stabilized GNP (Absorption max: 600nm, Sigma Aldrich) with density of $2 \cdot 10^{10}$ to $17 \cdot 10^{10}$ particles/ml were used to make pregel solutions of 10 wt% acrylamide (AAM) and 2 mol% N,N-methylenebisacrylamide (BIS). Ethanol (VWR) and milliq water solutions were used to stimulate a change in volume of the hydrogel. The fiber optic (FO) instrument illustrated in Fig. 1 consist of following components; light source 1 (MBB1F1, 470-850nm, Thorlabs), light source 2 (S5FC1005S, 1550nm, 50nm bandwidth, Thorlabs), 2x2 coupler multimode (MM) (50/50, FCMH2-FC, 400-1600nm, Thorlabs), 2x2 coupler single mode (SM) (50/50, 84075633, 1550nm, Bredengen), doubled cladded optical fiber (DCOF) 2x2 coupler (DC1300LEB, 400 - 1600 nm, 1250 - 1550 nm, Thorlabs), spectrometer 1 (QE65Pro, Ocean Optics), spectrometer 2 (NIRQuest-512-1.7, Ocean Optics), loose fiber-end terminated with index matching gel (G608N3, Thorlabs), sensor segment of Ø125 μm DCOF (DCF13, Thorlabs), program Spectrasuite (Ocean Optics). Optical fibers (OF) were connected using a Fitel Fusion Splicer (Furukawa Electric).

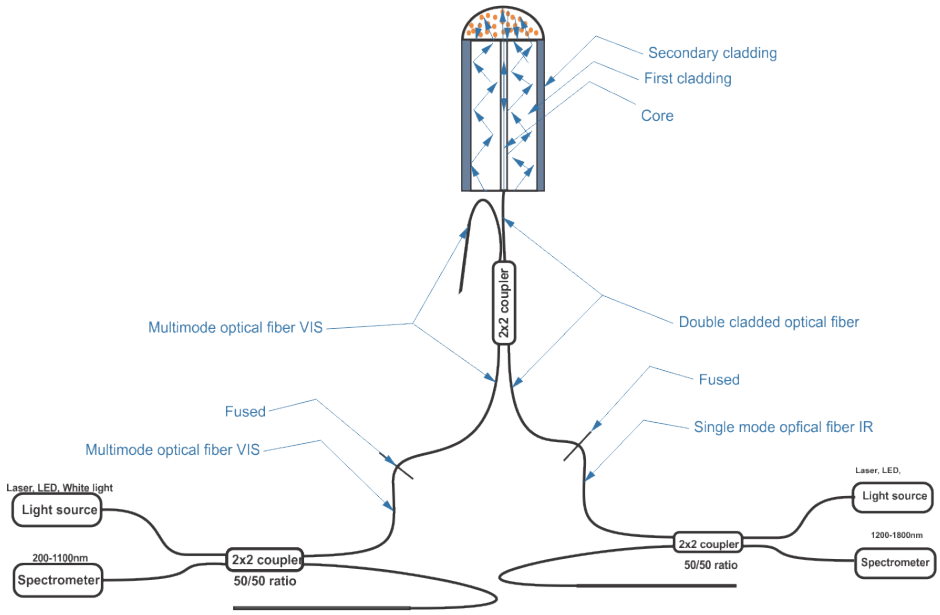
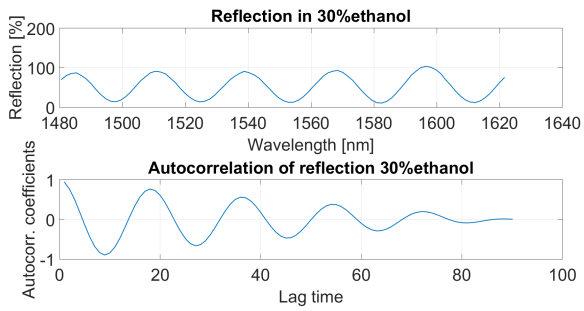


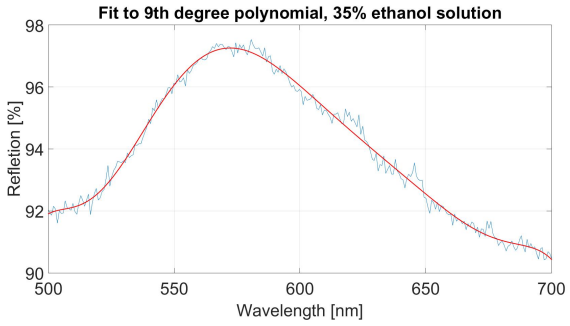
Figure 1: Set up of the fiber optic instrument based on reflection measurements

3. RESULTS AND DISCUSSION

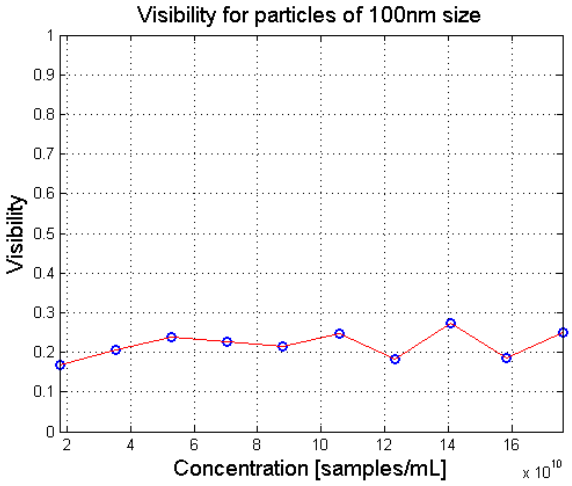
The measurements of the interferometric and LSPR signals were carried out by taking autocorrelation and polynomial fit of them, respectively. From figure 2a the FSR is determined by finding the position of the first peak of the autocorrelation function and its position that is non-zero. No fitting was used for the autocorrelation to find the peak and its position. It is possible to apply algorithms as described from previous work to obtain fast and accurate measurements from the same setup.[3,6] The interferometric signal in figure 2a shows to have a shape of a low-finesse FP etalon. The LSPR peak position and its width shown in figure 2b deviates from the original GNP-citrate solution where a LSPR peak at 600nm is observed. GNP in the acrylamide gel shows to have LSPR peak at 575nm. A broadening and blue shift of the LSPR peak and position, respectively, may be



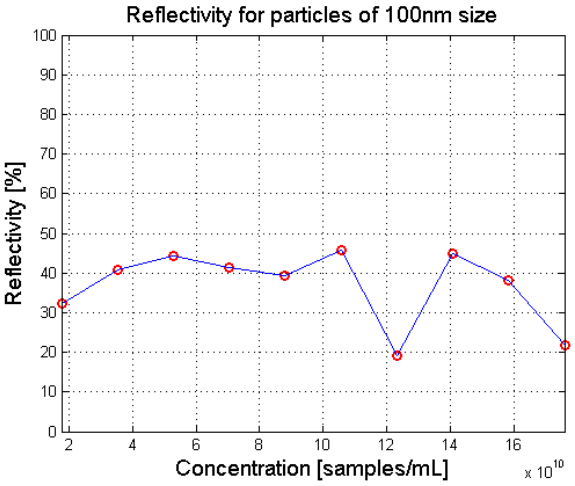
(a) IR reflection of hydrogel in 30% ethanol with its corresponding autocorrelation



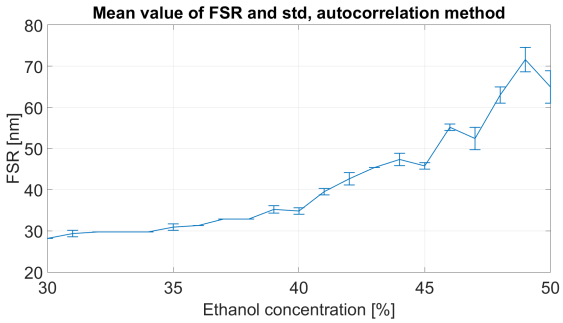
(b) VIS reflection of hydrogel in 35% ethanol with its corresponding polynomial fitting



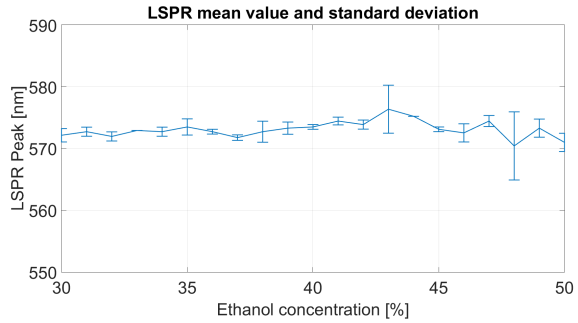
(c) Visibility of interferometric signal as a function of GNP density



(d) Reflectivity of interferometric signal as a function of GNP density



(e) FSR as a function of hydrogel swelling degree in ethanol concentration



(f) LSPR as a function of hydrogel swelling degree in ethanol concentration

Figure 2: FSR and LSPR measurenemts of the reflected spectrum of hydrogel in ethanol solutions

due to a local refractive index surrounding the GNP in acrylamide hydrogel that is different from the refractive index of the original GNP-citrate solution. In figure 2c and 2d the visibility and reflectivity of the interferometric signal is characterized for an increasing density of GNP in the gel. Up to a GNP density of $17 \cdot 10^{10}$ particles/ml the visibility is fluctuating between 0.15 and 0.25 while the reflectivity is decreasing after GNP density of $14 \cdot 10^{10}$ particles/ml. The GNP in the hydrogel does not have significant effect on the visibility and reflectivity with respect to loss factor, which also mean it is still possible to increase the GNP density or changing their size or

shape to increase the LSPR signal. There are however limitations concerning the stability of NMNP solutions when increasing their density. Figure 2e and figure 2f shows mean (4 samples per data point) and standard deviation of FSR and LSPR peak position, respectively, as a function of hydrogel swelling degree stimulated by ethanol solutions. The change in FSR from 30 to 70nm for ethanol concentrations from 30 to 50% in figure 2e indicates that the size of the hydrogel change to more than half of its initial size. Despite having GNP embedded inside the hydrogel, the readout of FSR shows to give useful interpretation of the swelling dynamics of a stimuli-responsive hydrogel, which is also evident from the visibility measurements in figure 2c. The measurements of FSR or change in phase of stimuli responsive hydrogels on end face of OF have in previous work been developed towards medical applications for label free sensing of specific biomolecules.[3,7] The LSPR peak position in figure 2f shows to stay relatively constant having fluctuations between 573 and 578nm with increasing ethanol concentration and simultaneously, the increased density of the acrylamide polymer. Changing the ethanol concentration from 30 to 50% results in a change of bulk refractive index of the gel (n_{gel}) from both the solution itself and the increase of acrylamide polymer density. The increase of surface refractive index around NMNP shifts the LSPR peak position to red for dipoles as seen in the Drude model and Mie theory.[4] This is however not observed for the measurements in figure 2f indicating that the bulk refractive index is not related to the refractive index located on the GNP surface. The difference between bulk and surface refractive index may be due to the orientation of water or ethanol molecules inside the polyacrylamide network relative to the spatially distributed GNP. LSPR based FO sensor shows however promising results in obtaining label free and selective sensing of specific biomolecules for medical purpose.[1,2] NMNP immobilized in hydrogel may improve the selectivity of LSPR sensing compared to the previous work mentioned above since the LSPR peak position depends on the n_m of the surface rather them the n_m of the bulk.

4. CONCLUSION

A first step demonstration towards a single point, two parametric fiber optic sensor have been demonstrated in this paper. Hydrogel swelling dynamics and the measurements of FSR and LSPR have been recorded as a function of ethanol solutions. Despite having GNP embedded in the hydrogel it shows to have little influence on the visibility of the FP etalon with respect to the loss-factor. The LSPR of the GNP shows also to be sensitive towards the surface n_m rather than the bulk n_m. Further work will be focused on continuing the development of this setup towards a proof-of-principle system for intravenous medical applications.

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