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Selective detection of cadmium ions using plasmonic optical fiber gratings functionalized with bacteria

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Abstract: Environmental monitoring and potable water control are key applications where optical fiber sensing solutions can outperform other technologies. In this work, we report a highly sensitive plasmonic fiber-optic probe that has been developed to determine the concentration of cadmium ions (Cd^{2+}) in solution. This original sensor was fabricated by immobilizing the *Acinetobacter* sp. around gold-coated tilted fiber Bragg gratings (TFBGs). To this aim, the immobilization conditions of bacteria on the gold-coated optical fiber surface were first experimentally determined. Then, the coated sensors were tested *in vitro*. The relative intensity of the sensor response experienced a change of 1.1 dB for a Cd^{2+} concentration increase from 0.1 to 1000 ppb. According to our test procedure, we estimate the experimental limit of detection to be close to 1 ppb. Cadmium ions strongly bind to the sensing surface, so the sensor exhibits a much higher sensitivity to Cd^{2+} than to other heavy metal ions such as Pb^{2+}, Zn^{2+} and $CrO_4{}^{2-}$ found in contaminated water, which ensures a good selectivity.

1. Introduction

Heavy metals are categorized as environmental pollutants due to their toxic effect on humans, animals and plants. They are persistent in all parts of the environment since they cannot be degraded or destroyed [1]. Contamination of the environment with heavy metals, including cadmium, is a serious problem of the modern world. As one of the most toxic heavy metals, the acute poisoning by the effect of cadmium is manifested in a variety of symptoms which include kidney damage, hypertension, anemia, high blood pressure or cancer, among others [2,3]. It is estimated that annually around 30,000 tons of cadmium are released into the environment, of which 13,000 tons result from human activity [4]. The provisional tolerable weekly input of cadmium recommended by the World Health Organization (WHO) on food additives is 0.4–5.0 mg, based on a tolerable intake of 1 μg/kg of body weight per day [5]. In addition, the maximum allowable cadmium ions concentration in unpolluted natural waters is 1 μg/L or 1 ppb [6]. It is therefore crucial to develop cost-effective chemical sensors exhibiting high selectivity and sensitivity, low limit of detection and fast response, to be able to detect cadmium ions in drinking or tap water, allowing continuous monitoring of the environment.

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In recent years, the analytical field has evolved with growing concern for the welfare of the environment, requiring both qualitative and quantitative information on the nature and concentration of pollutants. Several complex analytical techniques have been developed to determine the trace amounts of cadmium ions (Cd^{2+}) in water samples including electrochemical sensing [7–9] and fluorescent and colorimetric detection [10–13] methods. These techniques can be adapted for *in situ* portable sensor deployment and real-time monitoring of the environment. They also provide highly selective, sensitive and low-cost sensing methods, but a relatively high limit of detection (LOD). Alternatively, other analytical techniques have been reported, including atomic absorption spectrometry [14–18], inductively coupled plasma optical emission spectrometry [19,20], inductively coupled plasma mass spectrometry [21,22], and high-performance liquid chromatography [23]. These techniques require expensive instrumentation, time-consuming measurements and are not portable for *in situ* analysis, particularly for real-time environmental monitoring. Additionally, the use of labelled moieties can induce undesired effects in the optical detection of target molecules in solution. An alternative approach to overcome this drawback is a label-free optical detection scheme, in which no fluorescent tag is required for the detection of target heavy metal ions in water samples.

Optical fiber-based sensors have arisen as well, especially in biochemical sensing applications, providing numerous advantages as safety, corrosion resistance or suitability for remote sensing in very small sensing volumes [24–28]. Based on their principle of operation, some examples are exposed cores [29,30], interference-based [31,32], tapered fibers [33], microfibers [34], or fiber grating sensors [35,36]. To date, numerous optical fiber-based sensing techniques have been reported, such as surface plasmonic resonance (SPR) [26], localized surface plasmonic resonance (LSPR) [27], and lossy mode resonance (LMR) [37,38].

Here, we report a label-free surface plasmon resonance-based (SPR) optical fiber sensor for *in vitro* detection of cadmium in a water sample. The optical structure proposed in this work is shown in Fig. 1. It consists in a gold-coated tilted fiber Bragg grating (TFBG) [39] functionalized with *Acinetobacter* sp.. The TFBG couples some light modes out of the fiber core and into the cladding [40] so that an SPR is excited at the interface between the metal coating and the surrounding medium [41]. In this case, the sensor can perform in the range of cadmium concentrations from 1 ppb to 1 ppm. It therefore allows to provide environmental monitoring. Our test procedure (dip coating the optrode in tenfold growing concentrations of Cd^{2+} from 0.1 to 1000 ppb) confirms that the experimental limit of detection (LOD) is close to 1 ppb, which is highly relevant considering the target applications.

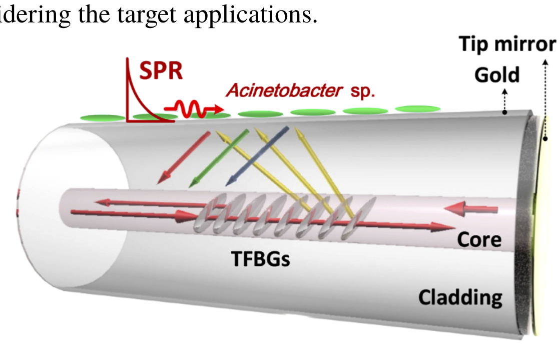

Fig. 1. SPR excitation with *Acinetobacter* sp.-functionalized gold-coated TFBGs.

2. Sensor conceptualization

2.1. Fabrication and biofunctionalization of the sensor

First, TFBGs with a length of 1 cm and a tilt angle of 8° were photo-inscribed in the core of a hydrogen-loaded single-mode optical fiber by excimer laser radiation at 193 nm, using a Noria

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FBG Manufacturing System from NorthLab Photonics. The period of the phase-mask that was chosen allowed to have the spectral resonance comb of the TFBGs located within the wavelength limits of the optical interrogator. After that, TFBGs were heated at 100 °C during 12 h in order to remove the residual hydrogen content still present in the fibers and stabilize their behavior at room temperature. Then, a gold coating of ~50 nm was deposited around the TFBGs location through sputtering and its adhesion to the fiber was improved by a thermal annealing process (2 hours at ~200°C).

A three-time diluted 869 medium was used to cultivate bacteria. The medium contained 3.33 g/L of tryptone (CAS-No: 91079-40-2, Sigma-Aldrich), 1.66 g/L of yeast extract (CAS-No: 8013-01-2, Merck), 1.66 g/L of NaCl (CAS-No: 7647-14-5, VWR International LLC), 0.33 g/L of glucose (CAS-No: 50-99-7, Sigma-Aldrich) and 0.115 g/l of $CaCl_2 \cdot 2H_2O$ (CAS-No: 10035-04-8, Sigma-Aldrich) and the pH was adjusted to 7.0 by using NaCl and HCl. Different concentrations of Cu^{2+}, Pb^{2+} and $CrO_4{}^{2-}$ (1.0 mM, 1.5 mM and 2.0 mM) were used to isolate metal-resistant bacteria. In order to enrich bacteria, bacteria colonies were first incubated in a liquid medium overnight without metal ions. Then, bacteria were incubated with gold-coated TFBGs at a temperature of 30 °C and a rotational speed of 150 rpm with 2 mM of $CrO_4{}^{2-}$ for one week. The $CrO_4{}^{2-}$ served as environmental stress to ensure the purity of bacteria. Once bacteria reached sufficient concentration, TFBGs were observed by optical microscopy and the biofilm formation on the optical fiber surface can be seen in section 3.

Biofilms are defined as matrix-enclosed microbial populations that adhere to biotic or abiotic surfaces [42]. They are considered to be the dominant lifestyle of bacteria both in the environmental ecosystems and human hosts [43]. Generally, the biofilm formation of bacteria on biotic and/or abiotic surfaces is a complicated process consisting of two phases: an initial adhesion phase and the subsequent biofilm development phas. The process of bacterial biofilm formation on material surface is shown in Fig. 2. Each phase further consists of multiple steps. In the adhesion phase, bacterial cells first approach to the substratum by intrinsic mobility, Brownian motion, convection, gravitation and so on. Then, cells reversibly interact with the substrate through physicochemical interactions such as van der Waals, electrostatic and hydrophobic interactions. In the biofilm development phase, while growing and secreting EPS, cells form microcolonies and then gradually develop biofilms [44].

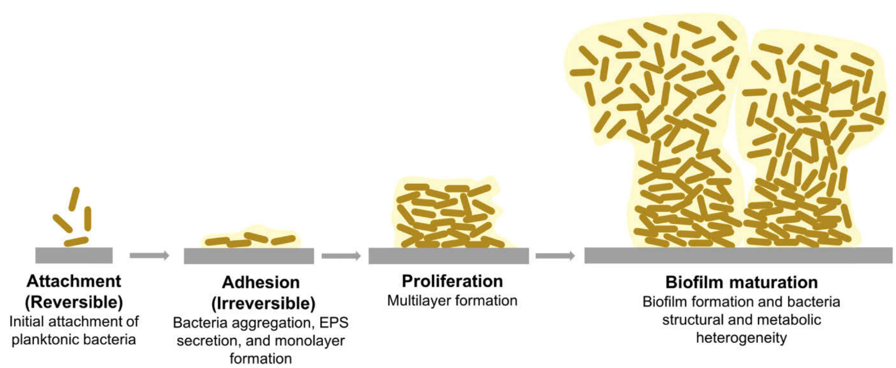

Fig. 2. Schematic drawing showing the two phases of biofilm formation on the material surface: adhesion phase (bacterial attachment and adhesion) and biofilm development phase (bacterial proliferation and biofilm maturation).

Acinetobacter sp., gram-negative bacteria belonging to *Grammaproteobacteria*, have potential applications in bioremediation of heavy metals, e.g. Pb^{2+}, Zn^{2+} and Cr^{6+} [44–47]. On the surface of bacterial cells, the presence of electron-rich and negatively charged groups, such as carboxyl, hydroxyl, amine and phosphate groups, allow the interactions with heavy metal ions and thus play a significant role in heavy metal removal and detoxification [46–47]. The interaction mechanism of *Acinetobacter* sp. with heavy metal ions is shown in Fig. 3. Therefore, the bacteria can be considered as possible receptors grafted on the surface of gold-coated TFBGs aiming to sense heavy metal ions. The greatest contribution of the refractive index changes around gold-coated TFBGs is biosorption, which is a complex process, involving several mechanisms, such as ion exchange, surface complexation, chelation, reduction, precipitation and electrostatic attraction [48]. In the present study, *Acinetobacter* sp. strain 6, isolated from a metal-contaminated soil and resisting to 2 mM CrO_4^{2-}, was used to form biofilm and was immobilized on the surface of TFBGs to detect Cd^{2+} among other metal ions (Pb^{2+}, Zn^{2+}, and CrO_4^{2-}). Two other bacteria, *Cupriavidus* sp. and *Pseudomonas* sp. were also incubated with gold-coated TFBGs to confirm the selective interaction performed by *Acinetobacter* sp. for Cd^{2+} detection.

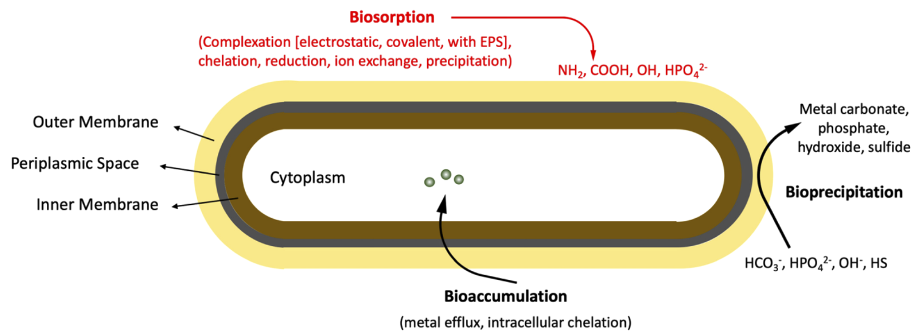

Fig. 3. Interactions of *Acinetobacter* sp. with heavy metal ions by biosorption, bioaccumulation and bioprecipitation.

2.2. Initial response of the sensor

The full reflection spectrum of the sensor is shown in Fig. 4(a). As it can be seen, the SPR region, highlighted in green, is clearly identifiable in the spectrum although other computational techniques can be used for this purpose otherwise [49]. The most sensitive mode is pointed out with a star and further studied in Fig. 4(b), which illustrates the intensity change of the sensor when it is exposed to cadmium environment with concentrations ranging from 0.1 ppb to 1 ppm. Due to the reaction of the bacteria immobilized on the gold surface to cadmium, a refractive index change occurs around the sensor [28]. The sensor can be interrogated both in wavelength

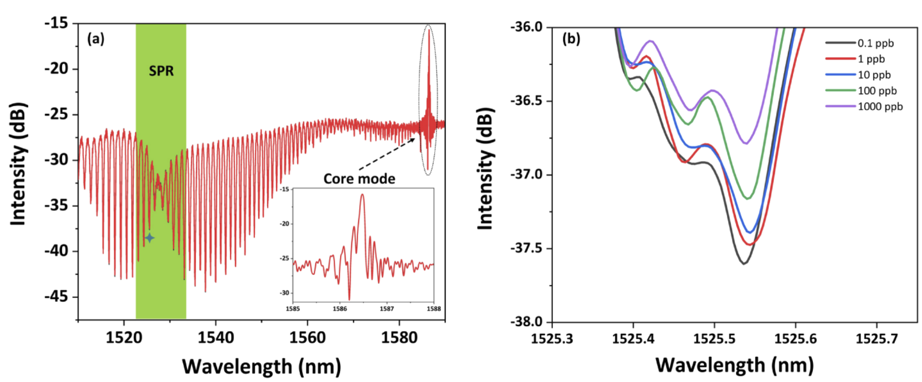

Fig. 4. (a) Reflection spectrum of the sensor and (b) relative intensity change of a selected cladding mode with the sensor immersed into different solutions containing cadmium ions.

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and intensity [50] but the second method is used in this case since the intensity change is the predominant change in the spectrum. Additionally, the core mode is located at 1586.4 nm and can be used as a temperature reference, because it is insensitive to refractive index variations of the surrounding medium.

3. Results and discussion

The performance of the sensor and its suitability for cadmium detection were evaluated by immersing the probe into the metal ion solution by using the setup illustrated in Fig. 5. The plasmonic TFBG sensor was connected to an optical fiber interrogator (NI PXIe-1071 from National Instruments) to record its response. A polarization controller (PC) was also used to select a radial (P) polarization and maximize the coupling of energy to the plasmon. The measurements were carried out in reflection to avoid curvatures on the optical fiber and make easier measurements in small volumes, and a gold mirror was deposited on the fiber tip in order to reflect the cladding modes backwards. The distance between the TFBG and the fiber end is kept below 1 cm to enable the optrode to be immersed into small vials.

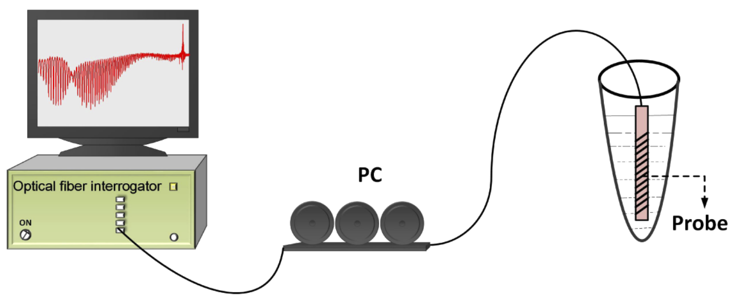

Fig. 5. Setup used to evaluate the response of the probe in the cadmium solution.

Three metal-resistant bacteria, *Acinetobacter* sp., *Cupriavidus* sp. and *Pseudomonas* sp., isolated from metal-contaminated soil, were used and tested in response to different concentrations of Cd^{2+}. They were all functionalized around some TFBGs following the process described in section 2. When incubating the bacteria with gold-coated TFBGs, the *Acinetobacter* sp. presents faster growth rate than the other two bacteria. After one week incubation, the biofilm formation of *Acinetobacter* sp. was also higher than the other bacteria. To obtain a similar density of biofilm on the fiber surface, the other two bacteria were incubated with the fibers for longer time than *Acinetobacter* sp.. The biofilms formation by these three bacteria was observed by microscopy and is shown in Fig. 6. Subsequently, several tests were performed by immersing the bacterial functionalized sensors into different cadmium solutions, obtaining the response plotted in Fig. 7. As it can be seen, there is a difference of roughly 0.7 dB when the concentration of cadmium increased from 1 ppb to 1 ppm. Considering the metrological performances of the measurement device (i.e. 0.05 dB resolution for amplitude changes), these results show the possibility to detect a minimum concentration of 1 ppb. The results also reveal that the other two bacteria do not react to Cd^{2+} as the TFBG response remains almost stable. Therefore, *Acinetobacter* sp. has a much higher selectivity to Cd^{2+} than the other two bacteria.

The response of *Acinetobacter* sp.-immobilized TFBGs to different heavy metal ions, such as Pb^{2+}, Zn^{2+}, Cd^{2+} was also investigated. These ions have been previously detected using various modified optical fibers [51–53]. In this study, $CrO_4{}^{2-}$ was used as a control. The sensor tests with Cd^{2+}, Zn^{2+}, Pb^{2+} and $CrO_4{}^{2-}$ ions were carried out at room temperature. Figure 8 shows the relative intensity changes of the selected cladding mode when the sensor was immersed into different kinds of heavy metal ion solutions at the same concentration of 10 ppb. The

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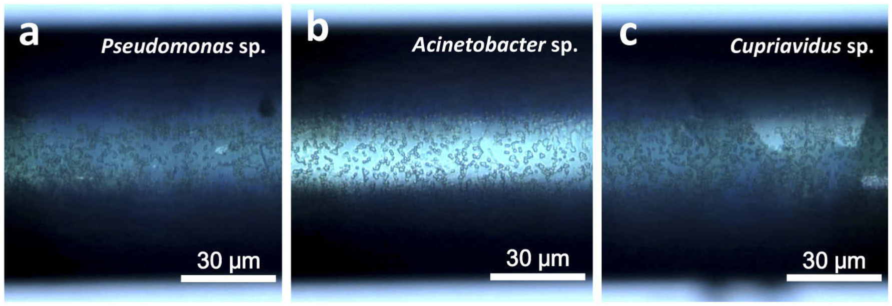

Fig. 6. Microscopic views of biofilms formation by different bacteria: (a)*Pseudomonas* sp., (b) *Acinetobacter* sp., and (c) *Cupriavidus* sp. on the sensor surface.

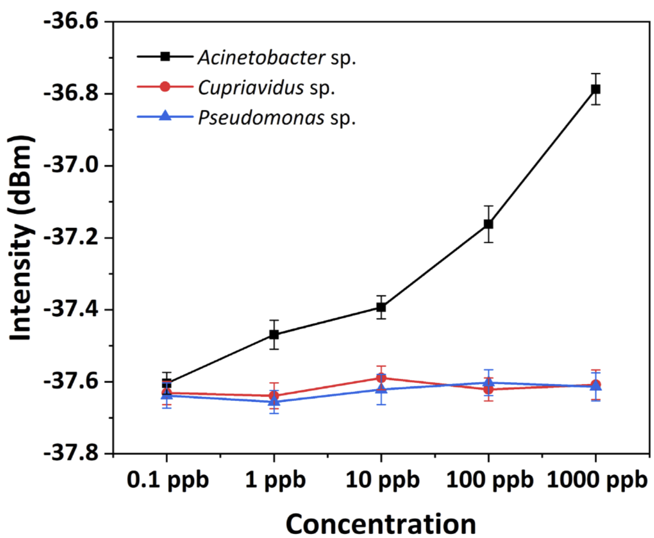

Fig. 7. Relative intensity changes of a selected cladding mode when the sensors immobilized with bacteria were immersed in different cadmium solutions.

intensity change is higher when the sensor reacts to Cd^{2+}, exhibiting a maximum difference of approximately 0.21 dB. When the sensor reacts to other heavy metal ions such as $CrO_4{}^{2-}$, Pb^{2+} and Zn^{2+}, all of their intensity changes were below 0.05 dB. As shown in the figure, the average stabilization time is roughly 15 minutes when the sensor reacts to Cd^{2+}. During the first minute, the intensity change when the sensor reacts to Cd^{2+} is the largest and peaks at ~0.20 dB while others remain below 0.05 dB.

The different responses of the sensor to all the ions tested are shown in Fig. 9. The higher response to Cd^{2+} is due to the carboxyl groups of peptidoglycans, which serve as a main metal-binding site on the cell wall. Additionally, thiol groups in bacterial cells, which is a kind of soft Lewis based, have a high affinity for Cd^{2+}, as soft Lewis acids then form a coordinate covalent bond [54]. When immersing *Acinetobacter* sp.-functionalized TFBGs into $CrO_4{}^{2-}$ solution, the relative amplitude change is even negative, elucidating a weak or null interaction between bacteria and $CrO_4{}^{2-}$. This negative change is probably due to the repellant interaction of negatively charged functional groups on the cell walls with $CrO_4{}^{2-}$. It was concluded that the developed sensor provides a high selective response to Cd^{2+} when tested against other heavy metal ions.

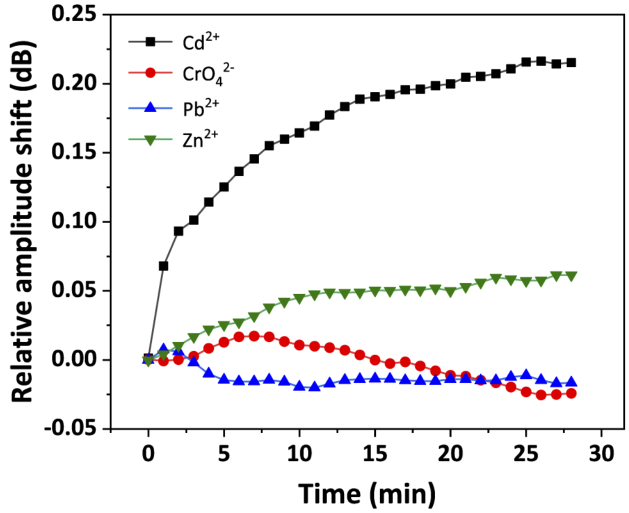

Fig. 8. Relative intensity changes of the selective cladding mode when the sensor immobilized by *Acinetobacter* sp. was immersed into solutions containing cadmium (Cd^{2+}), lead (Pb^{2+}), zinc (Zn^{2+}) and chromium ($CrO_4{}^{2-}$) ions.

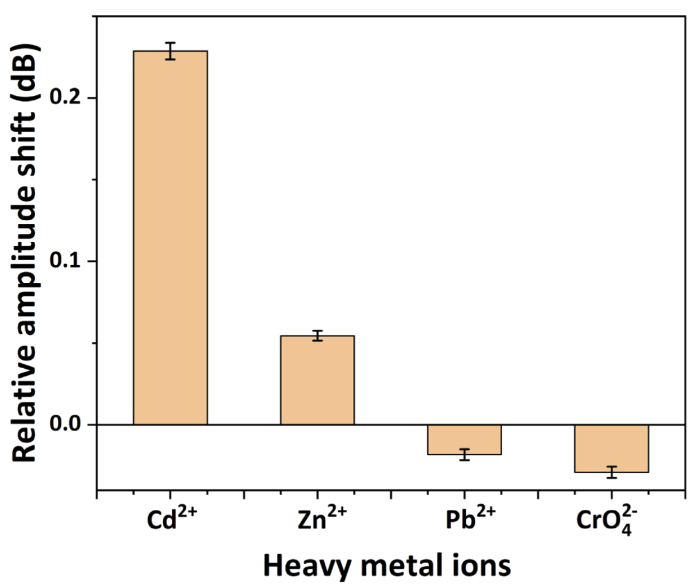

Fig. 9. Selectivity of the sensor immobilized with *Acinetobacter* sp. when tested against other heavy metal ions, such as Cd^{2+}, Zn^{2+}, Pb^{2+}, and $CrO_4{}^{2-}$ at the same concentration of 10 ppb.

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4. Conclusion

A label-free sensor based on a gold-coated tilted fiber Bragg grating has been developed, aiming for the specific detection of Cd^{2+} ions in water. *Acinetobacter* sp. bacteria were immobilized on the gold surface and used as receptors. The sensor showed a very high performance for the specific detection of Cd^{2+} in Milli Q water. Among the characteristics of the sensor, it is worth mentioning a fast stabilization time estimated to roughly 10 minutes and the possibility to detect a concentration of Cd^{2+} as low as 1 ppb while being selective. This fiber grating sensor configuration is intended to be used for *in situ* environmental monitoring and drinking water quality control.

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Disclosures

The authors declare no conflicts of interest.

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