JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 25, No. 7-8, July – August 2023, p. 387 - 394

Tribond bridged bipyridine complex-functionalized all-fiber interferometric sensor for heavy metal ions in water

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An optical fiber interferometric sensor for heavy metal ions in water is composed with tribond bridged bipyridine complex L coating Mach-Zehnder refractometer. Many heavy metals, include Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} are investigated. The sensing performance of copper (II) ions is particularly studied. In 0 μM~25 μM, sensitivity of the sensor is 16.5 pm/μM with 99.6% linearity, and 3.03 μM limit of detection (LOD). In 25 μM ~250 μM, the sensitivity is 1.2 pm/μM with 41.67 μM LOD. The response time of the sensor is 101.97 s, 182.62 s, and 253.05 s of 20 μM, 200 μM, and 300 μM Cu^{2+} concentrations, respectively.

(Received September 28, 2021; accepted August 10, 2023)

Keywords: Optical fiber interferometric sensor, Mach-Zehnder refractometer, Heavy metal ion, Coating, Water

1. Introduction

Heavy metal ion in water has serious biological toxicity even with low concentrations, which mainly comes from industrial wastewater polluted by arbitrary discharge of industrial pollutants such as metallurgy, printing and dyeing, chemical industry, etc.[1–3]. In recent years, due to the influence of modern industry, it has a wide range of mobility in groundwater and other environments, which has great toxicity to fish and phytoplankton. Furthermore, heavy metal ions will produce ecological toxic effects, like biological accumulation and sustainability, seriously affecting the ecological sustainable development and human health[4,5]. Heavy metal water pollution has become a major environmental problem affecting agricultural safety and human healthy [6,7]. Hence the detection and monitoring of heavy metal ions in water becomes essential.

So far, many kinds of heavy metal detection methods have been proposed such as electrochemical [8–11], optical [12, 13, 14], chemical and biological [15–21]methods. These methods and techniques can detect trace concentration and have good selectivity and sensitivity to metal ions. However, these existing techniques are difficult to achieve in situ detection and have disadvantages of high equipment price, complex operation, long respond time. Therefore, a high-precision, low-cost, real-time, and fast detection method is needed to be developed to detect heavy metal ions in water.

In recent years, various heavy metal ion optical fiber sensors have been proposed due to its high sensitivity, anti-interference, low cost, small size, and real-time performances. In these studies, the methods of constructing sensors by combining the substances that react with the heavy metal ions with various optical fiber sensing structures are widely used [19–22]. Existing types of heavy metal ion optical fibers sensors mainly include colorimetric fluorescence sensors[23], fiber grating coating sensors [24, 25, 26], electrochemical surface plasmons resonance fiber sensors[27, 28, 29].

In this paper, a novel tribond bridged bipyridine complex L [4-methyl-2, 6-bis(pyridine-3-ylethynyl) aniline] coating all optical fiber Mach-Zehnder (M-Z) heavy metal ion sensor is proposed and demonstrated. In our experiments, L-film with 0.75 μm thickness is coated on the surface of an all-optical fiber M-Z interferometer, which is composed with single mode-thinned core-single mode (STS) optical fiber structure. First, the electivity of various heavy metal ions of Zn (II), Mn (II), Co (II), Ni (II), Cd (II), and Cu (II) at different concentrations of the sensor is studied experimentally. The results show that the sensor has the highest sensitivity to Cu (II). And then, the sensing properties of copper (II) are investigated. In our experiments, the dip wavelength of the interference spectrum of the sensor presents red-shift with the increase of ion concentration, due to the combination of Cu (II) and L coating material can reduce the effective refractive index (RI) of the coating film. From 0 μM to 250 μM Cu (II) concentration changes, the dip wavelength increases nonlinearly. In the range of 0 μM~25 μM concentration, the sensitivity of the sensor is 16.5 pm/Mm. In the range of 25 μM~250 μM concentration, the sensitivity of the sensor is 1.2 pm/μM. The LOD of this sensor for Cu^{2+} is 3.03 μM in the ion concentration range of 0 μM ~25 μM, which is significantly lower than the World Health Organization (WHO)'s requirement for the threshold limit of Cu (II) in drinking water (~15.625 μM)[30, 31, 32]. Response time of the sensor at different Cu (II) concentration is also investigated, which results show that the lower the ion concentration, the shorter the sensor response time. In our experiments, for concentrations of 20 μM, 200 μM, and 300 μM, the response times of the sensor are 101.97 s, 182.62 s, and 253.05 s, respectively. In short, the sensor can achieve high precision, fast, real-time detection of heavy metal ions, and has the advantages of low cost, simple structure and easy fabrication.

2. Sensor fabrication and principles

L is coated on the surface of an in-line optical fiber Mach-Zehnder interferometer, which is composed by a single-mode fiber (SMF)-thinned core fiber (TCF)-single-mode fiber (SMF) structure. It is fabricated by splicing a 30mm length TCF with 4.5/125 μm core/cladding diameter between two SMFs. Its structure diagram is shown in Fig.1 (a), the light is injected into the TCF through SMF and divided into two beams at the first cores mismatch point, one passes through the core and excites core mode and the other passes through the cladding and excites cladding modes in the TCF, then cladding part light is recoupled into the core of the SMF at the second cores mismatch point and interferes with core mode. Therefore, this structure can be regarded as a M-Z interferometer. When cladding modes passing through the cladding of the TCF, it will carry surrounding material refractive index (RI) information, and as they are coupled into the core and interfere with the core mode, the RI information will be brought with the output spectrum of the interferometer, therefore, it can be regarded as a M-Z refractometer.

L is coated on the surface of the TCF of the M-Z refractometer to sense the heavy metal ions. Coating process: the optical fiber is placed in a microgroove and immersed in 0.1 g/L L solution in a dust-free and thermostatic box for 3 hours. After dried, a firm L film on the surface of the optical fiber is formed. Microscope photo of optical fiber before and after coating is shown in Fig. 1(b) and Fig. 1(c), respectively. The thickness of the L coating film is nearly 0.75 μm.

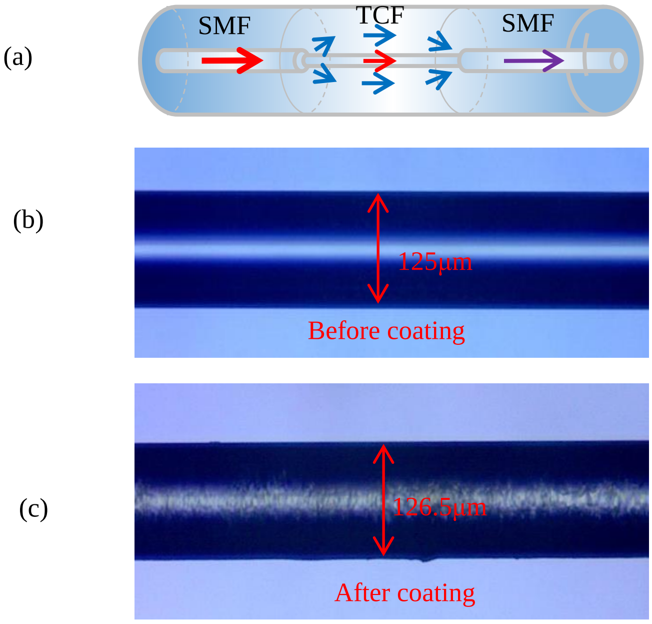

Fig. 1. (a) Diagram of the M-Z interferometer and (b) its microscope photo. (c) Microscope photo of interferometer coating with L film (color online)

In our experiments, the L[4-methyl-2, 6-bis(pyridine-3-ylethynyl) aniline] is synthesized by an improved Sonogashira reaction though one-pot synthesis by Chemical and Environmental Engineering Laboratory in our University[33]. The structure of L crystallized in orthorhombic crystal system, Pca21 space group, with parameters a=10.178Å, b=10.972Å, c=28.949Å, $\alpha = \beta = \gamma = 90^o$. L has conjugated large π bonds in molecules, which makes the coating film on the refractometer has good properties of electron transfer and energy transfer, which atomic structure diagram is shown in Fig.2(a). From Fig.2(a), it can be found that the coating film contains C-N-N / N-N metal coordination bonds to coordinate with transition metals ions. Once the sensor is put into a metal ion solution, these ligands and metal ions can form novel and stable molecular complexes, which is shown in Fig.2(b). L contains unsaturated covalent bond, there is empty orbit and flowing electron cloud in the ligand, which interacts with heavy metal ions and produces complexation reaction, so it shows the change of the optical RI of the coating film of the sensor.

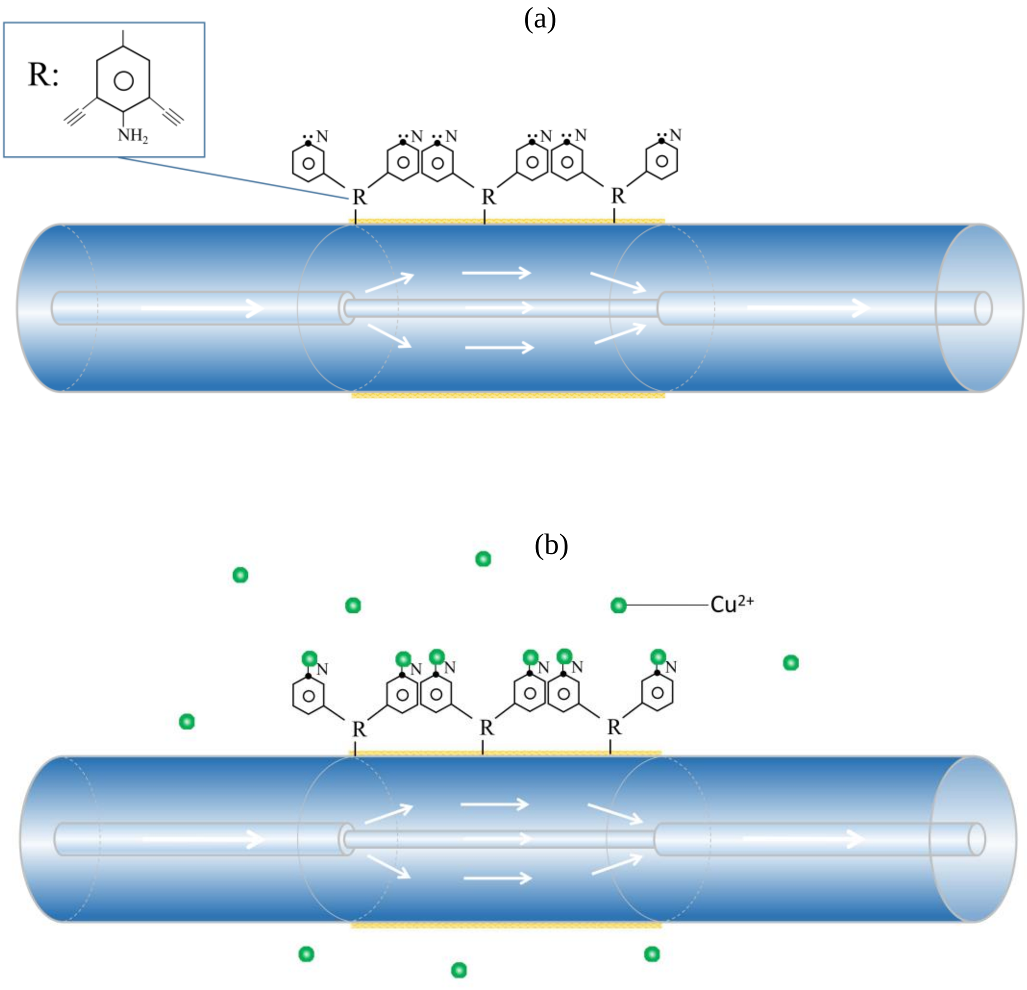

Fig. 2. (a) Diagram of the coating refractometer with surface L atomic structure. (b) L film interacts with heavy metal ions (color online)

The RI change of the L film with metal ions can be obtained through measuring the output interference spectrum of this L coating M-Z refractometer. The relationship between the dip wavelength λ_{dip} and the coating film RI can be expressed as follows [34]:

$$\lambda_{dip} = \left[\left(n_{core} - n_{coating} \right) l \right] / m \qquad (1)$$

among them, n_{core} and $n_{coating}$ is the effective refractive index of the optical fiber core and the coating, m is mode order and an integer, and l is the length of the TCF.

3. Experiments and discussions

3.1. Heavy metal ions in water experiment

The experimental setup is shown in Fig.3, in which a Broad Band Source (BBS) is used to provide broadband light with wavelengths from 1530 nm to1570 nm. Its output port is connected to the input end of the sensor and an Optical Spectrum Analyzer (OSA) with 0.05 nm resolution is connected to the output end of the sensor to detect its output spectrum. The sensor is placed in a miniature slot and immerged in the heavy metal ion solution.

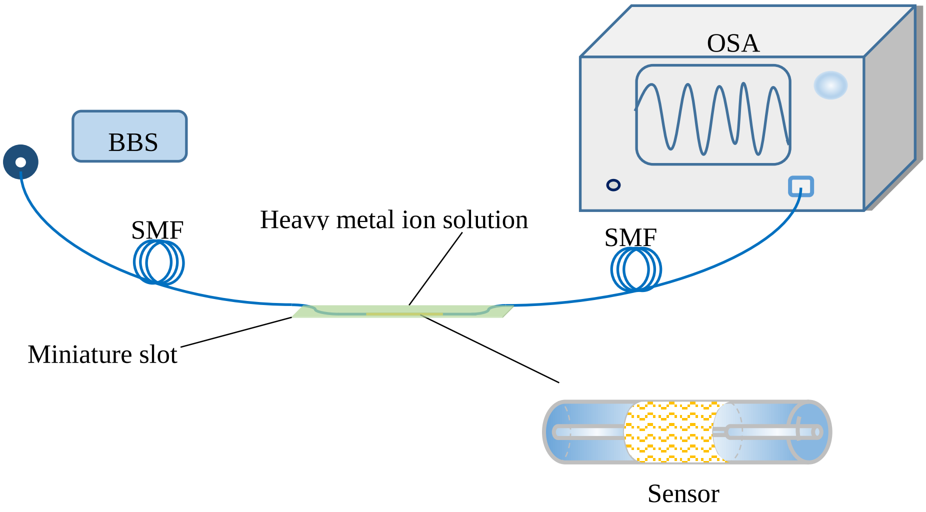

Fig. 3. Experimental setup (color online)

In our experiments, different heavy metal ion of Zn (II), Mn (II), Co (II), Ni (II), Cd (II), and Cu (II) with concentrations of 20 μM (micro-mol/L) and 200 μM response of the sensor is experimentally investigated, respectively. Bar graph of sensor responses to 20 μM concentration heavy metal ions of the sensor is shown in Fig. 4 (a). It can be found that the dip wavelength of the sensor response to Zn^{2+}, Mn^{2+} presents blue-shift with -0.0625 nm and -0.0525nm the maximum wavelength shift, respectively, to Co^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} presents red-shift with 0.125 nm, 0.045 nm, 0.165 nm, and 0.435 nm the maximum shift, respectively. Bar graph of sensor responses to 200 μM concentration heavy metal ions of the sensor is shown in Fig. 4 (b). It can be found that dip wavelength of the sensor response to Zn^{2+}, Mn^{2+} presents blue-shift with -0.05 nm and -0.0725 nm the maximum, respectively, to Co^{2+}, $Ni^{2+,}$ Cd^{2+}, and Cu^{2+} presents red-shift with 0.325 nm, 0.05nm, 0.375 nm, and 0.675 nm the maximum, respectively. According to Eq. (1), these results means that Zn^{2+} and Mn^{2+} combine with L materials, resulting in an increase in the effective refractive index of the coating, and Co^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} combine with L materials, resulting in a decrease in the effective refractive index of the coating, respectively. Meanwhile, it can be found that the sensing characteristics of the L coating all-fiber interferometric sensor relates to the type and concentration of the heavy metal ion, the sensor is the most sensitive to Cu (II) at both concentrations. This is due to when copper (II) ions encounter the lone pair electrons of nitrogen atoms in water, they would be converted into coordination compounds based on $[CuN_4]^{2+}$, such as tetra-amino copper (II). The nitrogen atoms in the ligand L are separated by the heterocyclic structure which made them could replace ammonia to form the coordination compound. The special selectivity for copper (II) ions of the ligand lead to establish of coordination structure when there exist a variety of transition metal ions.

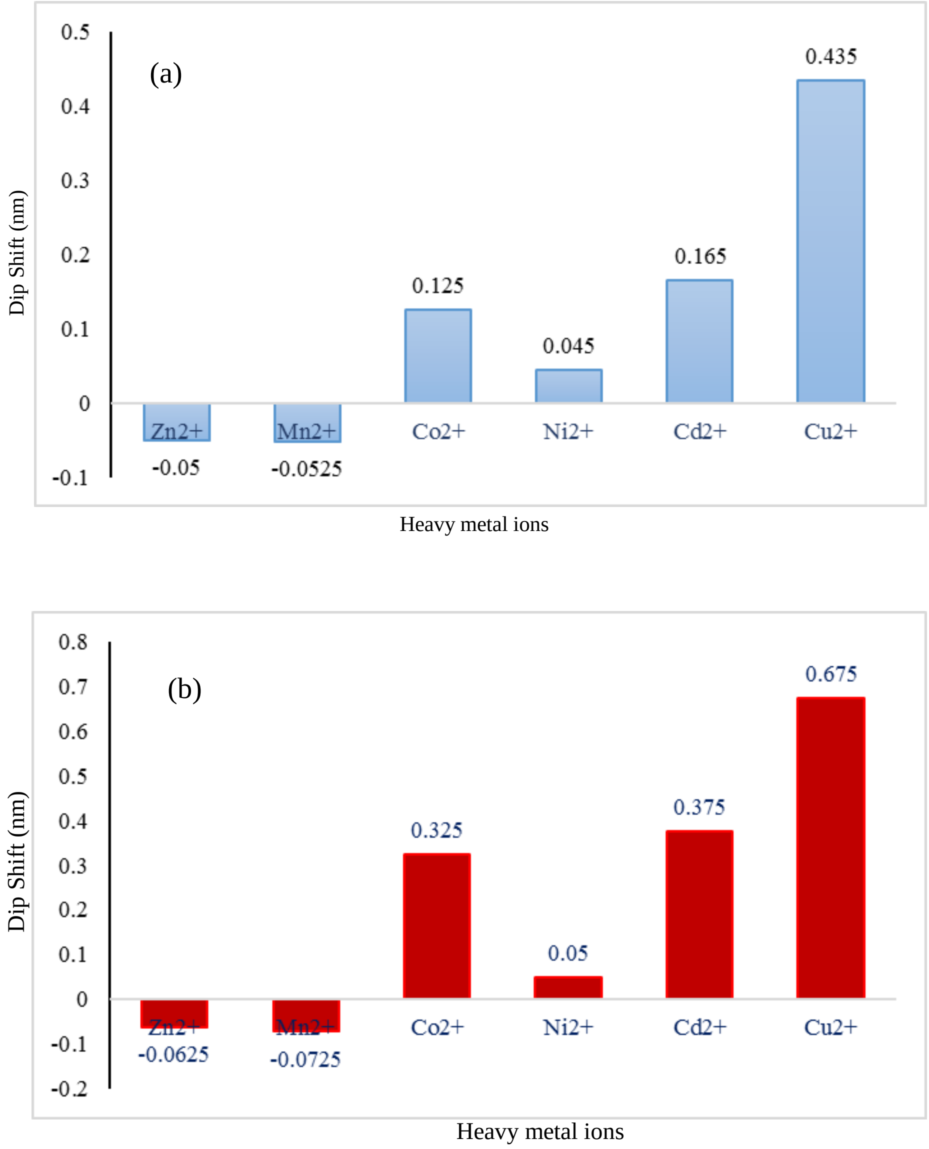

Fig. 4. Bar graph of sensor responses to different heavy metal ion of Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} solutions at (a) 20 µM and (b) 200 µM concentrations, respectively (color online)

3.2. Cu (II) in water sensing experiments

Heavy metal ions sensing performance of L coating all-fiber interferometric sensor is experimentally studied by taking Cu (II) solution as the example. In our experiments, with the Cu (II) solution concentration changes from 0 µM to 250 µM, the dip wavelength of the sensor output spectrum drifts gradually to the long wavelength (red-shift). The spectral superposition diagram and the wavelength-concentration scatter plot is shown in Fig.5(a) and Fig.5(b), respectively. From Fig.5(b), we can find that the dip wavelength of the sensor increases nonlinearly with the increasing of the Cu (II) concentration. To investigating its linear sensitivity of this sensor, piecewise linear fitting method is adopted. Linear fitting of dip wavelength shifts with Cu Cu (II) concentration in range of 0 µM~25 µM is shown in Fig5. (c), from which it can be found that the dip wavelength presents red-shift with 16.5 pm/µM sensitivity and 99.6% linearity. The limit of detection (LOD) of this sensor for Cu^{2+} at this concentration range can get 3.03 µM, which is significantly better than the World Health Organization (WHO)'s requirement for the detection of Cu (II) in water. Linear fitting of dip wavelength changes with Cu^{2+} concentration in range of 25 µM ~250 µM is shown in Fig.5(d), it can be found that the sensor presents linear red-shift with 1.2 pm/µM sensitivity and 91.37% linearity. The LOD of this sensor for Cu (II) at this concentration range is 41.67 µM.

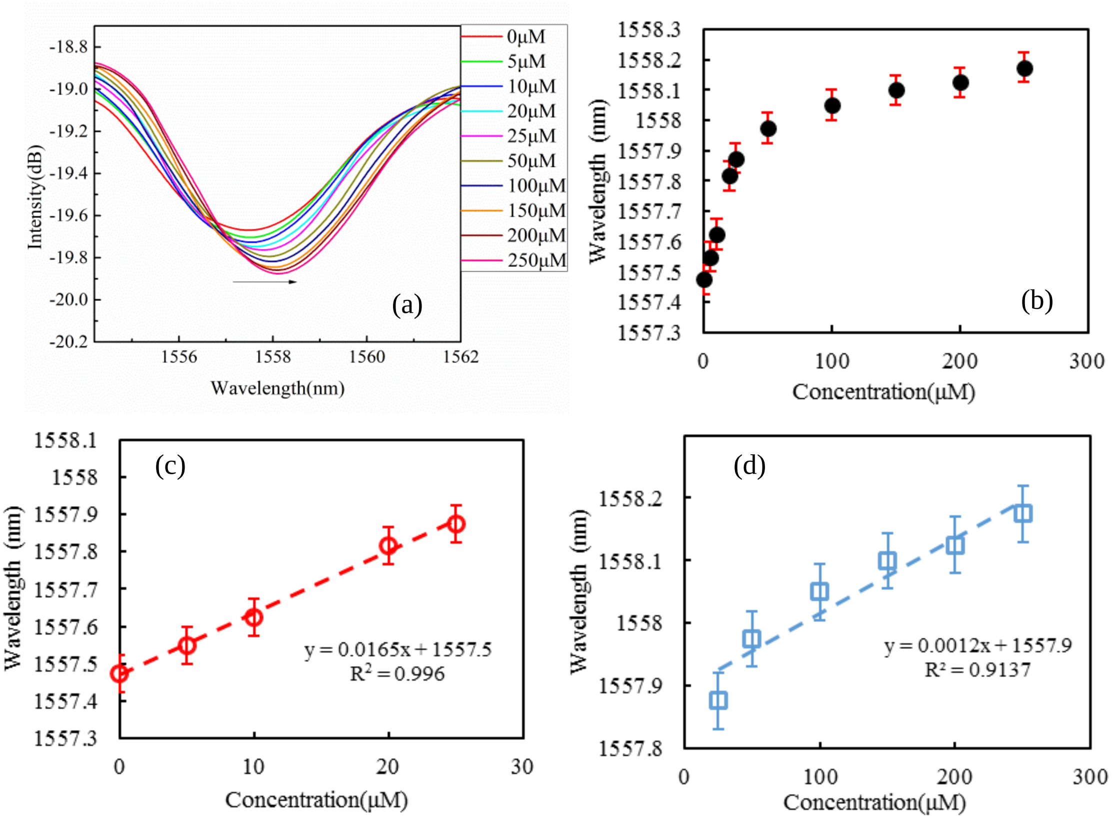

Fig. 5. (a) Sensor spectral superposition diagram of the Cu2+ concentration changing from 0 µM~250 µM and (b) its wavelength-concentration scatter plot. Linear fitting curves of the sensor dip wavelength versus ion concentration at the range of (c) 0 µM~25 µM and (d) 25 µM~250 µM (color online)

3.3. Response time of the sensor

Chemical reaction between Cu (II) and L coating causes the effective refractive index of the film on the surface of the sensor progressive change, which presents as the shift of dip wavelength gradually. In this process, the time experienced from the beginning of the dip wavelength shift to the stability invariant is measured as the response time of the sensor. Investigation of the relationship between response time and Cu (II) concentration of the sensor is carried out. Experimental scatter plots of dip wavelength versus time at different Cu (II) concentrations of 20 µM, 200 µM, and 300 µM are shown in Fig.6. From this figure, it can be found that for concentrations of 20 µM, 200 µM, and 300 µM, the response times of the sensor are 101.97 seconds, 182.62 seconds, and 253.05 seconds, respectively. The response time of the sensor is inversely proportional to the ion concentration, which mainly due to the high ion concentration, the longer reaction time is.

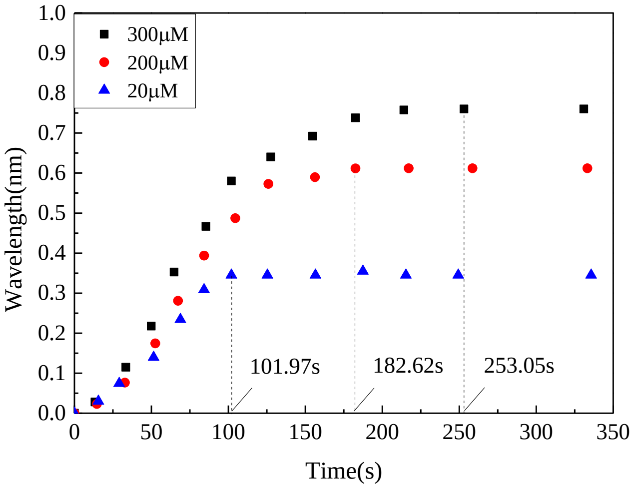

Fig. 6. Response time scatter plots of the sensor at 20 µM, 200 µM, and 300 µM Cu (II) concentrations (color online)

4. Conclusion

In conclusion, an L coating all optical fiber interferometric sensor for heavy metal in water and its sensing characteristics is proposed and demonstrated. The sensor is composed by a novel L material as heavy metal ions sensitive film coating on an M-Z interferometer as refractometer to sense the effective refractive index changing of the coating film. Various heavy metal ions of Zn (II), Mn (II), Co (II), Ni (II), Cd (II), and Cu (II) with concentrations of 20 μM and 200 μM response of the sensor is experimentally investigated, respectively. The experimental results show that the sensor presents different sensitivities to different ions due to the difference effective refractive index change can be produced by the combination of the L film and the ions. The sensor is most sensitive to Cu (II) ion. Therefore, taking copper ion as an example, the sensing characteristics of the sensor are studied. The sensor dip wavelength presents red-shift with the Cu (II) concentration increasing from 0μM to 250μM due to the decrease of the effective RI of the L film. The linear fitting of the sensing results in 0μ M~25 μM concentration range shows that the sensitivity of the sensor is 16.5 pm/μM with 99.6% linearity. The limit of detection (LOD) of this sensor for Cu (II) at this concentration range can get 3.03 μM, which is significantly better than the World Health Organization (WHO)'s requirement for the concentration of Cu (II) in water. Response times of the sensor at different Cu^{2+} concentration of 20 μM, 200 μM, and 300 μM are 101.97 s, 182.62 s, and 253.05 s, respectively, are obtained. In a word, a novel kind of heavy metal ions optical fiber sensor is demonstrated experimentally, which has the advantages of high precision, fast, real-time, low cost, and easy fabrication, which makes it has potential applications in industry, agriculture, medicine, health, environmental engineering and human life.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fundings

This work was supported by the State Key Laboratory of Mining Disaster Prevention and Control, Shandong University of Science and Technology (MDPC201602, MDPC2022ZR04); Department of Education of Shandong Province (J06P14); The Qingdao Feibo Technology Co., Ltd (02040102401); Postdoctoral Research Foundation of China (200902574, 20080441150).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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