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Luminescent optical fiber Hg^{2+} sensor based on an oligodeoxyribonucleotide sequence

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Abstract:
A luminescent optical fiber sensor fabricated by Layer-by-Layer nanoassembly for mercury detection is presented in this work. The luminophore, Atto-390, has been linked to a mercury sensitive oligonucleotide sequence: due to the strong selective binding of the mercury ions to the thymine-thymine pairs of this sequence, its shape changes in the presence of that metal ion. This change involves a variation of the luminescent intensity that is coupled to the optical fiber, which allows the mercury concentration to be monitored. The sensor detects 10^{-7} M Hg concentrations and shows a reversible behavior.

Key words: Mercury detection, oligodeoxyribonucleotide sequence, Layer-by-Layer nanoassembly, luminescence quenching, optical fiber sensor.

Introduction

Owing to its adverse consequences for the environment and for human health, the detection of water contaminants in low concentrations has become a huge challenge for scientists in the last decades. Thus, many electronic and optic devices have been developed for that purpose. Among the last ones, luminescence-based sensors have been widely employed: they are usually based on a sensitive indicator whose luminescence is attenuated by the target pollutant. The luminescent indicator utilized in this work for the development of a mercury ions (Hg^{2+}) sensor has been linked to the 3' end of an oligodeoxyribonucleotide (ODN) sequence that is sensitive to that metal ion. When the Hg^{2+} ions link to the thymine-thymine (T-T) pairs of the ODN sequence, it acquires a hairpin structure that produces changes in the luminescent intensity emitted by the sensor. As the combination of ODN sequences with the optical fiber has led to highly sensitive devices [1], this material has been chosen as the substrate for the sensor developed in this work. That sensor, apart from detecting Hg^{2+} concentrations as lower as 10^{-7} M, also exhibits a reversible behavior.

Materials and methods

The ODN sequence (5'-TTCTTTCTTCGCGTTGTTTGTT-3') functionalized with a carboxy group (COOH) and a fluorophore (Atto390) at its 5' and 3' ends, respectively, has been used as mercury ions (Hg^{2+})-sensitive material. As reported previously [2], Hg^{2+} ions bind selectively to the T-T pairs, thus, the ODN sequence can be divided in three parts: the first and the third one consist of T-rich sequences, whereas the second one is a linker that enables an easier binding between the Hg^{2+}-sensitive sequences. In presence of this metal ion, the ODN sequence aquires a hairpin shape as a consequence of the binding between of the Hg^{2+} ions to the T-T pairs, as shown in Figure 1.

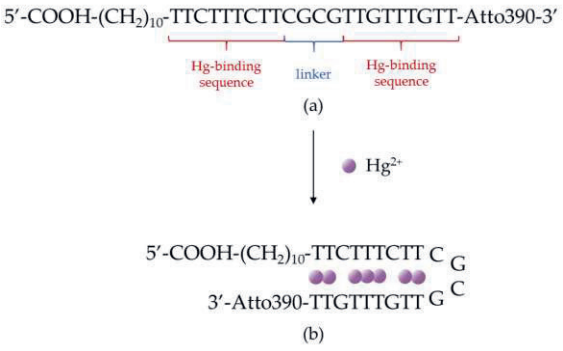

Fig. 1. Structure of the Hg^{2+}-sensitive ODN sequence in the absence of H^{l2+} ions (a) and in its presence (b).

Owing to its negative superficial charge and its water-solubility, the ODN sequence was deposited on the tip of a 1000 µm-core fiber by means of the Layer-by-Layer nanoassembly technique as follows: first of all, five pairs of

layers of oppositely charged polyelectrolytes poly(allylamine hydrochloride) or PAH (cationic) and poly(acrylic acid) or PAA (anionic) were deposited onto the tip of the fiber, followed by five bilayers of PAH and the ODN sequence, giving rise to the sensing structure $(PAH/PAA)_5(PAH/ODN)_5$.

The sensor was characterized by using a reflection architecture: it was connected to the common branch of a 600 µm-core bifurcated fiber, to whose independent branches were connected a LED centered at 395 nm and a Maya LSL spectrometer.

The illumination at 395 nm of the Atto390 molecules gave rise to a luminescence emission centered at 463 nm, whose monitoring allowed the measurement of Hg^{2+} concentration in aqueous solutions.

Results and discussion

For its characterization, the sensor was alternatively immersed into Tris-HCl buffer solutions at pH 7.6 of different Hg^{2+} concentrations: 0 M Hg, 10^{-7} M Hg, 10^{-6} M Hg, 10^{-5} M Hg and 10^{-4} M Hg.

The luminescence peak of the sensor under illumination at 395 nm can be observed in Figure 2. The same graph also shows how the luminescent intensity decreases as the concentration of the metal ion increases.

The behavior of the sensor under dynamic variations of the Hg^{2+} concentration is displayed in Figure 3: apart from the different intensities of the luminescence for the distinct Hg^{2+} concentrations, it is also observable that the sensor recovers its original luminescent intensity once the metal ion is removed from the aqueous solution.

Conclusions

The sensor presented in this work is based on a luminophore linked to an ODN sequence to which Hg^{2+} ions bind: as a consequence of this binding, the shape of this sequence changes and also does the luminescent intensity of the device. The sensor is not only capable to detect low Hg^{2+} concentrations, but it also exhibits a reversible behavior. Further work should try to improve the limit of detection and check the selectivity of the sensor.

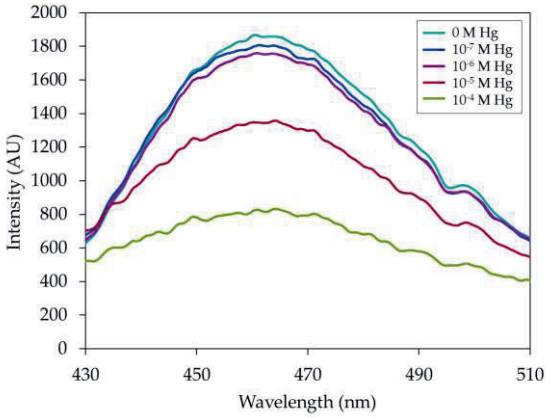

Fig. 2. Luminescent intensity of the sensor for different Hg^{2+} concentrations.

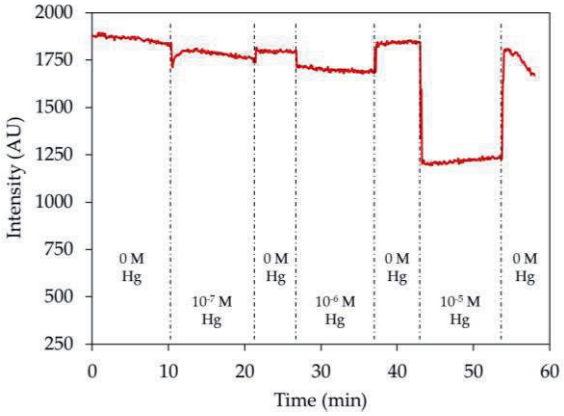

Fig. 3. Variation of the luminescent intensity under changes of the Hg^{2+} concentration.

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