

FIBER-OPTIC ARRAY SENSORS

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ABSTRACT

Despite many innovations and developments in the field of fiber-optic chemical sensors, optical fibers have not been employed to both view a sample and concurrently detect an analyte of interest. While chemical sensors employing a single optical fiber or a non-coherent fiber-optic bundle have been applied to a wide variety of analytical determinations, they cannot be used for imaging. Similarly, coherent imaging fibers have been employed only for their originally intended purpose, image transmission. Recently, we have used coherent imaging fibers to make fiber-optic chemical sensors. First, imaging fibers can be used to fabricate array sensors that can concurrently view a sample and detect a single analyte. Second, sensors can be made with spatially-discrete sensing sites for multianalyte determinations. Applications will include studying corrosion processes from remote locations.

INTRODUCTION

An imaging fiber is comprised of thousands of individual 2- μm -diameter optical fibers that are melted and drawn together in a coherent manner such that an image can be transmitted from one end of the fiber to the other. These imaging fibers (200-500 μm in diameter) have been utilized to construct several types of novel chemical sensors.[1]

In one approach, we have demonstrated the ability to combine two types of useful measurements (visual and chemical) using a single imaging fiber.[2] A pH-sensitive fluorescent dye was incorporated into a porous polymer layer after it was spin-coated directly onto the distal surface of an imaging fiber. When the pH-sensitive layer was sufficiently thin ($\leq 2 \mu\text{m}$), the fiber's imaging capabilities were not compromised. By combining the distinct optical pathways of the imaging fiber with a charge coupled device, visual (white light) and chemical (fluorescence) measurements could be acquired concurrently with 4- μm -spatial resolution. This technique has many potential applications for remote in situ analyses. For example, recent work has involved imaging a copper/aluminum corrosion cell with a pH-sensitive imaging fiber.[3]

In another approach, discrete arrays of micrometer-sized sensing regions have been photodeposited onto the distal tip of a single imaging fiber.[4] Using a charge coupled device, the fluorescence from each of the different sensing regions immobilized on the imaging fiber could be spatially resolved. The creation of spatially discrete sensing sites on a single optical sensor solves many of the problems associated with designing multianalyte optical sensors such as spectral overlap of multiple indicators and the need to use individual optical fibers for each analyte. Simultaneous measurements are especially important in a number of environmental applications, especially when the dynamics of different analytes are closely interrelated (e.g., pH, pCO_2 , and pO_2). This technique has many potential applications since numerous indicating chemistries (including those for metal ions) can be co-immobilized on a single imaging fiber to form compact multianalyte sensor arrays.

EXPERIMENTAL

Approach #1: pH-sensor fabrication begins by successive polishing of the distal and proximal faces of a 350- μm -diameter imaging fiber (Sumitomo Electric Industries, Torrance, CA) with 30- μm , 15- μm , 3- μm and 0.3- μm lapping films (General Fiber Optics, Fairfield, NJ). Residual polishing material was removed by wiping the faces of the imaging fiber with an acetone-soaked cotton swab. The polished distal face of the imaging fiber required treatment to activate the glass surface with a polymerizable double bond. Surface activation was achieved by silanizing the fiber surface for 2 h using a 10% solution of 3-trimethoxysilylpropyl methacrylate in acetone. After rinsing the fiber with acetone, the surface-bound acrylate was cured at room temperature for a minimum of 30 min. This procedure functionalizes the surface with a polymerizable acrylate to facilitate adhesion of a photopolymer to the glass surface of the optical fiber. A thin layer of polyHEMA/N-fluoresceinylacrylamide was then polymerized at the distal tip using photochemical polymerization in conjunction with

spin coating methods. The stock photochemical polymerization solution consisted of 10 mL HEMA, 200 μ L ethyleneglycol dimethacrylate, and 1 mL of dye solution (50 mg N-fluoresceinyl-acrylamide (synthesized from fluoresceinamine isomer I and acryloyl chloride) in 10 mL *n*-propanol). Individual solutions were prepared with 0.5-mL stock polymerization solution and 30 mg benzoin ethyl ether. Deoxygenated stock polymerization solution (100 mL) was stirred in a 6 x 50 mm test tube and prepolymerized with 366-nm light for 45 s. The resulting viscous oligomer was spread uniformly across the imaging fiber surface by placing a drop of it (approximately 1 mL) on the distal tip of a functionalized imaging fiber (held vertically in a Servodyne mixer head (Cole Parmer, Chicago, IL)) and spinning the fiber at 2000 RPM for 20 s. After spin coating, the polyHEMA/ fluorescein-modified imaging fiber was illuminated with 366-nm light for 1.5 min to complete the polymerization and bond formation. The modified epifluorescence microscope used for fluorescence measurements and imaging has been described previously.[2] The system is capable of making continuous ratiometric measurements through the use of a CCD camera and computer-controlled filter wheels and shutters. During fluorescence measurements, the filter wheels are positioned at the dye's excitation and emission maxima with the fluorescence images being captured by the CCD camera.

RESULTS AND DISCUSSION

The main objective of this work is to create a planar array of thousands of optical sensors in a unitary, flexible fiber format. This approach benefits from the commercial availability of coherent imaging fibers comprised of thousands of micron-sized optical fibers fused together in a fixed arrangement. By coating one end of the imaging fiber with an analyte-sensitive material, we obtain thousands of microsensors capable of simultaneously measuring chemical concentrations with 4- μ m spatial resolution over tens of thousands of square microns. In addition, the image carrying capabilities of the fiber are preserved allowing the operator both to position the sensor and to couple the chemical measurements to visual information.

Recent work has involved imaging a copper/aluminum corrosion cell with a pH-sensitive imaging fiber (Figure 1). In these experiments, the electrodes were placed in aqueous buffer and the distal end of the pH-sensitive imaging fiber was brought into contact with the metal surface. Fluorescence images were taken before and after the surface was exposed to a buffer solution with the change in fluorescence being attributed to the generation of hydroxide ion from the reduction of water that accompanies the anodic dissolution of a metal (Figure 2). Such studies provide information regarding the chemical and physical changes during the initial stages of corrosion.

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REFERENCES

- [1] Pantano, P. and Walt, D. R. *Anal. Chem.* 1995, *67*, 481A-487A.
- [2] Bronk, K. S.; Michael, K. L.; Pantano, P. and Walt, D. R. *Anal. Chem.* 1995, *67*, 2750-2757.
- [3] Panova, A. A., Pantano, P. and Walt, D. R. *Anal. Chem.* 1997, *69*, 1635-1641.
- [4] Healey, B. G.; Foran, S. E. and Walt, D. R. *Science* 1995, *269*, 1078-1080.

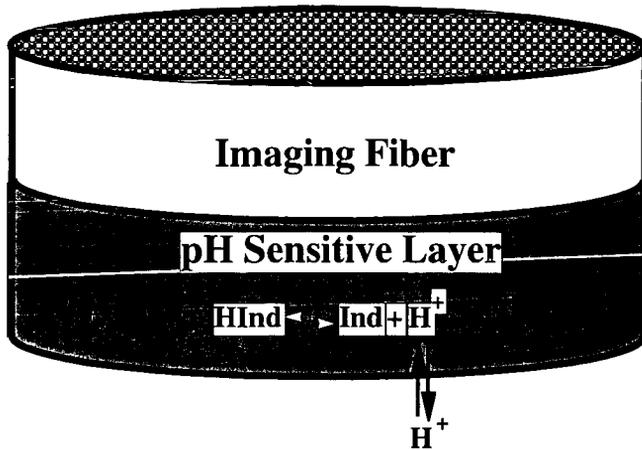


Figure 1. Schematic diagram of a pH-sensitive indicator immobilized to an imaging fiber's distal face.

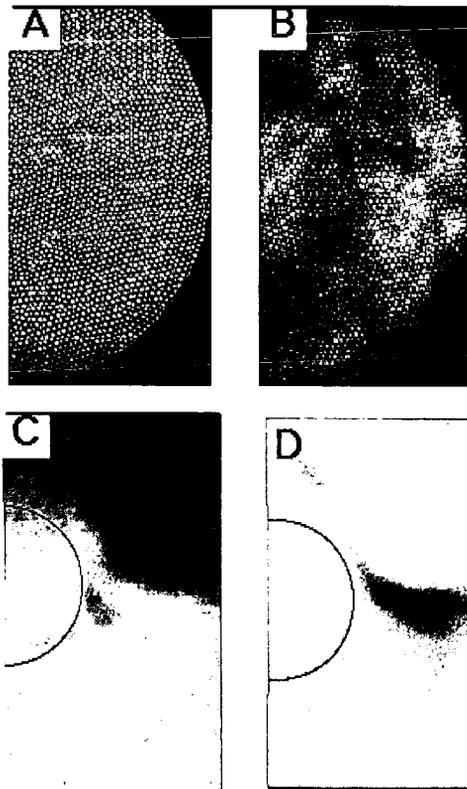


Figure 2. (A) fluorescence image taken at 490-nm excitation and 530-nm emission acquired through a pH-sensitive imaging fiber placed in contact with buffer. (B-D) images acquired through a pH-sensitive imaging fiber placed in contact a polished aluminum-clad copper wire (the image corresponds to half of the wire surface). (B) white light image, (C) fluorescence image after 1-min exposure of the metal surface to buffer, (D) background-subtracted fluorescence image taken after 5-min exposure. High fluorescence intensities (high pH) are denoted by white. The black half-circle denotes the Al/Cu border.