ABSTRACT
In this article, we present a micro-fluidic device that has integrated pH optical sensing capabilities based on polyaniline (PAni) suitable for pH detection in continuous flow. The polyaniline coating is covalently attached to the inner wall of the micro-channel using the “grafting” approach [1]. The optical proprieties of these polyaniline coatings change in response to the pH of the solution that is flushed inside the micro-channel. These unique properties offer the possibility of monitoring pH in continuous flow over a wide pH range across the entire channel length.

KEYWORDS: Polyaniline, pH sensor, Adaptive Coatings, Optical Sensor

INTRODUCTION
In recent years, a number of optical pH sensors have been developed because they offer advantages in terms of size, costs, and response time. By using optical fibers as optical pH sensors, the optical beam can be transported over a long distance, allowing remote sensing [2].

In the last few years conducting polymers have been used to prepare optical pH sensors. Through oxidative polymerisation of an appropriate monomer, conducting polymer films with suitable optical properties for pH sensing can be obtained. This technique eliminates the need of using organic dyes as in conventional optical sensors. Among these conducting polymers, polyaniline has received significant attention because of its suitability over a wide pH range [3-5]. By focusing on PAni nanofibres we can dramatically increase the surface area of the material, which manifests in improved response times and sensitivity. Therefore our approach presents a new, simple, and fast photometric method to measure pH using PAni based coatings in micro-channels. The pH measurement can be carried out in continuous flow mode by using fiber-optic light guides, or along the entire micro-fluidic system by using digital imaging.

THEORY
Usually, the development of optical chemical sensors employ a dye or indicator that should be immobilised onto a solid support material. These type of optical chemical sensors present two main problems: firstly, the dye should retain its optical properties after the immobilisation process and secondly, it should not leach to the solution. Therefore, the development of such sensors has focused on the search for new materials which overcome these problems. One alternative has been the development of optical chemical sensors based on conducting polymers. These materials display optical properties in the visible-near IR region which change upon doping-dedoping. The polymer itself, therefore, acts as the matrix support and the indicator dye. Further more, if in an ideal organic sensing material the essential properties like high sensitivity and penne ability to the analyte could be combined in a single polymeric compound, then no additives would be required. In this way, due to the absence of any leaching effects long-time stability and reproducibility could be realised if the polymer is itself stable. Being an intrinsically pH-sensitive polymer with good environmental stability, PAni is an excellent candidate for the use in fabrication of optical sensors in the visible-near IR detection.

EXPERIMENTAL
Micro-chip fabrication
A PDMS layer is formed by pouring PDMS onto a master mold. Following curing, the PDMS layer is peeled from the master mold. The surfaces of the two pieces - PDMS and glass (or another PDMS layer) were cleaned and oxygen plasma oxidased. Following this, the two pieces of PDMS and glass were immediately brought into conformal contact to form an irreversible seal.

Micro-channel functionalisation process
The functionalisation of the inner walls of the micro-fluidic channel with PAni nanofibres was achieved using the procedure described in Figure 1-left. Briefly, immediately after exposure of the PDMS chips to oxygen plasma and sealing to the glass slide/PDMS layer, the activated channels (1000x100μm) were flushed with a 20%wt solution of N-[3-(Trimethoxysilyl) propyl]aniline in ethanol for 60 min at a flow rate of 0.5 μl/min. The channel was then washed with ethanol and filled with 1M HCl solution containing the oxidant (ammonium peroxydisulfate) and aniline. After polymerisation, the channels were washed extensively with water to remove any unattached polyaniline nanofibres.
RESULTS AND DISCUSSION

Using the technique described, homogeneous PAni coatings were obtained, covalently attached to the internal walls of micro-channels made of PDMS/glass or PDMS/PDMS, Figure 1-right.

Figure 1: Scheme describing the polyaniline nanofibres functionalisation procedure of the micro-channel(left); Photos of the polyaniline functionalised PDMS/PDMS micro-channel (right).

The transformation of PAni between its Emeraldine Salt form (ES) to the Emeraldine Base (EB) in response to basic solution passing through the channel is accompanied by significant changes in colour, Figure 2.

Figure 2: Photos of the micro-channel when solutions of different pHs are flushed through the channel. The photos are accompanied by a scheme showing the differences in the chemical structure of polyaniline in the 2 different states: Emeraldine Salt and Emeraldine Base.

The UV–VIS absorption spectra of PAni films are measured for each pH solutions that is passed through the channel, Figure 3-left. The spectra is highly pH dependent and changes from the green ES to blue EB. Increasing the pH from 2 to 12 leads to a shift in the absorption lambda maxima of PAni from 420 (at pH 2) to 610 (at pH 12). These shifts are obviously due to doping–dedoping of PAni coatings and can be explained by the different degree of protonation of the imine nitrogen atoms in the polymer chain [6]. More specifically, in a low pH environment, a characteristic PAni band appears at 412 nm and represents the doped state. The band at 610 nm is ascribed to exciton formation in the quinonoid rings [7] and this absorption gives rise to the blue colour of the PAni base solutions. Two isosbestic points can be distinguished at 465 and 775 nm, which shows that ES passes to EB without any intermediate oxidation states. The pH dependence of the absorptions at 580 nm was plotted in Figure 3-right. A graduate changes behavior from pH 2 to 10 has been observed showing that these type of coatings can be used as sensor to determine the pH of solutions over a wide pH range region (2–10) in micro-fluidic devices.
CONCLUSION

In conclusion, a new, simple, and fast photometric method to measure pH using PANi based coatings is presented. The pH measurement is done in continuous flow using a syringe pump for the solution while pH measurements are realised using fiber-optic light guides. The main advantage of these sensors are that no reagent indicator is needed because the PANi itself acts as the indicator. Moreover, the functionalisation process can be easily achieved. The covalent attachment and the inherited stability of polyaniline overcomes problems like leaching, in the case when normal pH dyes are employed and presents long-time stability and reproducibility.

ACKNOWLEDGEMENTS

The project has been carried out with the support of the Irish Research Council for Science, Engineering and Technology (IRCSET) - Embark Initiative and Science Foundation Ireland under grant 07/CE/I1147.

REFERENCES


CONTACT

*F. Benito-Lopez, tel: +353-1-7007603; fernando.lopez@dcu.ie*