Development of a fiber-optic chemical sensor for the detection of cadmium

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***Abstract*—The detection of cadmium in the environment is very important and in this work the development of an optical fiber chemical sensor for the detection of Cd^{2+} is described. To achieve this, an optical fiber-based technique has been developed using a sensing layer containing a coumarin fluorophore and dipicolylamine receptor. This was covalently attached to the distal end of an optical fiber and exhibited a significant increase in fluorescence intensity in response to Cd^{2+} in the µM concentration range *via* a photoinduced electron transfer (PET) mechanism. Selectivity for Cd^{2+} over other metal ions has also been demonstrated showing the value of the approach for environmental measurements.**

Keywords—optical fiber sensor; chemosensor; cadmium sensor; fluorescent sensor; photoinduced electron transfer

I. INTRODUCTION

Cadmium can be released to the environment in a number of ways[1], including natural activities, human activities and remobilization of historic sources, such as the contamination of watercourses by drainage water from metal mines. Atmospheric deposition of cadmium on arable soils often outstrips its elimination, resulting in higher levels of cadmium in soils and crops. In addition, agricultural soil cadmium pollution can significantly rise through application of municipal sewage sludge. The effects of cadmium exposure on the individual are both serious and well documented: cadmium exerts toxic effects on the kidney, the skeletal system and the respiratory system and is classified as a human carcinogen[1]. Therefore, the detection of cadmium is very important for both the protection of human health and the minimization of its exposure in the environment.

The detection of cadmium using chemical methods is now new and several cadmium sensors based on fluorescence or surface plasmon resonance detection have been reported[2-11]. However, there are weaknesses with them and their application and most are not suitable for use in the field and often require extraction of samples prior to manipulation and analysis. Consequently, there is a strong industrial need for the development of a low-cost and portable alternative for the detection of cadmium, to create a compact device which will provide a fast screening solution to yield new information on what is an important aspect of improving the environment that we share.

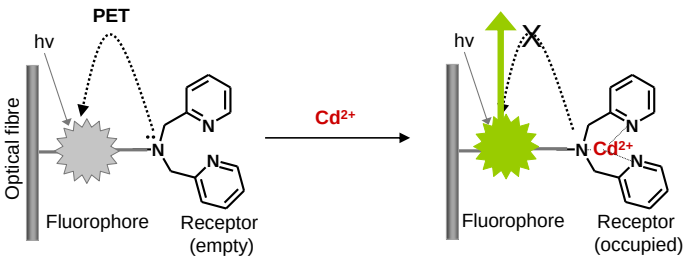

Fig. 1. Illustration of fluorescence switching on by Cd^{2+} binding *via* a PET mechanism.

In this work, a stable, compact and portable fiber optic sensing system which is capable of real time detection of cadmium ion (II) has been developed. The fiber optic approach is appropriate here as it offers advantages over conventional means in terms of small size, immunity to electromagnetic interference, remote sensing capability, resistance to chemicals and biocompatibility[12]. In addition, such sensors could be produced cheaply in quantity as required. The approach is based on a novel fluorescent polymeric material for Cd^{2+} detection, based on a derivative of coumarin (acting as the fluorophore) and dipicolylamine (acting as the cadmium ion receptor) that has been designed, synthesized and covalently attached to the distal end surface of an optical fiber. The approach taken is as follows: in this system, the presence of the amine significantly reduces the fluorescence of the fluorophore due to the quenching of its fluorescence by the nitrogen lone pair electrons through PET. Upon complex formation with Cd^{2+}, the nitrogen lone pair electrons are donated to Cd^{2+}, which therefore abolishes or tremendously reduces the fluorescence quenching. Consequently, binding of Cd^{2+} switches on fluorescence. This is shown schematically in Fig.1.

II. EXPERIMENTAL

A. Sensor fabrication

The fabrication of the Cd^{2+} sensing probe is straightforward, but required a multi-step process, using a novel polymerisable coumarin dye bearing a dipicolylamine

group (**CDA**). **CDA** absorbs at 336 nm and emits at 462 nm in H_2O/MeCN (7:3, v/v) (Fig. 2a). It shows a significant increase in fluorescence intensity in response to Cd^{2+} in an aqueous acetonitrile mixture (Fig.2b). **CDA** was covalently bound to the optical fiber by copolymerizing with methacrylic acid and 1,4-bis(acryloyl)piperrazine cross linker on the surface of the fiber that was prepared and functionalized with polymerizable allyl groups following the previously reported method[13]. The sensor tip was washed in methanol and distilled water to remove all unreacted materials and the excess amount of polymer formed which was not directly bound to the fiber. The probe was then stored in a cool and dark place until its later use.

B. Experimental set-up

The set-up used for the measurements undertaken to evaluate the performance and thus calibrate the probe is as presented in Fig. 3, where light from a LED, emitting at a center wavelength of 375 nm is coupled through a multimode UV/Visible fiber, using collimation and focusing lenses, into one branch of a 2x1 multimode fiber coupler. The other end of the fiber coupler is connected to the sensor probe with the active sensing region being located at the distal end of the fiber. Following pH interaction with the active region, a portion of the total light emitted from the sensing layer is collected and guided through the other branch of the fiber coupler to an Ocean Optics USB2000 spectrometer, with the output being displayed on a computer screen.

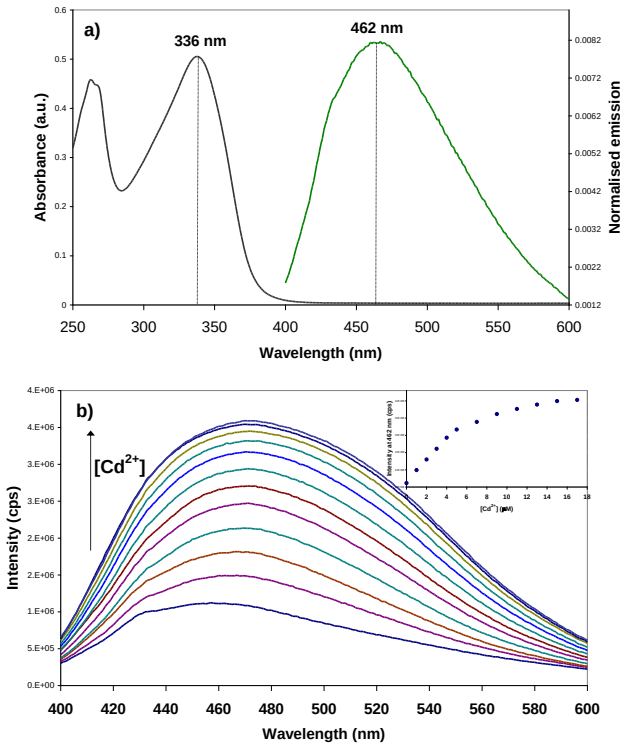

Fig. 2. a) Absorption and emission spectra of **CDA** (20 μM) in H_2O/MeCN (7:3, v/v). Emission spectrum recorded with λex = 336 nm. b) Emission spectra of **CDA** at [Cd^{2+}] ranging from 0 to 17 uM. The inset shows the titration plots at 462 nm (λex = 336 nm).

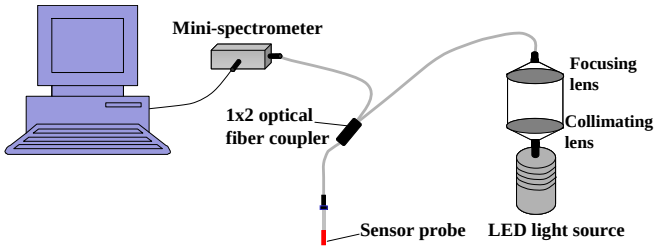

Fig. 3. Experimental set-up used in the evaluation of the performance of the probe designed.

III. RESULTS AND DISCUSSION

A. Response of the sensor to Cd^{2+}

The calibration of the sensor was performed using a series of solutions of cadmium nitrate tetrahydrate – a convenient source of cadmium(II) ions in deionized water. The probe was immersed in the Cd^{2+} solutions and the signals were allowed to reach constant values (~ 2 minutes) before being recorded. The sensor was rinsed with deionized water between measurements. In a way that is similar to that seen for the free dye, the sensor exhibited an increase in fluorescence intensity with increasing Cd^{2+} concentration in the range of 0 - 16 μM (Fig. 4). At higher concentrations of Cd^{2+}, no further change of intensity was observed due to the saturation of all available binding groups. It has also been noted that the emission peak of the immobilized form of the dye is slightly 'red shifted' compared to that of its free form in solution – that is to a longer wavelength. It seems that this probably can be attributed to the change in the polarity of the microenvironment.

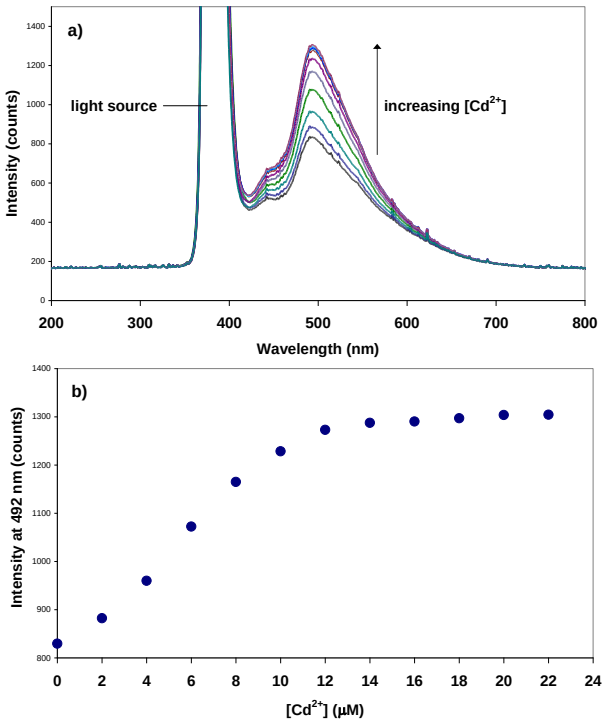

Fig. 4. a) Fluorescence spectra of the sensor probe in deionised water with the addition of Cd^{2+} b) Corresponding plot showing the change of fluorescence intensity with changing Cd^{2+} concentration.

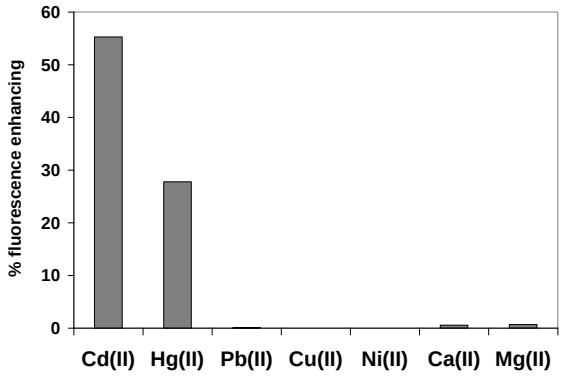

Fig. 5. a) Fluorescence spectra of the sensor probe in deionised water with the addition of Cd^{2+} b) Corresponding plot showing the change of fluorescence intensity with changing Cd^{2+} concentration.

B. Selectivity of the sensor towards other cations

Cross-sensitivity is an important issue for such probes and the responses of the sensor probe to the presence of various biologically and environmentally relevant metal ions were investigated and the results are illustrated in Fig. 5. The concentration of all the ions tested was fixed at 14 µM, where a significant increase in fluorescence intensity was seen for Cd^{2+}. The fluorescence profiles of the probe were almost unchanged in the presence of Pb^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+} and Mg^{2+}, indicating excellent selectivity for Cd^{2+} over these cations and a very important result for the in the field use of a sensor like this where such cross contamination is likely. In the tests carried out, the only metal ion that seems to interfere significantly with the determination of Cd^{2+} is Hg^{2+}. However, the sensor is two fold more selective for Cd^{2+} than to Hg^{2+}. This is the subject of on-going work to reduce this effect.

IV. CONCLUSIONS

A proof-of-concept simple optical fiber sensor able to detect cadmium selectively in dilute aqueous solutions has been demonstrated. The sensor has showed an increase in fluorescence intensity in response to Cd^{2+} in the uM concentration range *via* a photoinduced electron transfer mechanism. Sensors of this type are potentially inexpensive to produce in quantity and the large Stokes shift shown allows for more accurate measurements due to the minimum interference between light source and fluorescence signals generated. For industrial applications, the sensors would require 'packaging' to withstand use by inexperienced operators but prior work with, for example, optical fiber relative humidity sensors by some of the authors and others has shown an effective model to protect the sensitive fiber tip[14]. Referencing schemes to allow for corrections due to fluctuations in the source light or environmental perturbation to the sensor system will be considered to be incorporated into such a sensor either through dynamic calibration or a built-in software correction algorithm. As mentioned above, attention to cross-sensitivity issues is the subject of on-going work. Once its performance is further refined, this type of sensor has the potential to be an important tool for better environmental monitoring.

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