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Etching of multimode optical glass fibers: A new method for shaping the measuring tip and immobilization of indicator dyes in recessed fiber-optic microprobes

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ABSTRACT

We describe a new procedure for making recessed tips on multimode optical glass fibers. The method is based on etching fiber tips in 40% hydrofluoric acid for defined immersion times. As the etching velocity decreases radially from the core center in multimode graded index fibers, a recess can be formed in the tip of flat-cut tapered or untapered fibers. Etched fiber tips showed improved focussing of excitation light coupled into the fiber at the opposite end, and very efficient excitation of thin layers of optical indicators immobilized into the recess. The sensor chemistry is well protected when immobilized in recessed fiber tips and allows the construction of O_2 microoptodes with improved mechanical stability that can measure repeatedly even in very cohesive biofilms, tissue and dry soil.

1. Introduction

Fiber-optic chemical microsensors (microoptodes) allow measurements at high spatio-temporal resolution and have been developed for various analytes [1,2]. Such microsensors measure a chemical (e.g. O_2, pH, CO_2, salinity) or physical (e.g. temperature, refractive index) variable via an analyte-dependent reversible change in the optical properties of an indicator, which is embedded in a polymer matrix immobilized onto the fiber tip. The indicator chemistry has mostly been applied to the fiber tip via dip coating or by mechanical deposition of a small droplet onto the end of the fiber tip. The first microoptodes were developed for microscale measurements of O_2 [3] and were based on the dye, ruthenium(II)-tris-4,7-diphenyl-1,10-phenanthroline ($Ru(dpp)_3$) immobilized in polystyrene, but several other combinations of O_2 sensitive dyes and immobilization matrices have been described in recent years [4–9], and microoptodes are commercially available (www.pyro-science.com; www.presens.com).

Although the tip configuration of fiber-optic microsensors plays an important role for their performance, not much attention has been given to improve the design of the measuring tip and the immobilization of the indicator with respect to improved mechanical and optical properties. Various fiber taper geometries and their influence on the performance of e.g. biosensors and lensed fibers [10–13] have mainly involved use of single mode fibers, and it was shown that tapered fibers have a superior performance in collecting and transmitting light as compared to untapered fibers [11,12]. Furthermore, it was shown that fiber tips with relatively steep and conical tapers collect/focus light more efficiently than fiber tips with long and slender tapers [14].

Tapering of optical glass fibers can be done either by etching the fiber tip in hydrofluoric acid (HF) [11,13,15,16] or by pulling the fiber in an IR laser-beam, in an electric arc [17] or in a small flame from a micro torch (e.g. [2,18]). A constant tension during the melting process can be kept by a capillary puller [4,12] or by the force of gravity (as described here). The size of the flame, the pulling strength, and the timing all influence the final taper dimensions. While most work on chemical etching of optical fibers has been done on single mode fibers, we found that the cladding of fused silica multimode graded-index optical fibers is more resistant to hydrofluoric acid than the core and, therefore, a concave recess can be etched into the tip. In this study, we describe a simple method for etching recesses in tapered and untapered multimode optical fibers, we describe the optical performance of such etched fibers and explore whether immobilization of an

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optical O_2 indicator in the recess yields O_2 microprobes with improved mechanical stability.

2. Materials and methods

2.1. Fabrication of tapered fiber tips

We used fused-silica multimode graded index optical fibers with a 100/140 μm core/cladding diameter ratio. A 5 m long single strand optical fiber patchcord (Radiall Fiber-Optic GmbH, Rödermark, Germany) with a standard ST-connector at each end was cut in two. The protective PVC coating and Kevlar fibers were removed over a length of 5–10 cm, and the Tefzel® polymer jacket enclosing the fiber was removed mechanically over several cm's by use of a fiber stripper (Micro-Strip®, Thomas & Betts, Memphis, Tennessee). For better handling, the fiber was fixed in a hypodermic needle mounted on a syringe [2,18] or, alternatively, in a tapered Pasteur pipette. The fiber was secured with epoxy resin in such a way, that the exposed fiber was free of the needle or pipette tip. The syringe or the pipette was mounted vertically in a micromanipulator (MM33, Märtzhäuser, Wetzlar, Germany) with a small weight of 3.75 g attached to the bare fiber end.

A taper was made by heating the fiber with a small O_2/propane flame from a miniature brazing and welding set (Roxy-Kit®, Rothenberger, Frankfurt a. M., Germany). Thereafter, the taper was cut back manually under a dissection microscope with a ceramic knife and a sharpened forceps to the desired diameter of the tapered tip. The length of the taper and the tip diameter were measured using a calibrated compound microscope. Typical taper lengths and tip diameters were 300–800 μm and 20–40 μm, respectively. Finally, the tip was cleaned in hexane. Untapered fibers were cut with an optical fiber cleaving tool (Thomas & Betts, Raritan, New Jersey, USA) to obtain a straight and flat-cut fiber tip before etching and subsequent rinsing.

2.2. Etching of fiber tips

A recess in the fiber tip was made by etching a cavity with 40% hydrofluoric acid as follows:

A small volume (0.1 ml) of the HF was placed in an Eppendorf tube and carefully covered with 1 ml paraffin oil (Fig. 1). The paraffin oil prevented HF evaporation, the formation of aerosols, and removed adherent HF from the fiber tip when withdrawing it from the etching bath. The fiber was mounted vertically and was introduced into the etching bath with a computer-controlled motorized micromanipulator (Unisense A/S, Denmark). The micromanipulator software (Profix, Unisense A/S, Denmark) controlled the time the tip was immersed in the HF and the velocity with which the fiber was withdrawn from the etching solution. After etching, the fiber tip was cleaned by successive immersion in destilled water, acetone (99%), and xylene (98%).

For material etching rate experiments, only untapered fibers with straight and flat cut tips were used. Several 2–3 cm long fiber pieces were made from the same fiber cable and each piece was fixed with plasticine on the tip of a glass Pasteur pipette. The effect of etching on the fiber dimensions was observed and measured on a calibrated optical microscope.

For untapered fibers, the dimensions of the recess only depended on the time the tip was immersed in the HF, and the total depth of the recess could therefore be calculated from the etching rate. The actual recess depth was confirmed by observation of etched tips on a calibrated optical microscope. For tapered fiber tips, the shape of the recess also depended on the tip diameter and geometry, due to differences in the relative thickness of the cladding and core material in the tapered region after pulling. Thus for very thin and long tapers, the etching process became more undefined, but a central cavity was always formed in the fiber tip during etching for <15 min. By combining the etching procedure with sealing off parts of the fiber tip with polystyrene, it was also possible to create different shaped tips, e.g. conical tips.

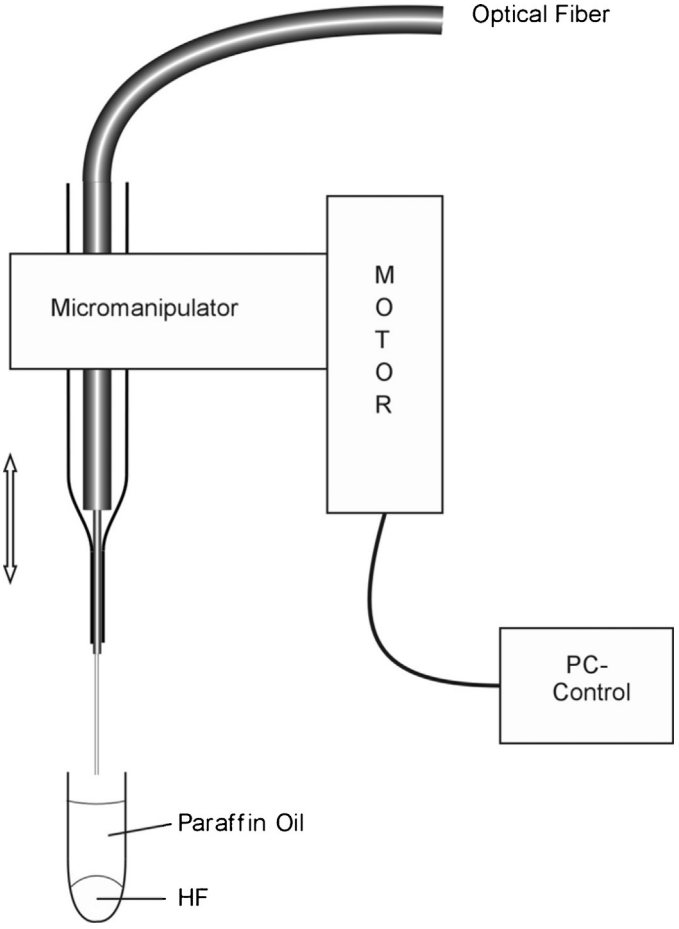

Fig. 1. Schematic diagram of the setup for etching optical fiber tips with hydrofluoric acid. The same setup was used for testing the mechanical stability of O_2 microoptodes. For this, the Eppendorf tube was replaced with a glass beaker containing the test media and a microoptode was connected to a fiber-optic O_2 meter.

2.3. Characterization of recessed fibers

The light emission from bare fiber tips was investigated under an optical microscope. For this, the fibers were coupled to either a fiber-optic fluorometer [19] or a fiber-optic O_2 meter (MICROX 1, Presense GmbH, Regensburg, Germany) from which light from a blue LED was coupled into the optical fiber. The light emitting fiber tip was placed into a flat glass capillary (internal dimensions 8 by 0.8 by 40 mm; VitroCom Inc., Mt.Lks., NJ, USA) filled with diluted milk. The milky suspension enabled visualization of the emitted light field from the fiber tip via scattering. The milky solution was replaced by an aqueous solution of ruthenium(II) tris(4,7-diphenyl-1,10-phenanthroline 4′,4″-disulfonic acid) dichloride, i.e., a water-soluble O_2 indicator. The indicator was synthesized according to Lin et al. [20] from potassium penta-chloro-aquoruthenate(III), which was changed from $RuCl_3$ (Fluka Chemie, Buchs, Switzerland) [21], and 4,7-diphenyl-1,10-phenanthroline 4′,4″-disulfonic acid (Fluka Chemie, Buchs, Switzerland). The emitted light field was monitored via the induced luminescence of the indicator around the fiber tip. Photographs of the fiber tips and the emitted light field were taken in a dark room with a Leica camera equipped with a 42 cm bellows and a light sensitive film Fujichrome Provia Daylight 400 F, RHP III