

Research on a fiber sensing system for metal ion detection based on SPF-PCF-SPF structure and coated LPFG*

GUO Junqi^{1,2}, ZHOU Yanfang^{1,2}, ZHENG Wenyue^{1,2}, XU Qianwen^{1,2}, LIU Yu^{1,2}, and LI Renpu^{1,2**}

1. Chongqing Key Laboratory of Autonomous Navigation and Microsystem, Chongqing University of Post and Telecommunications, Chongqing 400065, China

2. Chongqing Engineering Research Center of Intelligent Sensing Technology and Microsystem, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

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In order to provide a method for accurately detecting the concentration and types of heavy metal ions in water, a fluid ion detection system is designed. It consists of a side-polished fiber-assisted fluid structure and a long-period fiber grating (LPFG) coated with a metal chelating agent membrane. In this study, both theoretical and experimental investigations are conducted to examine the sensing characteristics of the system towards copper ion and iron ion solutions. The results demonstrate that under the premise of ensuring solution flow, the system can achieve specific identification of different types of heavy metal ions. Furthermore, it exhibits concentration sensing sensitivities of 9.23×10^4 mL·nm/mol and 7.13×10^4 mL·nm/mol for copper sulfate (CuSO_4) and ferric chloride (FeCl_3) solutions, respectively. Therefore, this sensing system offers the potential for real-time detection of metal ions.

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Heavy metal water pollution has become a prominent environmental problem today and must be addressed as a matter of priority. Atomic absorption spectrometry^[1], electrochemical analysis^[2], fluorescence colorimetry^[3,4], fiber optic sensing method^[5-7], etc are frequently used to identify metal contamination in solutions. Among them, fiber-optic-based ion detection sensors are compact, extremely interference-resistant and extremely sensitive^[8-10]. However, current fiber optic ion sensing is still difficult to achieve high sensitivity sensing of ions in fluids. Therefore, the study of a new fiber optic sensor with stable performance and real-time detection of heavy metal ion characteristics in fluids has important social significance and application value.

Recently, numerous fiber optic sensing techniques for metal ion detection have been reported. In 2019, SHUKLA et al^[11] proposed a U-shaped fiber optic probe modified with glucose-coated silver nanoparticles for the detection of mercury ions in water. A concentration detection limit as low as 2 ppb was achieved using the surface plasma principle and the reaction of glucose-coated silver nanoparticles with mercury ions. In 2020, a micro-tapered long-period fiber grating (LPFG) with graphene oxide coated on the surface was reported by WANG et al^[12] for the purpose of detecting Ni^{2+} concentration. The sensitivity of the resonant wavelength varia-

tion and intensity variation of micro-tapered LPFG to its concentration sensing is 5.12×10^{-4} nm/ppb and 3.07×10^{-4} dB/ppb, respectively^[12]. In 2022, LI et al^[13] designed a coreless fiber-less-mode fiber-coreless fiber structure by coating smart hydrogel on less-mode fiber. Sensitivity of 8.155×10^5 nm·L/mol for the detection of Pb^{2+} in water was achieved by using the Mach-Zehnder interferometer (MZI) principle and the specific binding of hydrogel. It can be seen that a fluid ion sensor with high response sensitivity and straightforward construction can be created by combining a fiber optic sensor with the physicochemical characteristics of the material to be measured. However, it is difficult for the fiber optic metal ion sensors studied so far to provide high sensitivity sensing of ion concentration and species while maintaining fluid flow.

In this work, a metal ion fiber optic sensor based on D-type fiber (SPF) and coated LPFG is studied. Simulations have shown that the metal ion species can be identified by observing changes in the amplitude of the coated grating, while the refractive index sensitivity of the system is 7 550 nm/RIU. The results of sensing experiments on copper sulphate and iron chloride solutions show that the system not only specifically identifies heavy metal ions in fluids, but also achieves concentration sensing sensitivity on the order of 10^4 nm·mL/mol.

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** E-mail: lirp@cqupt.edu.cn

The metal ion optofluidic sensing system designed in this study is depicted in Fig.1. The experimental setup includes a light source, a spectrometer, a coupler, a polarization controller, and a fiber grating cascade filled photonic crystal fiber (PCF). The SPF-PCF-SPF structure enables solution filling and replacement. The film layer material of LPFG contains chelating agent of metal ion to be measured, and the metal ion will change the refractive index of the film layer by chelation reaction with it.

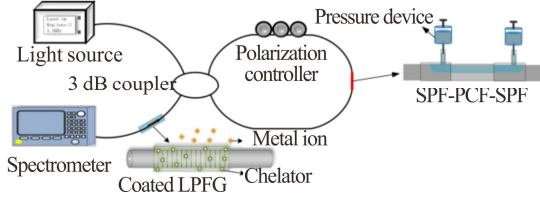


Fig.1 Diagram of system

For the detection of fluid ion concentration, this paper adopts SPF and PCF to form SPF-PCF-SPF fluid sensor. The SPF is processed from a single-mode fiber with cladding diameter, core diameter and polishing depth of 125 μm , 9 μm and 57 μm , respectively. The micro-structured fiber is PM-PCF-125-01 from Wuhan Changfei. It's mainly composed of two different sizes of circular air holes with apertures of 1.05 μm and 2.8 μm . According to Fig.2, when this PCF is fused to an SPF fiber with a 57 μm polishing depth, it reveals precisely 5 layers of air holes that operate as fluid channels.

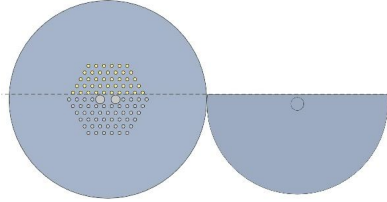


Fig.2 Diagram of fiber cross section

The SPF-PCF-SPF structure introduces significant asymmetry by filling some air holes in the micro-structured optical fiber. This allows for the detection of the refractive index of the filled fluid through birefringence principles. The concentration-refractive index relationship at a fixed wavelength can be approximated as $c = An + B$. That is, the fluid sensing structure can monitor fluid material concentration in real time. However, this structure alone cannot identify the ion species.

This work adopts the way of adding metal ion chelator to the film layer of coated LPFG. Each metal has its own corresponding chelating agent and chelation reactions occur to obtain chelates with special colors^[14]. This paper takes copper ions as an example, ammonium pyrrolidine dithiocarbamate ($\text{C}_5\text{H}_{15}\text{N}_3\text{S}_2$) is selected as the chelating agent for copper ions. In acidic or neutral solutions, $\text{C}_5\text{H}_{15}\text{N}_3\text{S}_2$ can react with divalent copper ions to form dark brown cuprous sulfide. In the preparation of the film material, the chitosan powder is first dissolved

in acetic acid solution and then the chitosan is modified by adding glutaraldehyde solution to obtain the chromogenic solution. The copper ion indicator solution is obtained by dissolving $\text{C}_5\text{H}_{15}\text{N}_3\text{S}_2$ in deionized water. Finally, the two solutions are stirred thoroughly to obtain the coating solution required for the experiment. As shown in Fig.3, the LPFG is coated using the above coating solution to obtain a thin and uniform film.

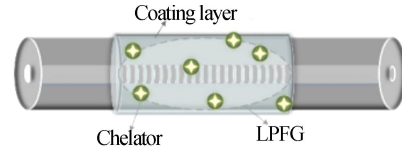


Fig.3 Structure of the coated LPFG

According to the Sagnac interferometer transmission principle^[15], the transmission spectrum expression can be given as Eq.(1), where λ is the resonant wavelength, l is the length of PCF, and $B(\lambda)$ is the birefringence.

$$Tr(\lambda) = \frac{[1 - \cos(2\pi l B(\lambda) / \lambda)]}{2} \quad (1)$$

Therefore, the combination of SPF-PCF-SPF and Sagnac interferometer gives a higher refractive index sensing sensitivity. To investigate the feasibility of this system for refractive index sensing, Fig.4(a) displays the transmission spectra of a Sagnac interferometer filled with liquids of various refractive indices. The wavelength of the resonance peak is red-shifted with the increase of refractive index of the solution. The lowest resonance peak near 1 120 nm is selected as the observation point. The linearity fit is 99.97%, and the refractive index sensing sensitivity is about 7 550 nm/RIU. Thus, the drift of the resonance peak wavelength can be observed to obtain the refractive index of the solution. Based on the above theoretical analysis, the sensing system can realize the sensing of fluid metal ion concentration.

To achieve the identification of ion species, the effect of refractive index of the coated LPFG film layer on the transmission spectrum is investigated theoretically. The phase-matching condition of LPFG can be represented as Eq.(2), where λ_{res} is the resonant wavelength, $n_{\text{eff}}^{\text{co}}$ is the effective refractive index of the core, $n_{\text{eff}}^{\text{cl}}$ is the effective refractive index of the cladding mode, and Λ is the period of the fiber grating.

$$\lambda_{\text{res}} = (n_{\text{eff}}^{\text{co}} - n_{\text{eff}}^{\text{cl}}) \Lambda \quad (2)$$

The grating transmission spectrum is analyzed numerically in the commercial software MATLAB based on the three-cladding model of coated LPFG and mode coupling theory. The variation of the resonant peak waveform of the coated fiber grating with only changing the refractive index of the film layer is shown in Fig.4(b). The wavelength of the resonant peak is blue-shifted slightly with an increase in the refractive index of the film layer, while the depth of resonant peak loss dramatically reduces. It can be seen that the change

of refractive index of the film layer has a significant effect on the amplitude of the loss peak. Thus, the ion species can be distinguished by observing the change in the amplitude of the resonance peak of the coated LPFG.

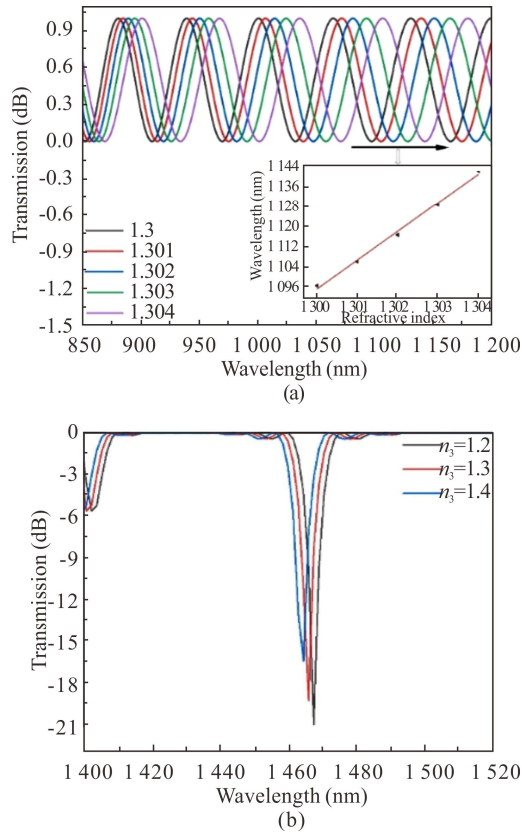


Fig.4 (a) Transmission spectra of Sagnac interferometer and refractive index fitting curve; (b) Coated LPFG resonance peak variation curves

The relationship between copper ion concentration and refractive index is investigated. Six sets of copper sulfate (CuSO_4) solutions are prepared. The refractive indices of each concentration are measured separately using an Abbe refractometer. The fitting results are shown in Fig.5(a), and the linear regression equation is obtained as $n = 1.32753 + 0.00268 \times 10^4 c$. Therefore, concentration sensing properties can be obtained by studying refractive index sensing.

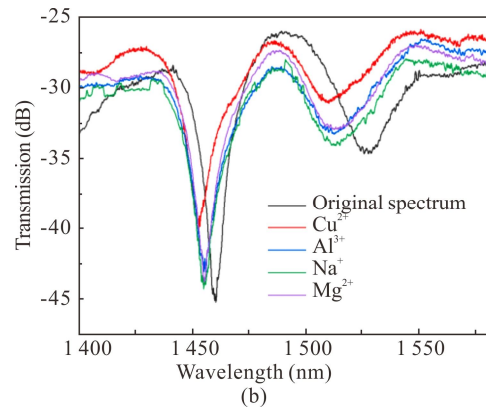
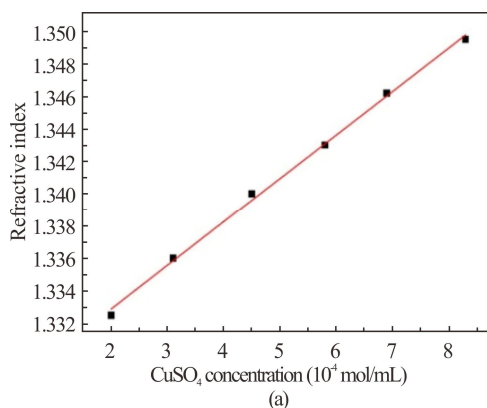
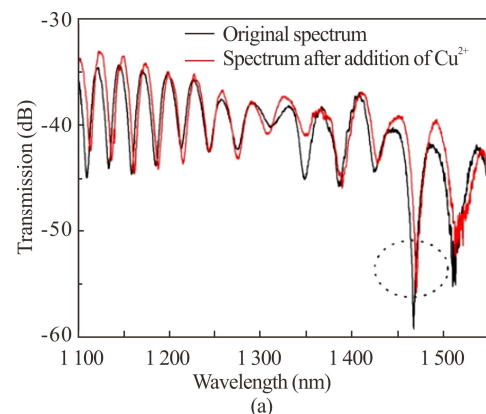


Fig.5 (a) Fitting curve of CuSO_4 solution concentration and refractive index; (b) Transmission spectra of the coated LPFG at the same concentration of different ionic solutions

In order to verify the above theory, the LPFG is produced by using a CO_2 laser pulse device. The coated LPFG is immersed in Cu^{2+} , Al^{3+} , Na^+ , and Mg^{2+} solutions at a concentration of 1%, respectively, to verify the specific recognition of metal ions by the coated LPFG. The transmission spectra are shown in Fig.5(b). The resonant peak loss depth of the coated LPFG in Al^{3+} , Na^+ , and Mg^{2+} solutions is reduced by about 1.6 dB due to the sensitivity of the fiber grating itself to changes in the external refractive index. In contrast, the depth of resonant peak loss of the coated LPFG immersed in the Cu^{2+} solution changed significantly, with a total reduction of about 5 dB, indicating that the $\text{C}_5\text{H}_{15}\text{N}_3\text{S}_2$ in the film had changed the refractive index of the film by chelating with Cu^{2+} . This coated LPFG specifically recognizes the presence of Cu^{2+} in solution.

The capability of the overall system to recognize copper ions is experimentally evaluated. The CuSO_4 solution with a concentration of $1.312 \times 10^{-5} \text{ mol/mL}$ is introduced into the SPF-PCF-SPF fluid channel using a pressure device and dripped into the coated LPFG reaction chamber, and the experimental results are shown in Fig.6(a). The resonant peak amplitude dropped by 3.37 dB with the addition of the CuSO_4 solution. It proves that the system is capable of recognizing copper ions precisely.

The transmission spectra are obtained after introducing six groups of CuSO_4 solutions with different concentrations into the system. As the concentration of CuSO_4



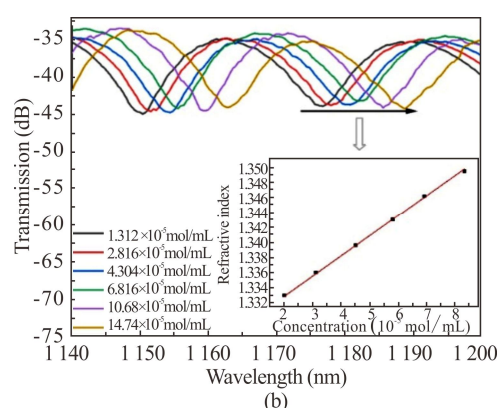


Fig.6 (a) Copper ion identification transmission spectrum of the fusion system; (b) Transmission spectra obtained after introducing six groups of CuSO_4 solutions with different concentrations into the system

solution increases, the interference fringe is red-shifted and the amplitude of the resonance peak decreases significantly. The interference fringe near 1180 nm is magnified as shown in Fig.6(b), and select the lowest point of the interference peak as the observation point. The wavelength of the observation point is red-shifted by 12.4 nm from 1.312×10^{-5} mol/mL to 14.74×10^{-5} mol/mL. The linearity fit is calculated to be 99.95%, and the concentration sensing sensitivity is about 4445.7 nm/RIU.

To enhance the versatility of the system, experimental studies are also conducted for the detection of iron ion solution properties. The chelating agent in the film layer is replaced with sulfosalicylic acid, which will chelate with Fe^{3+} to produce a dark red chelate. The other structures of the system are kept unchanged, and the same color-developing film and coating method are used to obtain the coated LPFG sensitive to Fe^{3+} . Fig.7(a) demonstrates the changes in the transmission spectra before and after the introduction of Fe^{3+} solution in the system. The resonance peak amplitude dropped by 2.12 dB after the addition of the iron ions solution. The structure has the same recognition ability for iron ions.

In order to investigate the effect of Fe^{3+} concentration on the wavelength of the interference peak, six groups of ferric chloride (FeCl_3) solutions with different concentrations are introduced into the fluid channel of SPF-PCF-SPF and the reaction cell of coated LPFG using a pressure device. The interference fringes near 1150 nm are magnified for analysis as shown in Fig.7(b), and the interference peak is red-shifted as FeCl_3 solution concentration rises. Select the lowest point of the interference peak as the observation point. The wavelength of the observation point is red-shifted by 12.76 nm from 3.892×10^{-5} mol/mL to 21.8×10^{-5} mol/mL. The linearity fit is calculated to be 99.97%, and the concentration sensing sensitivity is about 7.13×10^4 mL·nm/mol.

In summary, the system proposed in this work not only specifically identifies heavy metal pollution ions in water such as copper and iron ions, but also provides highly sensitive real-time sensing of their concentration

characteristics.

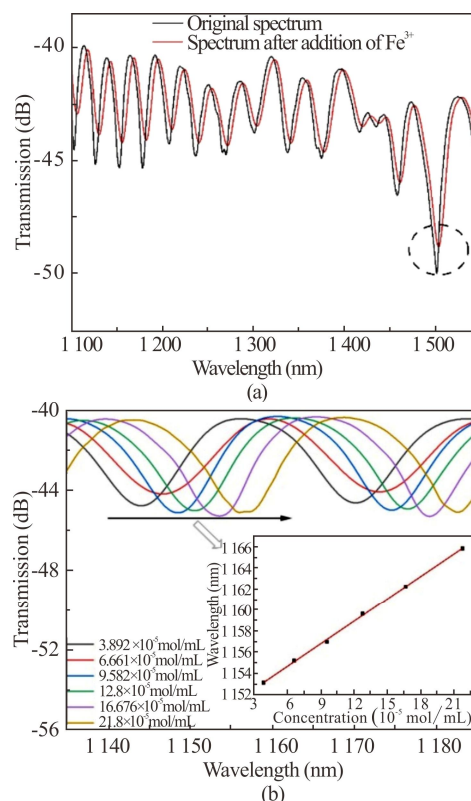


Fig.7 (a) Iron ion identification transmission spectrum of the fusion system; (b) Concentration response fitting characteristics of FeCl_3 near 1150 nm

A metallic ion optofluidic sensing system based on coated LPFG and SPF-PCF-SPF structures is proposed. The relationship between solution concentration and refractive index, as well as the relationship between the resonance peak variation of coated LPFG and the refractive index of the coating layer, is analyzed theoretically and experimentally. The sensitivity of the system for sensing the concentration of CuSO_4 and FeCl_3 solutions is 9.23×10^4 mL·nm/mol and 7.13×10^4 mL·nm/mol, respectively. By observing the change in the amplitude of the resonance peak, the metal ion species can be specifically identified. The system enables the sensing of metal ion types and concentrations in fluids. And its high sensitivity, compact structure is easy to further package and process for industrial wastewater treatment, water pollution detection and other applications.

Ethics declarations

Conflicts of interest

GUO Junqi is an editorial board member for Optoelectronics Letters and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

References

- [1] ALI M. Preconcentration and determination of trace

- amounts of heavy metals in water samples using membrane disk and flame atomic absorption spectrometry[J]. Chinese journal of chemistry, 2007, 25(5): 640-644.
- [2] SI Y, LAO J, ZHANG X, et al. Electrochemical plasmonic fiber-optic sensors for ultra-sensitive heavy metal detection[J]. Journal of lightwave technology, 2019, 37(14): 3495-3502.
- [3] LIN H, HUANG J, DING L. A recyclable optical fiber sensor based on fluorescent carbon dots for the determination of ferric ion concentrations[J]. Journal of lightwave technology, 2019, 37(18): 4815-4822.
- [4] MU J, LIU J, GAO L. Upconversion fluorescence modulation of CaTiO₃: Yb³⁺/Er³⁺ nanocubes via Zn²⁺ introduction[J]. Optoelectronics letters, 2022, 18(3): 129-134.
- [5] SI Y, LAO J, ZHANG X, et al. Electrochemical plasmonic fiber-optic sensors for ultra-sensitive heavy metal detection[J]. Journal of lightwave technology, 2019, 37(14): 3495-3502.
- [6] SHAKYA A K, SINGH S. State of the art in fiber optics sensors for heavy metals detection[J]. Optics and laser technology, 2022, 153: 1879-2545.
- [7] CAI S, PAN H, GONZÁLEZ-VILA Á, et al. Selective detection of cadmium ions using plasmonic optical fiber gratings functionalized with bacteria[J]. Optics express, 2020, 28(13): 19740-19749.
- [8] BASHAN G, LONDON Y, DIAMANDI H H, et al. Distributed cladding mode fiber-optic sensor[J]. Optica, 2020, 7(1): 85-92.
- [9] ABDULKAREEM H D, ALWAHIB A A, MAHDI B R. PCF-multimode/endless fiber sensor for respiratory rate monitoring[J]. Optoelectronics letters, 2023, 19(1): 8-13.
- [10] LI Y, LI Y, MIAO Y, et al. Micro-displacement sensor based on an asymmetric wavy multimode fiber interferometer[J]. Optoelectronics letters, 2023, 19(3): 134-138.
- [11] SHUKLA G M, PUNJABI N, KUNDU T, et al. Optimization of plasmonic U-shaped optical fiber sensor for mercury ions detection using glucose capped silver nanoparticles[J]. IEEE sensors journal, 2019, 19(9): 3224-3231.
- [12] WANG R, REN Z, KONG D, et al. Graphene oxide functionalized micro-tapered long-period fiber grating for sensitive heavy metal sensing[J]. Applied physics express, 2020, 13(6): 067001.
- [13] LI G, LIU Z, FENG J, et al. Pb²⁺ fiber optic sensor based on smart hydrogel coated Mach-Zehnder interferometer[J]. Optics & laser technology, 2022, 145: 107453.
- [14] RYBARCHUK O V, DRAGUNSKY A V, DUDAREV V I, et al. Sorption reaction of chromium (VI) ions with carbon adsorbents[J]. Protection of metals and physical chemistry of surfaces, 2021, 57(3): 464-468.
- [15] LIU S, LU G W, LÜ D Y, et al. Sensitivity enhanced temperature sensor with cascaded Sagnac loops based on harmonic Vernier effect[J]. Optical fiber technology, 2021, 66: 102654.