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Absorption detection of cobalt(II) ions in an index-guiding microstructured optical fiber

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ABSTRACT

We reported the absorption detection of cobalt(II) ions (Co^{2+}) in aqueous solutions which is filled into the air-holes of a pure-silica microstructured optical fiber (MOF). The evanescent field in MOF which changes with solution of absorbing species is numerically investigated with respect to the change of refractive index, wavelength as well as the microstructure pattern in a systematic manner. Good linear calibration curves for samples concentration and length of MOF were obtained. Moreover, the MOF possesses good thermal and bending stabilities, thus allowing its use for absorption detection of an analytes even in harsh environment. The MOF may be developed into absorption sensors or integrated with microchips.

1. Introduction

Optical fiber based sensors have been increasingly explored for the interrogation of ambient index changes due to many advantages such as high sensitivity, immunity to electromagnetic interference, accessibility to harsh and hostile environment, small size and cost effectiveness [1]. While fiber optic sensor presents an attractive platform for sensing, the use of conventional fiber requires the removal, physically or chemically, of the cladding in order to make close proximity of the measurand to the fiber core, thereby compromising device reliability. In recent years, the boosting development of a new type of microstructured optical fibers (MOFs) with an array of air-hole along the propagation direction has attracted immerse research interest worldwide [2]. There is a growing interest in exploring MOFs for advanced sensor components and devices by infiltrating the air-hole with gas, liquid and polymers [3]. The degree of freedom in designing the microstructured waveguides is greatly enhanced compared with that of conventional fibers for specific applications [4], such as the air-filling fraction, the air-hole pattern, etc. At every point of internal reflection at the silica–hole interface, a small portion of the field penetrates and decays exponentially into the cladding. This evanescent field overlap with the filled species is enhanced compared with the conventional evanescent field spectroscopy devices [5]. The results show that the enhancement of sensitivity is attributed to the long effective interaction length in compact fashion while only submicroliter sample volumes are needed. Recently, liquid core waveguide (LCW) cell has become very widely used to minimize source light loss to the cell. In an LCW cell, the tube material (cladding) has a lower refractive index than that of the fluid (core). The source light thus propagates through the LCW fluid by total internal reflection (TIR). Such cells have now been widely used for long path length spectrophotometry [6]. However, the construction material for LCW cells, Teflon® AF, is one of the most expensive commercial polymers. Moreover, Teflon® AF is highly gas permeable, which can cause problems of strong evaporation of water from the internal solution. In Ref. [5], we reported the absorption detection using a MOF with a central defected air-hole. However, a meniscus occurred at the end faces of the fiber, which tended to defocuses the light and makes it quite difficult for launching.

In this paper, we report a solid core index-guiding MOF as a miniaturized waveguide flow cell for long path-length axial absorbance detection. It solves the launching problem and offers several advantages over conventional absorption detection methods. As light is propagated along the fiber, the optical path is equal to the length of the fiber and in theory this could be any length, therefore, the sensitivity would be greatly enhanced due to the

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extraordinarily long optical path. In addition, MOF itself is a waveguide and stray light effects due to the increase of path length could be eliminated. The fiber is robust and can be wound up to keep a small footprint, which makes it amendable for on-chip integration. More importantly, the small cross section area of air-hole keeps the reagent consumption at minimum.

2. Theoretical analysis

Absorption spectroscopy is the most widely used detection method in general analysis. It refers to a range of techniques employing the interaction of electromagnetic radiation with matter. As defined by the Beer–Lambert's Law [7], absorbance A of light by a sample is proportional to the chromophore concentration c, the molar absorption coefficient ε, and the optical path length b. In the microstructured fiber, the fraction of light interacting with the aqueous solution P_{hole} will also determine the absorbance. Therefore, the term P_{hole} is included in the calculation of absorbance in the form of

$$A = \log \frac{I_o}{I_t} = \varepsilon b c P_{\text{hole}} + \alpha \quad (1)$$

where α is the attenuation of the MOF without absorption. In absorption spectroscopy, the intensity of a beam of light measured before and after interaction with a sample are related by $I_t = I_o \exp(-k_l L)$, where I_o is the intensity of the incident light; I_t is the intensity of the light passed through the layer of the substance; L is the thickness of substance layer, or the path length; k_l is the extinction coefficient dependent on the type of substance and wavelength of the incident light.

A solid-core MOF was fabricated using stack-and-drawing technique for this study. Solid-core MOFs based on total internal reflection guidance show some advantages over the hollow-core MOFs based on photonic bandgap guidance for chemical sensing. Firstly, solid-core MOF have broader spectral band propagation, hence more compounds may be detected. Secondly, the requirement for an accurate control of the air-hole size and periodicity of the air-hole is less stringent, thus increasing the fabrication tolerance. The MOF was made from pure silica with a refractive index ~1.45. Fig. 1(a) shows a scanning electron micrograph (SEM) of the MOF. During the MOF drawing process, a melting preform was drawn to the size of standard fiber diameter of 125 μm. The core region was surrounded by three layers of air-hole, serving as cladding. The average pitch size (Λ) is 5.2 μm and the average diameter of the air-hole in the cladding (d) is 3.2 μm. The MOF structure shown in Fig. 1(a) is modeled with a full-vector beam propagation method [8]. Transparent boundary conditions are used to enable the analysis of leaky modes. By infiltrating the air-holes with aqueous solution, the refractive index of cladding increases accordingly with the refractive index of solution. The fiber therefore exhibits increased leakage of light into the air-holes because the difference of refractive index between the core and cladding decreases. The core mode and the portion of evanescent field penetrating into the air-holes with infiltrations are shown in Fig. 1(b). Most of the guided light power is confined within the solid region of the core with ~0.78% of guided light power extending into the air-holes region (for refractive index of deionized water 1.33 at 510 nm). Moreover, the evanescent field is proportional to the concentration of the infiltrated solution. As shown in Fig. 2, when we increase the index of infiltrated aqueous solution from pure water n = 1.33–1.35, the ratio of evanescent field intensity in the holey region to the total confinement power increases from 0.78% to 0.92% linearly.

As the molar absorption coefficient varies with wavelength, the absorbance is wavelength-dependent. We calculated the fraction of light interacting with the aqueous solution P_{hole} as a strong function of wavelength, results shown in Fig. 3(a), this agrees well with literature [9]. Therefore, the fiber is expected to be more sensitive for absorption detection at longer wavelengths. The effect of the number of the layers of air-hole on the evanescent field is calculated and shown in the inset of Fig. 3(a). This, however, can be ignored when the number of layers is more than two. The microstructure pattern is characterized by two parameters, namely the air-hole diameter d and the pitch size Λ. More leakage of light occurs when we increase the air-hole size, therefore the interaction with the infiltrated liquid is enhanced. The effect of d and Λ on the evanescent field are calculated and shown in Fig. 3(b). Three values close to the dimension of the fabricated fiber have been considered, Λ = 4.8, 5.0 and 5.2 μm.

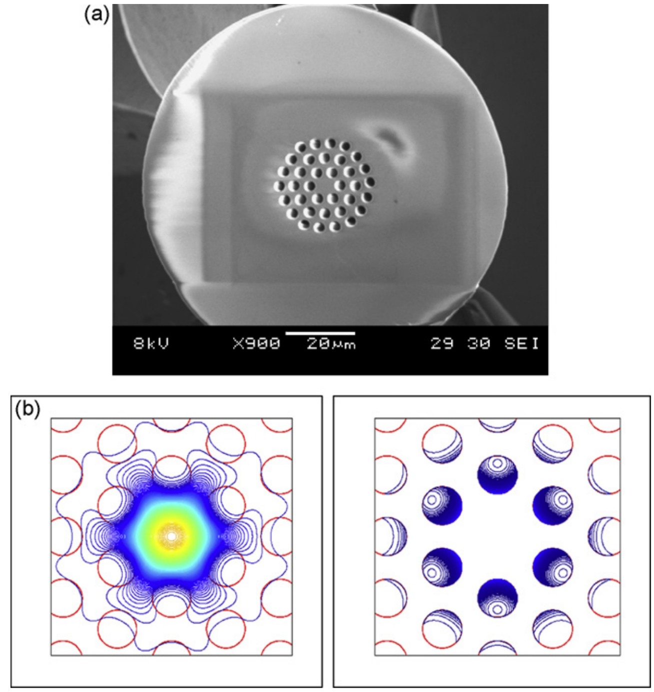

Fig. 1. (a) Scanning electron micrograph (SEM) of the pure-silica MOF. A solid core is surrounded by three layers of air-hole which serve as cladding. (b) Calculated fiber mode distribution, where most of the guided light power is confined within the solid region of the core (left) with 0.7% of total power extending into the holey region (right).

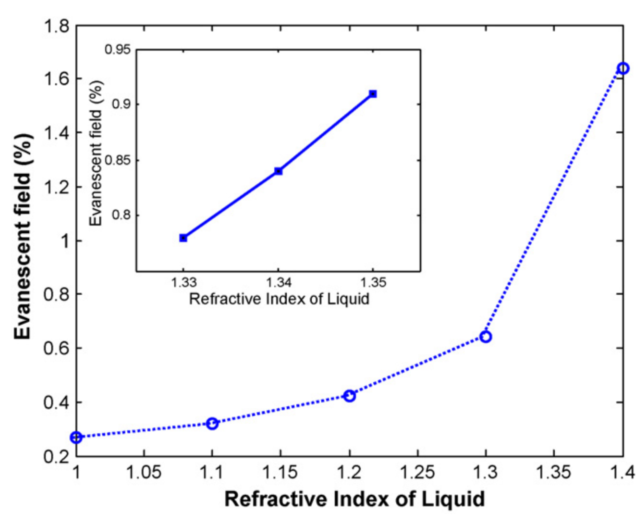

Fig. 2. Calculated percentage of evanescent field intensity in the air-hole region for different refractive indices of the infiltrations. *Inset*: percentage of evanescent field intensity when the refractive index is close to 1.33 (water).