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Surface plasmon resonance based fibre-optic chemical sensor for the detection of cocaine

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ABSTRACT

A surface plasmon based fibre-optic chemical sensor for the detection of cocaine has been developed using a molecularly imprinted polymer (MIP) film with embedded gold nanoparticles as the recognition element. The MIP was formed on the layer of gold thin film which was deposited on the surface of a fibre core. The sensing was based on swelling of the MIP film induced by analyte binding that shifted the resonance spectrum toward a shorter wavelength. The sensor exhibited a response to cocaine in the concentration range of 0 - 400 µM in an aqueous acetonitrile mixture. Selectivity for cocaine over other drugs has also been demonstrated.

Keywords: Optical fibre sensor, chemical sensor, cocaine sensor, SPR sensor, molecularly imprinted polymer

1. INTRODUCTION

The detection of cocaine, one of the most commonly abused drugs, is critically important for law enforcement and clinical diagnostics due to the adverse health effects and related dangers associated with its illicit use[1, 2]. Apart from several major analytical techniques available in the laboratory for the determination of cocaine and its metabolites, which are generally expensive, time consuming and cumbersome, existing sensor capabilities to detect the presence of cocaine are fairly limited and in many cases, the best technology continues to be employment of sniffer dogs that involves a high cost (due to the need for specially trained handlers) and is complicated by limited duty cycles and false alarms. There is a need, therefore, for the development of sensitive, selective and robust sensing systems which are capable of real time detection of the target drug. Fluorescence based molecularly imprinted polymer sensors have previously been successfully used for selective detection of cocaine[3-5]. However, fluorescence intensity detection schemes are affected by various potential interfering factors such as the fluctuation of excitation light source used, the aging of optical fibres and environmental condition changes. Therefore, a regular calibration is required in order to increase the reliability of measurements. In this research, a new sensor system which employs surface plasmon resonance (SPR) as the detection method has been developed. SPR is a resonance phenomenon in which surface plasmon waves (surface electromagnetic waves that propagate in a direction parallel to the metal/dielectric interface) are excited at the metal/dielectric interface. SPR based optical sensing systems are developed utilizing the sensitivity of SPR to the refractive index change at the metal/dielectric interface. The technique monitors the change in SPR wavelength, hence it is less affected by interferants.

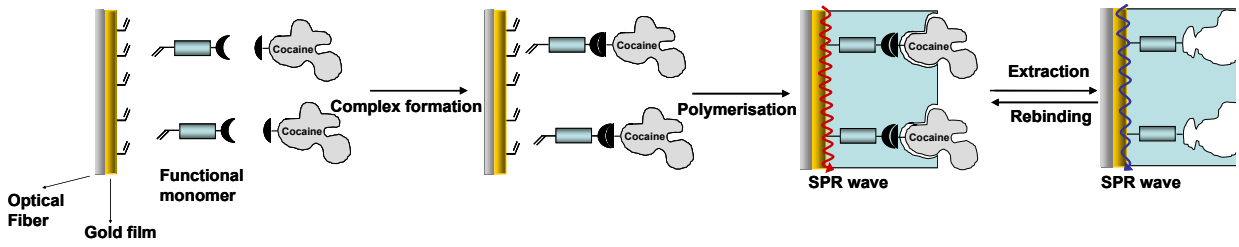

Figure 1. The preparation of a cocaine sensing MIP on the surface of a fibre-attached gold film which exhibits SPR changes upon template binding.

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The molecularly imprinted polymer (MIP) receptor which is selective for cocaine was coated on the layer of gold thin film which was deposited on the fibre core. The imprinting and sensing strategy is illustrated in Fig.1. A complex is formed between the functional group -COOH on the functional monomer (methacrylic acid) and the amine group on the template/analyte. The complex is copolymerised with cross-linking monomer on the surface of the gold film, which has been functionalised with polymerisable groups. Then the template/analyte is extracted from the polymer. The resulting MIP formed on the fibre contains recognition sites and exhibits a change in SPR signal selectively in the presence of the template/analyte. Selectivity arises from the functional group of the functional monomer and from the shape of the cavity. The sensor prepared in this approach benefits from the advantages offered both by the optical fibre in terms of small size, immunity to electromagnetic interference, remote sensing capability, resistance to chemicals and biocompatibility[6, 7] and by the synthetic polymer receptor in terms of robustness, thermal and chemical stabilities, low cost and long shelf-life[8].

2. EXPERIMENTAL

2.1 General

All chemicals were of analytical grade, purchased from Sigma-Aldrich and were used without further purification except for methacrylic acid (MAA) which was distilled under reduced pressure prior to use. 2 nm gold nanoparticles were prepared following a previously reported procedure[9].

2.2 Sensor probe fabrication

The distal end of a 1000 µm diameter UV-Vis multimode fiber with hard polymer cladding purchased from Thorlabs was polished in succession with 5 µm, 3 µm and 1 µm polishing pads (Thorlabs) and washed with acetone. The cladding in the 15-mm end segment of the fibre was removed manually with acetone and a 50 nm thick gold film was symmetrically deposited on the fibre core, using a sputter coater. A silver mirror was created at the distal end of the fibre using a chemical technique with Tollen's reagent[10].

The SPR fibre-optic sensing element is illustrated in Fig.2a, showing the gold film deposited on the fibre core and the silver mirror coated on the distal end of the fibre.

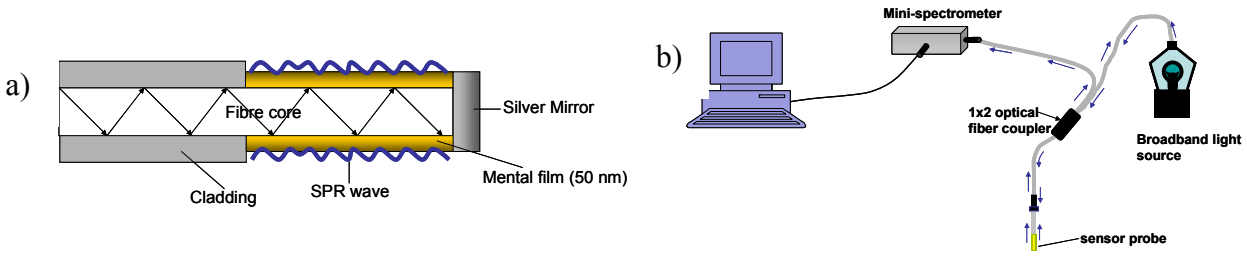

Figure 2. a) Illustration of the SPR fibre-optic sensing element. b) Experimental set-up used in the evaluation of the performance of the probe designed.

The gold-coated segment of the fibre was dipped in a gold surface cleaning solution purchased from Sigma for a period of 30 seconds with subsequent rinsing in copious amounts of distilled water and ethanol and dried with compressed nitrogen. After that, it was immersed in a solution of allyl mercaptan in ethanol (20 mM) overnight, rinsed with ethanol and dried with compressed nitrogen. This procedure functionalizes the gold surface with polymerizable allyl groups.

The pre-polymerization mixture was prepared by dissolving cocaine (30 mg, 0.1 mmol), methacrylic acid (34 µL, 0.4 mmol), 1,4-bis(acryloyl)piperazine cross linker (194 mg, 1 mmol), *N*-isopropylacrylamide co-monomer (91 mg, 0.8 mmol) and 2,2-dimethoxy-2-phenylacetophenone initiator (20 mg) in a solution of 2% (w/w) poly(vinyl acetate dissolved in dry diethylene glycol dimethyl ether (diglyme) (2.5 mL). 20 mg of 2 nm gold nanoparticles were added to the solution to enhance the sensitivity of the sensor. The solution was purged thoroughly with argon for 10 min and quickly transferred to a glove box. Polymerisation was carried out in the glove box by alternately immersing the fibre tip in the pre-polymerization mixture and curing with 365 nm UV radiation (10 times). The fibre was then washed overnight in toluene, followed by a 4h washing in a mixture of 1:4 acetic acid/methanol. Finally, the fibre was rinsed with methanol and dried under vacuum.

2.3 Experimental set-up

The set-up used for the measurements undertaken to calibrate the probe is as presented in Fig. 2b, where light from a broadband light source (purchased from Ocean Optics) is coupled through a multimode UV/Visible fibre with hard polymer cladding, 1000µm silica core and numerical aperture (NA) of 0.37 into a 2x1 Y fibre coupler, which is connected to the sensor probe with the active sensing region being located at the end of the fibre. Following interaction of cocaine with the active region, the reflected light is collected and guided through the other end of the fibre coupler to an Ocean Optics USB2000+ spectrometer, the output from which is processed using the reflection mode and then displayed on a computer screen.

3. RESULTS AND DISCUSSION

3.1 Response of the sensor to cocaine

The calibration was performed by immersing the probe in different cocaine solutions in H_2O/MeCN 9:1 (MeCN was added to solubilize the analyte) at various concentrations. The signals were allowed to reach constant values and then recorded. After each measurement, the probe was washed in MeOH-AcOH (8:2, v/v), followed by the same procedure with MeOH alone to remove bound cocaine. The sensor exhibited a shift in the resonance spectrum toward shorter wavelengths with increasing cocaine concentration in the range from 0 - 400 µM (Fig. 3). This was probably attributed to the swelling of MIP that was induced by analyte binding. At higher concentrations of cocaine, no further change in SPR wavelength was observed due to the saturation of all available binding sites.

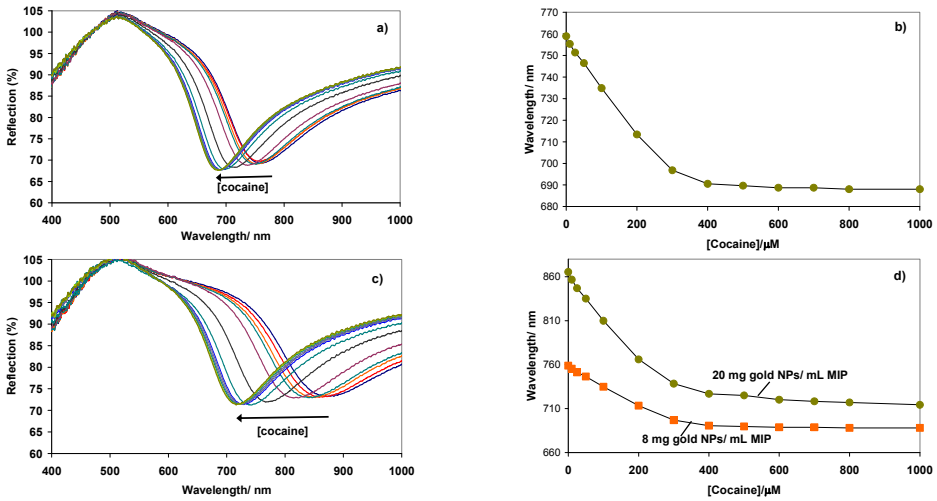

Figure 3. Response of the sensors to cocaine in the concentration range from 0 to 1000 µM. a) SPR spectra of sensor 1 - MIP with embedded gold NPs (8 mg/ mL MIP). b) Plot showing the dependence of SPR wavelength on cocaine concentration for sensor 1. c) SPR spectra of sensor 2 - MIP with embedded gold NPs (20 mg/ mL MIP) d) Plots showing the dependence of SPR wavelength on cocaine concentration for sensors 1 and 2.

It has been demonstrated that the incorporation of Au NPs into a MIP matrix enhanced the sensitivity of the corresponding MIP coated sensor because in addition to the change in dielectric constant, there is a change in coupling between the localised surface plasmon of the Au NPs and surface plasmon polarisation[11]. Sensor 1 and sensor 2 were prepared under identical conditions but with different densities of Au NPs (8 mg/ mL MIP solution and 20 mg/ mL MIP solution, respectively). It can be seen from Fig.3 that sensor 2 exhibits a greater shift in SPR wavelength upon cocaine addition compared to sensor 1 (-138.6 nm vs. -68.3 nm at cocaine concentration of 400 µM), showing the effectiveness of the Au NPs for enhancing the sensitivity. However, the density of Au NPs didn't affect the dynamic response range of the sensor as the number of available binding sites was supposed to be almost the same.

3.2 Selectivity of the sensor

Different drugs including cocaine, ketamine, codeine, amphetamine sulphate, ecgonine methyl ester and buprenorphine.HCl were used for an investigation into the selectivity of the probe developed to cocaine, as it is often seen in the presence of other agents. The concentration of all the drugs considered was fixed at 400 µM in H_2O/MeCN 9:1. It can be seen from Fig. 4 that the sensor responds less to any of these drugs than to the template cocaine. This indicates successful imprinting and selective recognition sites in the MIP. The difference in SPR response of the sensor to different competitors can be explained in terms of the difference in shape and functional groups of their structures to that of cocaine, which results in the difference in their binding capability to the imprinted sites in the MIP matrix and hence causing different degrees of swelling.

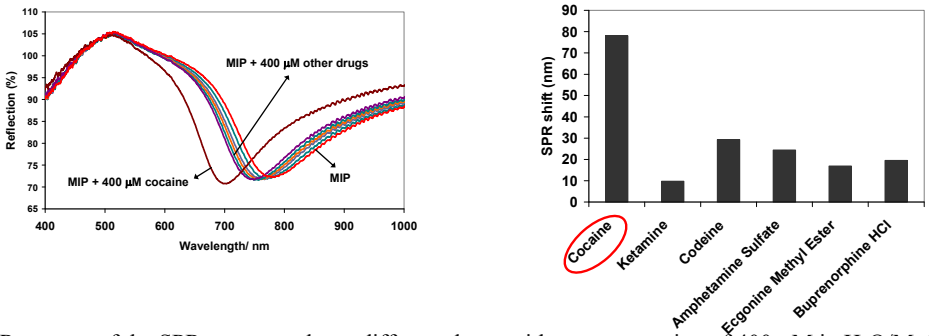

Figure 4. Response of the SPR sensor probe to different drugs with a concentration of 400 µM in H_2O/MeCN.

4. CONCLUSIONS

In this paper, a novel SPR based fibre optic chemical sensor for cocaine has been developed and evaluated and preliminary results reported. The sensor showed a shift in the resonance spectrum toward a shorter wavelength in response to cocaine in the concentration range of 0 – 400 µM in an aqueous acetonitrile mixture. It is also confirmed that gold nanoparticles embedded into the MIP are able to enhance the sensitivity. Selectivity to different drugs was also demonstrated. Research is currently ongoing to investigate the stability and reproducibility of the sensor and the suitability of this type of sensor for use in the homeland security sector.

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