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Simple Absorption Optical Fiber pH Sensor Based on Doped Sol−Gel Cladding Material

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Introduction

The transition from basic research in materials science to the useful application of a newly developed material has been a major standing challenge in this field, and doped sol−gel materials are no exception in this regard. Massive basic research in the past 15 years[1] is beginning now to point to a plethora of applications just around the corner, with some first products beginning to hit the market. This communication describes an additional step in the applicative direction.

Organically doped sol−gel ceramic materials proved their versatility in numerous chemical-reactivity applications, including photochemically active materials, bioactive materials, catalysts, materials for electrochemistry, and more.[1−5] Due to their attractive optical properties,[6,7] particularly intensive activity has characterized the area of reactive organically doped sol−gel materials for sensors applications.[3,4,8,9] Our early sol−gel sensors activity demonstrated the ability to detect metal cations, some anions, and protons (pH);[10] our latest has been the description of the sensing of alcohols by solvatochromically doped Ormosils.[11]

In the general area of sol−gel sensors, much attention has been devoted to the sensing of acidity. Sol−gel pH sensors have employed various doped indicators and various material configurations, using both emission[12] and absorption[13] spectroscopies. Some specific techniques included monoliths,[14] thin films,[15] capillaries,[16] and optrode tips[17] including miniaturized micron-size tips[18] and coated optical fibers,[19−21] all embedded with various routine pH indicators which interact with the diffusing protons or hydroxyls, changing thereby a measurable optical property. Since porosity allows the molecules to penetrate in and out, the optical effects are reversible and proportional to the concentration of the analyte.

The most common optical effect used in sol−gel fiber sensors has been fluorescence, not only for pH[19] but also for many other analytes.[20] In this configuration, the fiber pumps the doped sol−gel clad in an absorption wavelength and guides the broad-band fluorescent emission signal to detection. Pumping can be a continuous wave, measuring the fluorescence intensity, or pulsed in time-domain-reflectometry sensing, measuring the fluorescence decay temporal properties.[21,23] The use of absorption in this context was demonstrated successfully,[22] but despite inherent advantages this approach may offer in a number of applications, its full potential is yet to be explored.

Here we describe a simple low-cost sol−gel coated SiO_2 fiber optic pH sensor that is based on the absorption of α-naphtholphthalein. It is characterized by a high dynamic range (higher than in analogous fluorescence-based sensors), a behavior that does not seem to follow simple evanescent field considerations.

Construction of the pH Absorbance Optical Fiber Sol−Gel Sensor and Its Performance

General Description. The approach was to place a sol−gel coating on the fiber instead of the removed, original cladding layer. This allows the fiber to be used for both pumping, irradiating the doped sol−gel layer,

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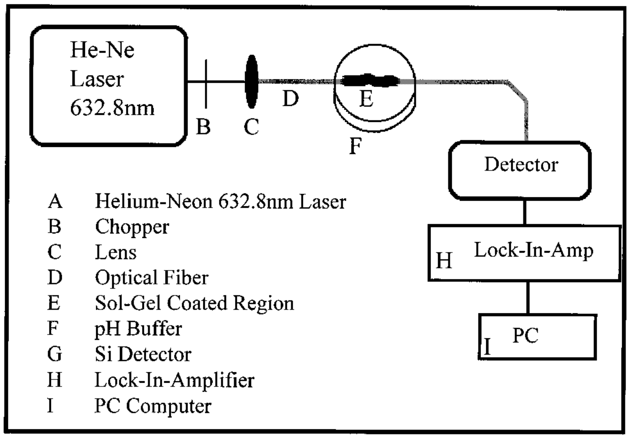

Figure 1. Absorbance sol–gel optical fiber sensor setup: the fiber is pumped by a He–Ne laser. Its middle part is recladded with α-naphtholphthalein-doped sol–gel and dipped in buffer solutions. The signal is detected at the tip of the fiber.

and as a collecting device that guides the optical signal to the detector. In the coated region, the absorbance of the replaced clad causes the fiber to lose power, in proportion to the analyte concentration, changing the amount of power transmitted through it. The selected indicator has been α-naphtholphthalein, which has a conveniently located broad absorption region around 630–660 nm. This allows the application of the widely used He–Ne lasers (632.8 nm) or the more compact low-power semiconductor diode lasers in the red region.

Preparation of the Coated Fiber. The fiber used was a 50 cm long 600 mm core multimode PCS (plastic coated silica) with numerical aperture 0.3. A 3 cm region in the middle of the fiber was decladded by exposing it to a flame which burned the plastic clad. The decladded region was immersed in NaOH solution 0.1 M for 24 h and washed in water and ethanol prior to coating. Several sol–gel procedures were tested, out of which our previously reported[7] one-step tetramethoxysilane (TMOS)/cetyltrimethylammonium bromide (CTAB) procedure was found suitable. Thus, 3.0 g TMOS, 0.72 g of 0.1 M aqueous HCl, and 3.0 mg of α-naphtholphthalein were mixed in an exothermic reaction for 1 min, after which 40 mg of CTAB were added, and the mixture further sonicated for 10 min. The addition of the CTAB after the initial stage is an important necessary modification over our original procedure. Coating was done by dripping the fresh mixture onto the decladded region at the middle of the fiber. The standard dipping and pulling in a steady low-velocity procedure is not convenient here because the decladded region is in the middle of the fiber. After coating, the fiber was dried for at least 72 h. All of the procedure was performed at room temperature.

Measurements. As mentioned above, the pump used was a 15 mW He–Ne 632.8 nm laser, due to the large sensitivity of the α-naphtholphthalein at this wavelength. The pumping laser was chopped in order to allow lock-in-amplifier detection via a 1 cm diameter Si photodiode detector. The signals were recorded on a PC via a communication port (Figure 1). The coated region of the fiber was fixed in a Petri dish in which the buffered solutions were placed and exchanged. The buffered solutions were in the range between pH 4 and 11 and were replaced by each other from pH 11 to 4 up and down, in steps of 1 pH unit. The absorption band is developed at the higher pH solution and bleaches out at the acidic pH. Thus, more power is absorbed under the basic pH, resulting in a decrease in the transmitted power at the detecting tip of the fiber; and changing the buffer to a lower pH solution increases the measured signal. Figure 2 shows typical measurement results: In Figure 2a the pH was changed from basic to acidic and in Figure 2b it was changed backward. The spikes reflect the changes of the buffer solutions, after a plateau was reached in each step. The response time is nonexponential: it is moderately fast for the rise to half-maximal value (~40 s), but the time to plateau, few minutes, is to be improved.

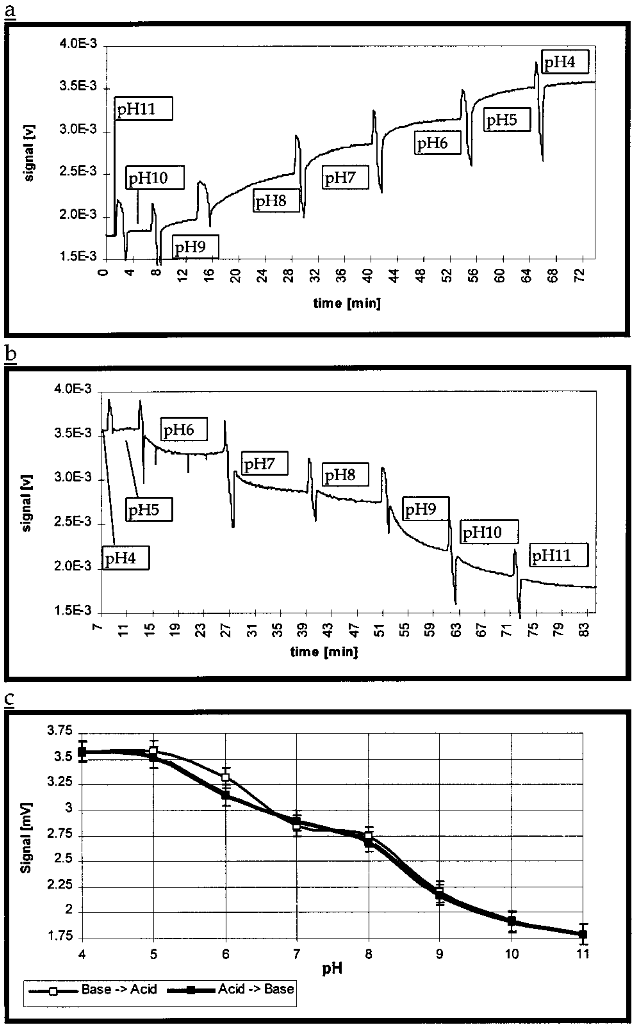

Figure 2. Typical response behavior: (a) from high to low pH (spikes are due to buffer exchange); (b) from low to high pH; (c) a full titration curve and its reversibility.

Figure 2c shows the resulting titration curve of the sensor; it is evident that the sensor exhibits good absorption and responsivity, with a change of ~100%: the signal almost doubles going from pH 4 to 11, allowing pH determination in about 0.2 pH unit accuracy. This large dynamic range is higher than the current status of fluorescence based sol–gel fiber sensors,[23] improving therefore accuracy in measurements.

Discussion

The exact optical mechanism of energy loss is yet to be fully studied. Evanescent field theory predicts[24] that the fraction of energy in the cladding is given in the

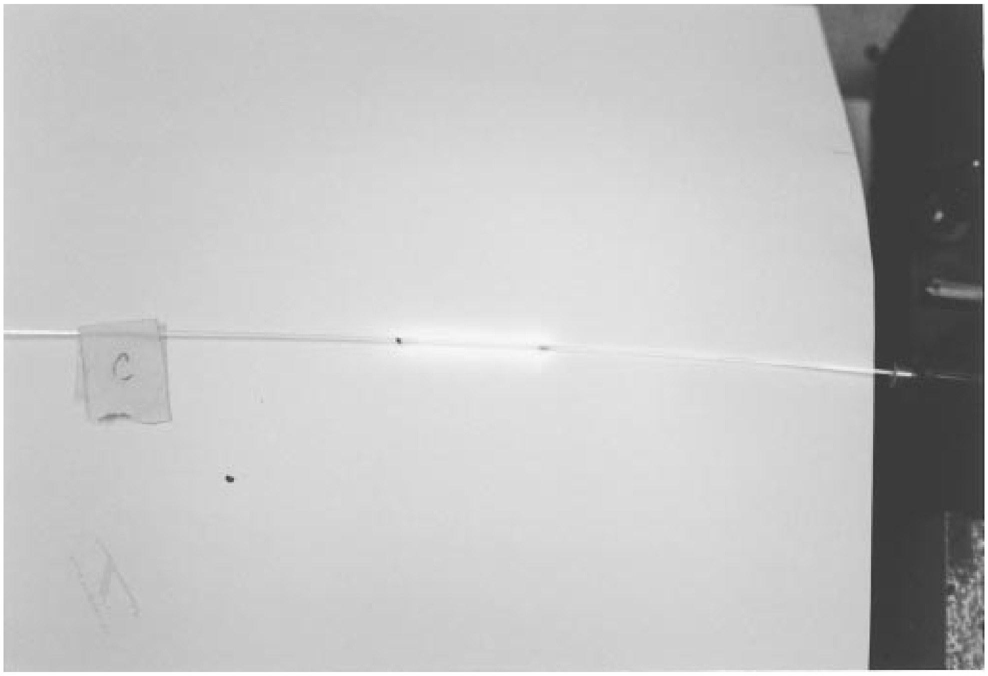

Figure 3. Middle part of the fiber re-cladded with α-naphtholphthalein doped sol−gel. He−Ne pumping results in intense irradiation from the coated part giving rise to strong absorbance dependence as pH changes.

weakly guiding approximation as $\eta = 2^{5/2}(3V)^{-1}$, where V is the fiber parameter ($V = 2\pi r_c(n_{core}{}^2 - n_{clad}{}^2)^{1/2}/\lambda$, where r_c is the core radius and n are the refraction indexes). This gives very small η values (fraction of percentage) for large-core multimode fibers. The consequent loss due to evanescent absorption is Loss = exp($-\eta\alpha L$), where L is the clad length (3 cm in this case) and α is the signal extinction. This extinction was measured directly form the absorption of α-naphtholphthalein in a sol−gel monolithic piece at the same concentration, 10 mm in thickness, obtaining $\alpha = 0.72$ cm^{-1}. To comply with this loss, the fraction of energy in the clad has to be very large, unlike typical values for multimode fibers. The irregular structure of the porous sol−gel coating, its thickness (about 1 μm), and the evident massive light emission from the sol−gel coating (Figure 3) suggest that a more complex treatment has to be applied.

The feasibility study reported here demonstrates that the absorption-based sol−gel sensor described here is quite attractive because of its large dynamic range, simplicity, and very low cost: The probe is disposable and is prepared in a straightforward way under regular room conditions; the decladding and recoating are simple; the fiber-optics disposable probe is easily replaceable; the optical setup is trivial and involves inexpensive common parts; in particular the light source can be the common compact red diode laser. A feature to be improved by manipulating the clad porosity, is the risetime from $t_{1/2}$ to the plateau, although the first halftime of rise is already convenient. Optimization in this direction as well as design of other similar low-cost absorbance based sol−gel fiber sensors, is in progress.[25]

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