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# Fiber-optic biochemical sensing with a colloidal gold-modified long period fiber grating

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**Abstract**

A novel class of fiber-optic evanescent-wave sensor, which is simple to construct and easy to use, is presented and analyzed. This fiber-optic sensor is based on the modification of the grating portion of a long-period fiber grating with self-assembled gold colloids. The transmission spectra and optical properties of gold colloids change with the different refractive index of the environment near the surface of gold colloids. The sensor response of gold colloids increases linearly with solvents of increasing refractive index. When the colloidal gold surface was modified with a dinitrophenyl compound (DNP), experimental results show that the signal increase linearly with increasing concentration of the analyte, and the detection limit of the sensor for anti-DNP is $1.4 \times 10^{-7}$ g/mL or $9.5 \times 10^{-10}$ M.


*Keywords:* Long-period fiber grating; Gold colloids; Localized surface plasmon resonance; Refractive index; Biosensor

## 1. Introduction

In recent years, considerable attention has focused on long-period fiber gratings (LPFGs) for a variety of applications owing to their low insertion losses, low back-reflection, polarization independence and relatively simple fabrication. These gratings have offered wide applications in optical communications and sensing systems, such as in-fiber band rejection filters [1] and various kinds of sensors [2,3] for temperature, strain and refractive index (RI) measurements. The LPFG is extremely sensitive to the RI of the medium surrounding the cladding, thus allowing it to be used as an ambient RI sensor. At the same time, there is a great interest in the optical properties (e.g., absorbance and peak wavelength) of noble metal nanoparticles, such as Au or Ag, partly due to their potential applications for chemical and biological sensing. Several nanoscale biosensors and chemosensors have been realized through shifts in the localized surface plasmon resonance (LSPR) extinction maximum of gold or silver nanoparticles [4–8]. The wavelength shifts are mainly caused by adsorbate-induced local RI changes at the surfaces of nanoparticles. Among the LSPR sensors, an optical fiber biosensor that exploits the LSPR of self-assembled Au colloids (SAGC) on the unclad portion of an optical fiber was demonstrated [6,9]. The attenuated total reflection spectrum of SAGC is sensitive to the refractive index of its surrounding medium, which can be used for monitoring the solution bulk and for label-free detection of antigen/antibody binding or DNA at the surface of the Au colloids. The advantages of this type of the sensor are their simple construction and ease of use. Moreover, the sensor has the potential capability for on-site and remote sensing, can be easily multiplexed to enable high-throughout screening of bimolecular interactions, and has the potential use for disposable sensors.

This paper proposes a new class of biosensor and/or chemosensor relying on the modification of the grating portion of a long-period fiber grating with self-assembled Au colloids, which is sensitive to the RI of the colloidal gold surface and, hence, is suitable for label-free detection of biomolecular binding at the surface of Au colloids.

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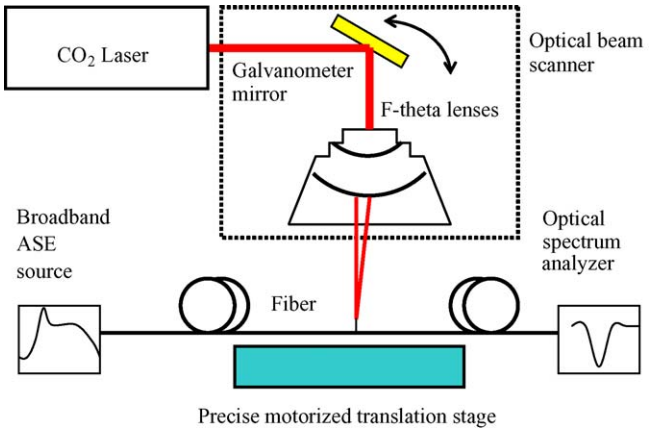


Fig. 1. Experimental setup for fabrication of long-period fiber grating.

## 2. Experimental

The experimental setup for grating fabrication is shown in Fig. 1. The experimental configuration consisted of a computer-controlled $CO_2$ laser associated with a high-speed optical beam scanner to direct and focus the laser at the desired location along the fiber. A translation stage is used to position the fiber in the alignment fixture. The $CO_2$ laser (SYNRAD, 48-2) provides a full power of 25 W at a typical frequency of 5 kHz (200-μs period), which is probably the best frequency for energy absorption of silica at 10.6-μm wavelength. The beam scanner consisted of a galvanometer mirror and F-theta lenses, capable of spanning the focused laser with 290-μm beam spot across a field size of 110 mm. The two-beam position resolution of the system is about 30 μm and the maximum speed of moving successive beam pairs can be up to 40 kHz (25 μs). A broadband ASE source and a spectrum analyzer (ANDO AQ6315A) were used to in situ monitor the transmission loss as the grating was written.

The LPFG studied in the paper was fabricated in hydrogen-free Corning SMF-28 fibers. The length of the LPFG was 22 mm long and the gratin period was about 550 μm long, written with a laser power of 0.8 W and a total exposure time of about 2 min. The transmission spectrum was interrogated during the writing and its characteristics, such as insertion loss, resonance peak wavelength and peak depth were analyzed after the grating was written. With suitable fabrication parameters, such as laser power, exposure time, grating period and scan speed, the resulting resonance wavelengths ranging from 1510 to 1600 nm with greater than 20-dB peak depth were obtained. In addition, the rapid motion of the scanner has made the fabrication process less time consuming. For a typical 20-mm long LPFG, the fabrication time was less than 2 min. The efficiency of the fabrication makes it possible to mass production of LPFGs economically.

The preparation of Au colloids can be found in Refs. [5,6]. Transmission electron microscopic (TEM) image analysis showed that the mean diameter of the Au colloids was $8.4 \pm 2.8$ nm. The average surface coverage (relative to a close-packed monolayer) of self-assembled colloid monolayer of gold ($CM_{Au}$) was estimated to be 30% by atomic absorption spectroscopy. The preparation of colloidal Au-modified long-period fiber gratings ($CM_{Au}LFPG$) followed the same procedure as that of colloidal Au-modified optical fibers ($CM_{Au}OF$) in Ref. [6]. A self-assembled colloid monolayer of gold on the grating surfaces of LPFG was used for further study. As shown in Fig. 2, the fiber-optic sensing system used to measure the transmission spectrum of the sensor consisted of a broadband ASE source, a sensing LPFG fiber, a cell, and an optical spectrum analyzer (Q8384, ADVANTEST). Each transmission spectrum was referenced to the background spectrum of a bare fiber in air.

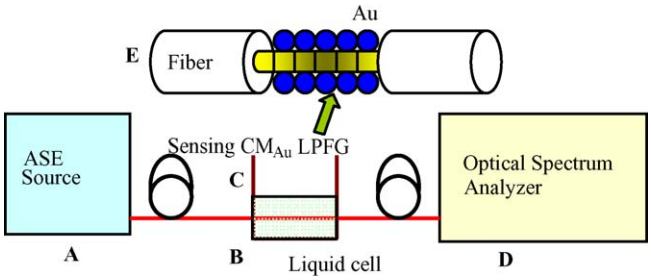


Fig. 2. Schematic representation of the experimental setup used to make measurements with the $CM_{Au}LFPG$. Apparatus used to obtain transmission spectra: (A) ASE light source, (B) liquid cell, (C) colloidal Au-modified long-period fiber grating, (D) optical spectrum analyzer and (E) magnified view of a sensing $CM_{Au}LFPG$.

## 3. Results and discussion

The ability of the colloidal Au-modified long-period fiber grating to detect changes in the surrounding RI was first studied. The control of surrounding RI is through the use of sucrose solutions with various concentrations. The relationship between RI and sucrose concentration is shown in Fig. 3 [10]. When the concentration and, hence, the RI of a sucrose solution increased in the range of 1.34–1.43, the transmission spectrum of the $CM_{Au}LFPG$ exhibited a decrease in the transmission loss or peak amplitude ($10 \log (I/I_0)$, where $I$ is the peak intensity of

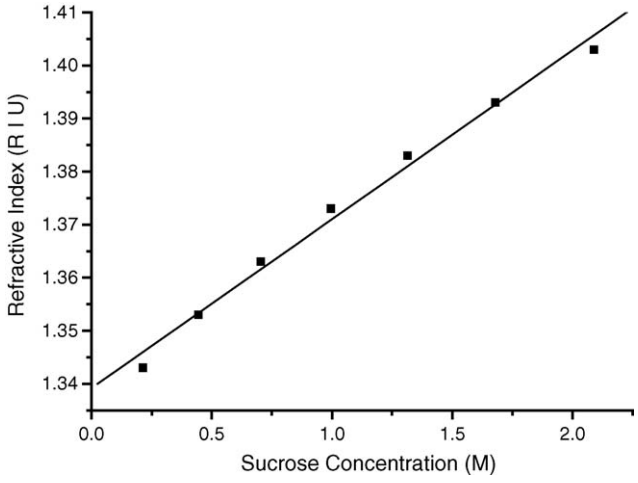


Fig. 3. A plot of solution refractive index vs. concentration of sucrose in the solution.

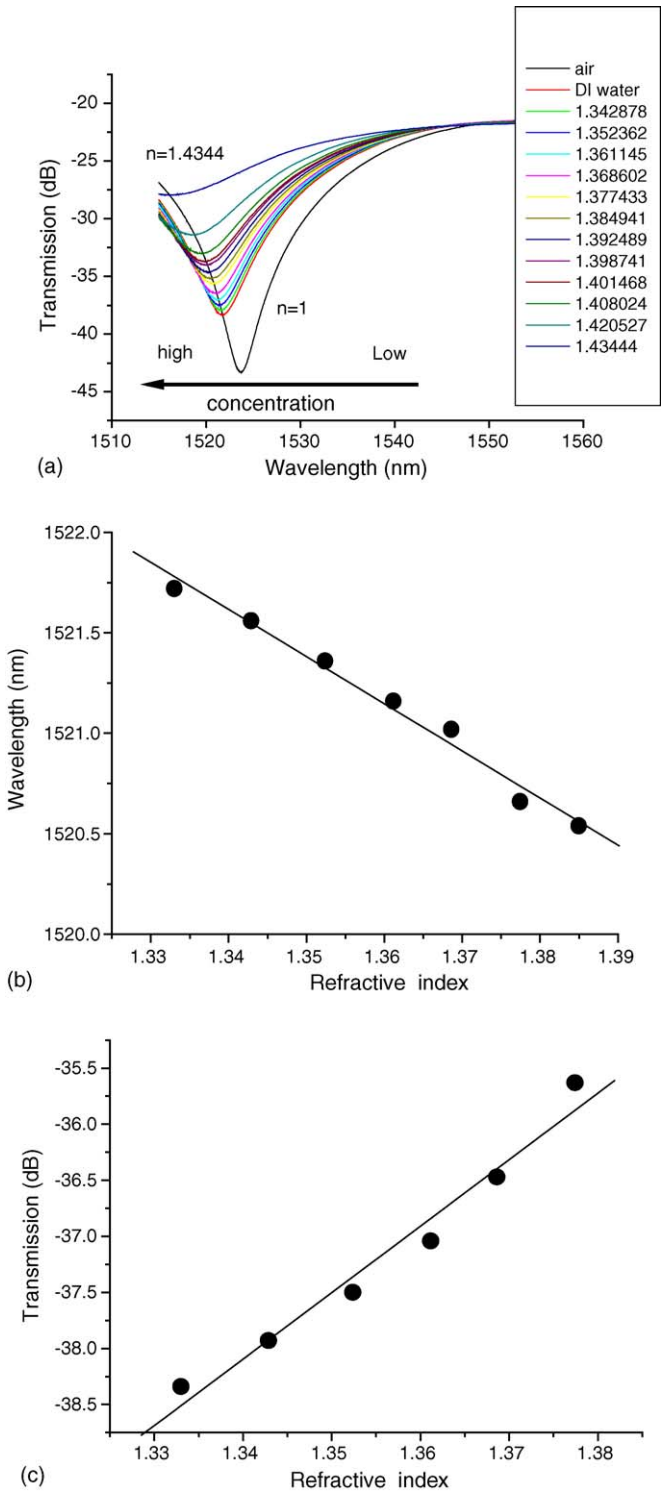


Fig. 4. (a) Transmission spectra of $CM_{Au}$LPFG in aqueous solution containing increasing concentration of sucrose (from bottom to top). (b) Plot of peak wavelength vs. refractive index of the sucrose solution. (c) Plot of the transmission loss vs. refractive index of the sucrose solution.

the optical signal from a $CM_{Au}$LPFG that is immersed in a sample and $I_0$ is the peak intensity of the optical signal from a bare fiber that is immersed in air) at the peak (resonance) wavelength and a blue shift in the resonance wavelength, as shown in Fig. 4(a).

Fig. 4(b) shows a linear fit (correlation coefficient, $R = -0.9919$) to the plot of peak wavelength as a function of refractive index $n$. The resonance wavelength of 1524.5 nm for LPFG at air is chosen because a maximum sensitivity is found at that wavelength. The sensitivity by wavelength interrogation was $-23.45$ nm/refractive index unit (RIU) in the range of $n = 1.33$–$1.39$, which is determined from the slope of linear fit. On the other hand, a plot of transmission loss as a function of RI is also linear ($R = 0.984$), as shown in Fig. 4(c). The sensitivity from the slope of Fig. 4(c) was 59.3 transmission loss unit (dB)/RIU. Another intensity measurement approach is by plotting transmittance ($I/I_0$) as a function of RI, which is more linear (correlation coefficient, $R = 0.998$) than the plot of transmission loss versus RI. Hence, transmittance was used as the sensor response in later studies.

In comparison to the data obtain from $CM_{Au}$LPFG, the same analysis was applied to the LFPG prior to the modification of Au colloids over the grating region. The sensitivities were $-17.93$ nm/RIU and 37.31 dB/RIU. It can be seen that an enhancement of sensitivity was obtained when the grating portion of the LPFG was modified by self-assembled Au colloids.

Previous work [6] has demonstrated that LSPR can be used to measure changes of local RI at the colloidal gold surface induced by analyte binding events to a functionalized $CM_{Au}$OF for the streptavidin-biotin pair with a limit of detection as low as $9.8 \times 10^{-11}$ M. The sensing mechanism is based on attenuated total reflection at the colloidal gold-modified surface that produces a large decrease in the reflectivity due to multiple reflections in the optical fiber [6]. To investigate the possible applications of $CM_{Au}$LFPG for biomolecular binding, a dinitrophenyl (DNP) antigen was formed on a $CM_{Au}$LFPG to study the binding of anti-DNP on the surface of colloidal gold using an antibody–antigen binding model. Considering a Langmuir absorption model for the general reaction in equilibrium between an antibody and an immobilized antigen, the following expression is derived [6]:

$$\frac{1}{I' - I} = \frac{1/k + 1}{kK_f[M]_0} \tag{1}$$

where $I'$ is the intensity from the $CM_{Au}$LPFG which is immersed in water, $I$ the intensity from the $CM_{Au}$LPFG that is immersed in a sample solution, $k$ the proportionality constant, $[M_0]$ the initial concentration of the analyte in solution and $K_f$ is the conditional formation constant of the reaction. Hence, a linear plot of $1/(I' - I)$ versus $1/[M_0]$ would allow the calculation of $K_f$ by dividing the $y$ intercept by the slope. As shown in Fig. 5(a), the concentration-dependent responses of a DNP-functionalized $CM_{Au}$LPFG were investigated in order to determine the sensitivity of this sensor for the study of DNP–anti-DNP binding. Over the range of anti-DNP concentration from $1 \times 10^{-6}$ to $3 \times 10^{-5}$ g/mL, the sensor response is linear ($R = 0.9976$). Using the intercept and slope of the plot as shown in Fig. 5(b), the conditional formation constant of the immobilized DNP–anti-DNP complex was calculated to be $7.8 \times 10^4$ $(g/mL)^{-1}$. Fig. 5(c) shows a plot of transmittance $I/I'$ as a function of anti-DNP concentration. The limit of detection (LOD = $3\sigma/m$,

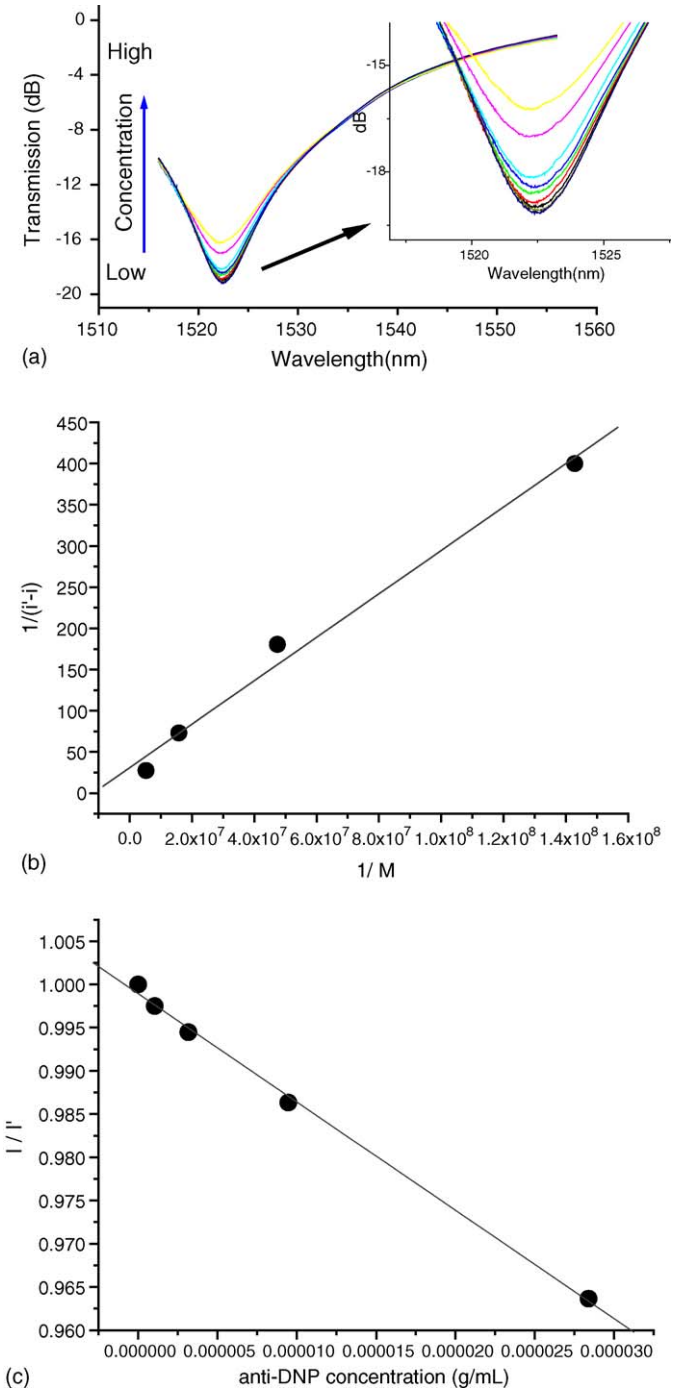


Fig. 5. (a) Transmission spectra of DNP-functionalized $CM_{Au}$LPFG in a buffer solution containing increasing concentration of anti-DNP (from bottom to top). (b) Plot of $1/(I' - I)$ vs. reciprocal concentration of anti-DNP. (c) Plot of $(I/I')$ vs. the concentration of anti-DNP.

$\sigma$ = standard deviation of $I$ in measuring the blank, $m$ = slope) of the sensor was determined to be $1.4 \times 10^{-8}$ g/mL or $9.5 \times 10^{-10}$ M.

## 4. Conclusions

In summary, we have demonstrated a class of refractive index sensor that exploits the LSPR of self-assembled Au colloids on the grating portion of an LPFG for monitoring the concentration of chemical solution and for label-free detection of biomolecular binding at the surface of gold nanoparticles. Studies presented in this paper illustrate the feasibility of making this colloidal Au modified long-period fiber gratings for chemical and biochemical sensing. The realization of the sensors is through the measurement of transmission spectra of the sensing fiber grating. The advantage of this type of sensor is its simplicity in construction and easy of use. When the colloidal surface was modified with DNP, results show that the detection limit of the sensor for anti-DNP is $9.5 \times 10^{-10}$ M. The sensitivity of the sensors is useful for biosensor applications but has not yet been optimized, which can be enhanced by the optimization of some key parameters, such as the size and density of immobilized Au colloids, surface structure of the functionalized monolayer, length of the LPFG fiber for immobilization of Au colloids and detection wavelength.

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