



Fast and long term optical sensors for pH based on sol–gels

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Abstract

Long lasting and fast response optical sensor for the detection of pH in the range of 6–12 is described. The sensor is fabricated by spin coating silica sol in the presence of phenol red (PR). The sol is in turn obtained by acidic hydrolysis of tetraethoxysilane (TEOS) and phenyltriethoxysilane (Ph-TriEOS). The performance of the sensor depends on the ratio of Ph-TriEOS to TEOS. At the optimal composition, the sensor has a response time of less than 20 s, the response is completely reversible and its life-time is over 12 months.

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1. Introduction

The sol–gel method is a low temperature process used to synthesize optically transparent, amorphous bulk glasses and thin films either by spin coating or dip coating techniques using organic precursors [1,2]. It involves a metal alkoxide, water and a solvent, which are mixed thoroughly to achieve homogeneity on a molecular scale. To make silica glass by this method, a silicon alkoxide such as tetraethoxysilane (TEOS) in solution (the sol) undergoes hydrolysis and condensation polymerization reactions at room temperature to produce a loose network (the gel). Drying and heat treatment will then progressively densify the gel by elimination of solvents and water. At the sol stage, films can be coated onto a variety of substrates including optical fibers and planar glass for optical chemical

sensor applications. Films can be aged prior to coating. During this aging or pre-polymerization stage, hydrolysis and condensation continues and this results in an increase in viscosity prior to coating. Sol–gel glass is well suited as support matrix in that it provides a chemically and physically stable environment with excellent optical clarity, and may be cast as thin films. The potential use of these materials as indicator phases in optical sensing devices has generated considerable research activity. Sol–gel materials containing colorimetric reagents, metal ions and complexed dyes, enzymes, antibodies and other proteins have been prepared and characterized [2–4].

Numerous works have been reported in the literature on dye-doped sol–gels for pH sensing [5–20]. For proton response in aqueous solutions, the type of alkoxide precursors used in the sol–gel process is limited to the TEOS or TMOS and their analogs that give hydrophilic gels. However, many dyes have limited solubility in hydrophilic medium, thus leaching from the sol–gel film into the bulk sample solution

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occurs [11–20]. Various efforts have been undertaken to improve the stability of dyes in the sol–gels, e.g. by adding organosilanes [21,22], attaching dyes on the organosilanes [22–24], adding surfactant [25], or attaching the functional dyes onto hydrophilic polymers [26,27].

While these methods are useful to prevent dye leaching, extended response times are observed with gels that use organic modifiers [19–23], and very often the pK_a of the dyes are shifted 2–3 units, thus, the response pH ranges are also changed [17,21]. The factors that affect the response time are the thickness of the films, pore size, and hydrophobicity of the doped sol–gel glass. Adding organic modifiers increase the hydrophobicity of the gel and may well change the pore size and thus resulting a prolonged response time of the sensor to hydrophilic species. Thus, only ultra thin films can be used to reduce the response time. This, however, reduces the size of the signals. Evanescent wave that employs multiple interactions with a planar film are often used to enhance the sensitivity when absorbance measurements are used [8,9,18,20].

In our work, we have doped phenol red (PR) in a sol–gel formed by co-condensing TEOS and phenyltriethoxysilane (Ph-TriEOS). By adding a small amount of Ph-triEOS to TEOS as precursor, the resulted sensor overcomes the common problems of leaching and small response signal. The relative thick film still gives short response time, in addition to the wide response range, high reproducibility and long life-time.

2. Experimental

2.1. Reagents

Phenol red, TEOS, Ph-TriEOS were obtained from Aldrich. Standard pH buffers of 4, 7, and 10 were obtained from Fisher Scientific. Sodium phosphates, sodium acetate, boric acid, sodium carbonate were obtained from Aldrich. All other chemicals were commercially available products. Standard solutions and buffers were prepared with distilled-deionized water.

2.2. Preparation of sensor layer sol–gels

Sol–gel solutions were prepared by mixing 4 ml of TEOS, 50–200 μ l of Ph-TriEOS, 5 ml of water, and

1.60 ml of 0.1 M of HCl and 10–20 mg of phenol red. The mixture was stirred at room temperature for 20 min. The resulting sol is stable at room temperature for more than 2 months when sealed tightly. Two hundred microliters of the sol was placed on a pre-cleaned microscopic slide (7.5 cm \times 2.5 cm) and then spin cast at 1500 rpm for 30 s. The resulting sol–gel coated glasses were dried and stored at room temperature. pH measurements were made at least 2 days after the sol–gel had been made to ensure stable spectra. Smaller size sensor slides (0.9 cm \times 3 cm) were cut from the coated glasses in order to be placed into the standard cuvette. The thickness of the sol–gel glass films was *approximately* 1 μ m measured with SEM.

2.3. Optical measurements

Absorbance measurements were made on a UV-Vis single-beam photo-diode array with large glass slides (4 cm \times 13 cm), or on double beam (LB6, Perkin-Elmer or DU-2, Shimadzu) spectrophotometers with the sol–gel coated glass slides placed in a commercial quartz cell (1 cm \times 1 cm \times 4.4 cm) containing the test solution. All quantitative measurements were made at 560 nm with the double beam DU-2. In most cases, sensors were first soaked for more than 20 min. in a pH 4 buffer to ensure a stable absorbance value before the first measurement was made. For most experiments, calibration was performed by immersing the films in 3 ml of the sample solution in the cuvette; absorbance was taken at 1 min. The spectrophotometer was auto-zeroed by zeroing the absorbance of the sensing sol–gel film at 700 nm with the double beam spectrophotometer. All measurements and pre-equilibration were carried out under ambient conditions (\sim 23 $^{\circ}$ C).

A universal buffer containing 0.1 M Na_2SO_4 , 0.04 M of NaOAc, 0.04 M of NaHPO_4 , 0.04 M of H_3BO_3 and 0.04 M of Na_2CO_3 , was used to make pH buffers of pH 4–12, the pH was adjusted with H_2SO_4 or NaOH using an Orion pH combination electrode. Standard buffers of pH 4 (acetic acid–acetate), pH 7 (phosphates) and pH 10 (borate and carbonate) were used for the standardization of the pH electrode.

Phenol red stock solution was prepared by dissolving 10.0 mg of phenol red in 100 ml of de-ionized water. Measuring solution at various pH were prepared by mixing the stock solution and buffers in a 1:1

ratio. Absorption spectra of phenol red solutions were taken in a standard cuvette at room temperature.

3. Results and discussion

3.1. pH response

Sol-gels made of TEOS have a yellow color. It changes to pink when in contact with a pH 10 solution. Phenol red has limited solubility in these sol-gels and leaching of the dye from the sol-gel glass film occurs. Addition of Ph-TriEOS enhances the solubility of phenol red dye in the gel, and practically no leaching of the dye was observed, as indicated by stable absorbances at 560 nm measured in pH 6 and 10 solutions for more than 10 cycles. However, large amount of Ph-TriEOS increased the response and recovery times of the gel significantly. Optimal ratio of the TEOS to Ph-TriEOS was determined to be 20/1 (v/v), for the best performance in terms of both signal size and response time.

3.2. Response spectra

Fig. 1a shows the spectra of phenol red doped in sol-gel glass. The absorption spectra of phenol red doped sol-gels reassembles to the spectra of phenol red in aqueous solutions (Fig. 1b). At low pH, the absorbance maximum is at 440 nm, and this peak decreases as solution pH increases. There is only a slight red shift of the absorbency maximum in the sol-gels comparing to the aqueous solutions, e.g. the absorbance maximum are 560 and 558 nm in sol-gel and in aqueous solutions, respectively. In the range of pH 6–12, the peak at 560 nm continually increases with the increased pH. There is an isosbestic point at 482 for the pH range of 5–9, corresponding to the isosbestic point to phenol red in aqueous solutions, which is 481 nm. However, at higher pH range this point shifts to 492 nm, indicating the dye, phenol red in the gel has two forms, possibly a free form and an adsorbed form.

Fig. 2 shows the sol-gel sensor response curve at 560 nm in the universal buffer solutions of various pH. For comparison, the response curve of the phenol red in the aqueous buffer solution is shown in Fig. 2. Both curves are normalized for the respective absorbance values at pH 13. From the curves, it can be seen that the phenol red in sol-gel (pH from 6

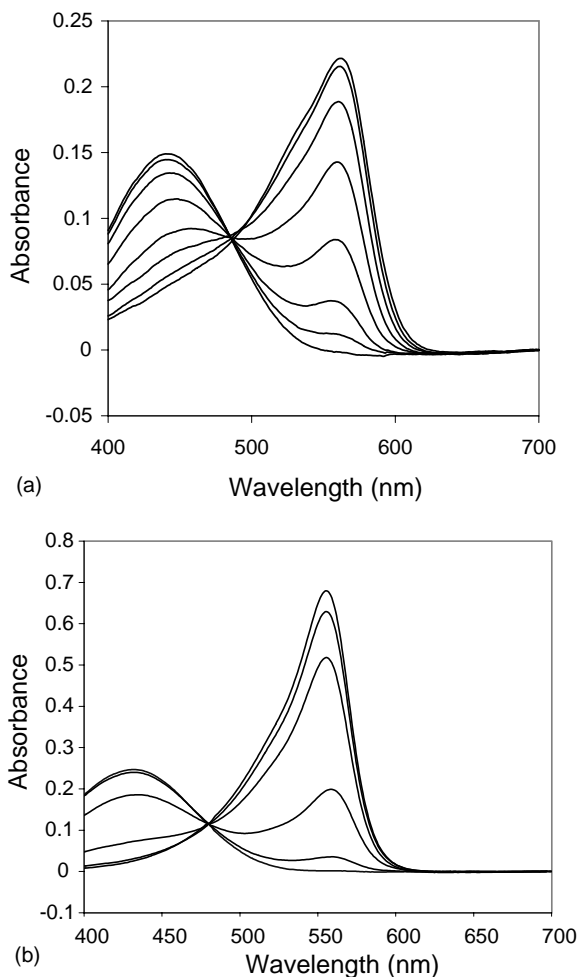


Fig. 1. (a) Absorption spectra of phenol red in TEOS/Ph-TriEOS (5%, v/v) sol-gel glass film in buffer solutions of varying pH. From bottom up: pH 5, 6, 7, 8, 9, 10, 11 and 12. (b) Absorption spectra of phenol red in buffer solutions of varying pH. From bottom up: pH 5, 6, 7, 8, 9 and 10. Phenol red concentration: 1.41×10^{-4} M.

to 12), has much wider response range than in aqueous solution (pH 6–10). This again suggests that the phenol red in the sol-gel exist in two forms. The adsorbed form is responsible for the higher pH range. From the calibration curve, it was calculated that the immobilized phenol red has an average pK_a of 8.5, which is only slightly higher than the respective pK_a of 7.9 in the aqueous solution [28].

It is well known that addition of organic modifier changes the hydrophobicity and the structure of the gel network [2,20–23], thus the gel pores are more

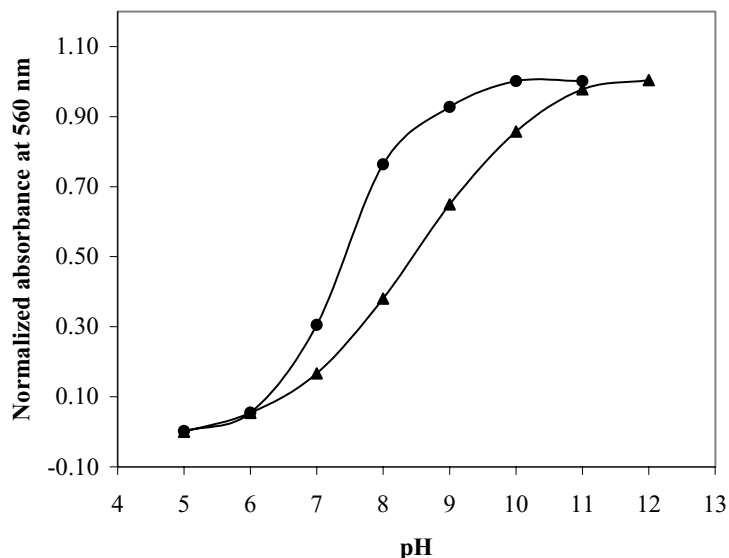


Fig. 2. Response curve of the (●) phenol red in solution (concentration: 1.41×10^{-4} M) and (▲) the phenol red/TEOS/Ph-TriEOS (5%, v/v/v) sol-gel glass film at 560 nm as a function of buffer pH.

suitable to accommodate phenol red molecules, thus increased the solubility of phenol red in the gel. When organically modified gels use relatively larger amount of organosilanes in the precursor, the resulted gels causes larger pK_a shifts of the dyes and the response time is longer [21–23]. The gels described in this paper only apply a small amount of organosilane, thus the pK_a shift is small. And also the relatively high hydrophilicity of the gel permits faster diffusion of proton ions in the gel, therefore the response is fast.

Common cations such as Na^+ , K^+ , NH_4^+ , Ba^{2+} showed insignificant influence when 0.1 M of the respective chloride salts were added into the pH 9 universal buffers. All the absorbance spectra and the absorbance at 560 nm are very close (see Table 1). However, the ionic strength does influence the absorbance. The absorbance values at 560 nm in the diluted buffer are (shown in Table 1) much lower than in the original buffers, indicating a higher hydrogen activity in the diluted buffers. This is due to that a diluted solution has a lower ionic strength and therefore a lower pH values.

3.3. Response time

The response time of the phenol red doped sol-gel sensor depends on the amount of the Ph-TriEOS added

into the sol-gel precursor mixture. Table 2 summarized the response time of the sol-gels at different compositions. With up to 5% (v/v) of Ph-TriEOS relative to the total silane precursor, the sensor gives very fast response in any direction of the pH changes. At 2.5% Ph-TriEOS in the silane precursor, the response time is less than 10 s. The response time for a 5% Ph-TriEOS in the precursor silane, as shown in Fig. 3, is less than 30 s. However, further increasing the Ph-TriEOS, will significantly increase the response time, e.g. the response is longer than 5 min

Table 1

Salt and ionic strength effect on the sensor absorbance at 560 nm when pH 9 universal buffer was mixed with various salts solution (0.1 M) or water

Solution	Absorbance
Buffer	0.157 ± 0.002
Buffer/NaCl (1:1, v/v)	0.159 ± 0.002
Buffer/KCl (1:1, v/v)	0.160 ± 0.002
Buffer/LiCl (1:1, v/v)	0.162 ± 0.002
Buffer/ $BaCl_2$ (1:1, v/v)	0.153 ± 0.003
Buffer only	0.157 ± 0.002
Buffer/water (1:1, v/v)	0.134 ± 0.002
Buffer/water (1:2, v/v)	0.132 ± 0.002
Buffer/water (1:3, v/v)	0.124 ± 0.002

Table 2
Response time ($t_{95\%}$) of the phenol red sol–gels with various Ph-TriEOS contents

Sol–gel no.	TEOS (ml)	Ph-TriEOS (μ l)	Phenol red (mg)	$t_{95\%}$ (s)
1	4	0	10	5
2	4	50	10	8
3	4	100	10	10
4	4	200	20	20
5	2	2000	20	600

$t_{95\%}$ was measured for pH change from 5 to 10.

when pH changed from pH 4 to 10 solution, and the response from pH 10 back to 4 is even slower for a 50% of Ph-TriEOS. This agrees with the results reported in [20,21]. These results can be interpreted by the increased hydrophobicity of the gel with the increasing amount of Ph-TriEOS in the precursor, therefore, the hydronium ions diffuse slower in these gels. Yet, the presence of a small amount of Ph-TriEOS as precursor in the sol is critical for the sensor's stability.

Extensive aging did not change the response time significantly. Within the first 2 weeks, the response time slightly increased, e.g. from 18 to 20 s for a pH change from 5 to 10, in day 5 and day 15 for the 5% Ph-TriEOS films. Further storage did not al-

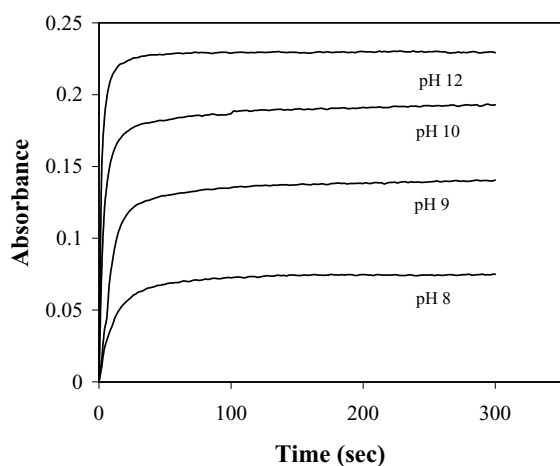


Fig. 3. Time response curve of the phenol red/TEOS/Ph-TriEOS (5%, v/v/v) sol–gel glass film in pH buffers when changed from pH 5 to various pH values.

ter the response time. Films tested at 1 month and 1 year showed that there was no change in response time.

3.4. Stability, reproducibility and life-time

The sensor requires aging time of ca. 5 days after the phenol red sol–gel is coated onto the glass slides. Within the first 5 days, the isosbestic point at higher pH (10–12) is much higher than the spectra at lower pH range. However, no obvious loss of the dye into the solution were observed, as indicated there is no absorbance at 560 nm in the soaking solution, and no decrease in the film absorbance at pH 10. After further aging, the spectra remain unchanged. Absorbance values measured at days 10, 30, 60, 90 and 120 days and 1 year are essentially the same and the relative standard deviation (R.S.D.) in pH 8 buffer is less than 5%. The reproducibility when measured 10 times in a cycle of pH 5–8–10 within a 2 h period gives R.S.D. of less than 5% for all the solutions. The slides are kept air dry when not used in room temperature and humidity. No obvious discoloration was detected with visual checking. Continuous usage of the sensor for over 3 months' period showed no decrease of the absorbance in the detected range. In fact, the above graphs are made 4 months after the sensor was made and the sensor was repeatedly used before and after these graphs were taken. Currently, these sensors are under test for the rapid and reversible sensing and detection of gaseous species, the results will be presented in a separate article.

4. Conclusion

Fast and long life-time optical sensors for pH were fabricated with phenol red in sol–gels. Addition of a small amount of organosilane is the key to the sensor's sensitivity, stability and life-time, due to the increased solubility of the dye in the sol–gel. However, large amount of the organosilane in the gel greatly decreased the mobility of the ions in the gel, therefore, the response time is prolonged. Due to adsorption of the dye by the gel component in the lipophilic gel, the response range is much wider than the dye response in the aqueous solutions.

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