

## Optical sensing of HCl with phenol red doped sol–gels

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### Abstract

A dye doped sol–gel for the sensing of hydrochloric acid in solution and/or gaseous phase is described. The sol–gel is obtained by acidic hydrolysis of tetraethoxysilane (TEOS) and phenyltriethoxysilane (Ph-TriEOS) in the presence of phenol red (PR) and further spin-coating onto glass slides. The sensitive response is based on an increase of the absorption band at 510 nm of phenol red entrapped in the sol–gel casting when exposed to HCl solution or gas, due to protonation of the dye. The detection limit of the sol–gel response to moisturized gaseous HCl is below 12 ppm, and its response to HCl in solution falls in the range of 0.01–6 M. The sol–gel coating has a response time of less than 40 s in steady-state, and life-time of more than a year. Weak acids such as acetic acid, benzoic acid, salicylate acid, citrate acid, and carbonic acid do not interfere the response. The responses in acid solutions are completely reversible. In the gaseous phase, response of HCl appears to be moisture sensitive.

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### 1. Introduction

Optical sensors using sol–gels have attracted great attention to researchers because of their optical transparency, ruggedness, ease of fabrication, and most of all, the possibility to be used directly for gas sensing in micro- and remote-samples [1,2]. A great number of optical sensors have been reported for detecting proton [2–13], O<sub>2</sub> [14,15], NO [16,17], and CO<sub>2</sub> [18] by using dye doped sol–gels. Most of the pH sensors reported are for the pH range of 2–12 [2–13] using pH indicators that have high pK<sub>a</sub> values. High acidity sensors using low pK<sub>a</sub> indicators such as chromoxane cyanine R, bromocresol purple, bromocresol green, and neutral red, are reported using sol–gel technique [18–20]. For some of the sensors, tetramethoxysilane was used as sol–gel precursor, ion exchangers such as nafion or cetyltrimethylammonium bromide was used as additives. These high acidity sensors

are highly dependent on the ionic strength of the solution [19,20]. In general, dye leaching was a major problem for pH sensors based on dyes entrapped in sol–gel.

HCl is a strong acidic gas. Its aqueous solution in commercial acid product is 36–37 wt.% with a high HCl gas vapor pressure. The strong acid property makes it highly toxic, and corrosive. OSHA identified HCl as a workplace hazard with a short-term exposure limit of 5 ppm. Thus, it is a great interest to develop sensors for the monitoring of HCl gas to protect our health, public safety as well as our environment. In fact a great deal of efforts have been undertaken to develop fast responding sensors for the HCl gas with low detection limits [21–27]. These sensors are based on porphyrin and other dyes doped in organic films. The drawback of these sensors is their limited life-time due to the instability of the porphyrins in organic films. Our approach is to use sol–gel materials to overcome such problem. Up to date, no gaseous HCl sensors based on sol–gels were reported in the literature.

Phenol red is widely used as an acid–base indicator for the basic pH range titration end-point indications, with color

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change from pH 6 (yellow) to 8 (pink). Many studies have impregnated phenol red into sol–gels or polymer matrices for the development of optical sensors [13–17]. We have reported in our earlier paper that phenol red doped sol–gels made from tetraethoxysilane and phenyltriethoxysilane have a yellow color and can be changed to pink when exposed to base. The sensor responds in the pH range 6–12 [28], has a very long life-time, high reproducibility and fast response. In this paper, we report the same sol–gel material doped with phenol red that responds to strong acids in solutions and very selectively responds to HCl in gaseous phases. The sol–gel coating response to HCl can be rationalized by diffusion of HCl into the gel, then followed by protonation of phenol red monoprotic acid form, the corresponding changes in absorbance of the gel were recorded at 510 nm, and correlated to HCl concentration.

## 2. Experimental

### 2.1. Reagents

Phenol red, tetraethoxysilane and phenyltriethoxysilane were obtained from Aldrich. Concentrated acids of HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and pure acetic acid, as well as standard buffers of pH 4, 7, and 10 were obtained from Fisher Scientifics. Sodium phosphates, sodium acetate, boric acid, sodium carbonate, citric acid, potassium bromide, potassium iodide, benzoic acid and salicylate acid, and ethanol (99.9%) were obtained from Aldrich. All the other chemicals were commercially available products. Standard solutions and buffers were prepared with distilled–deionized water. The diluted solutions of HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub> solutions were made from serial dilutions with the concentrated products, and the 0.1 M acids were standardized by the titration method using Na<sub>2</sub>CO<sub>3</sub> as standard. HCl gas in nitrogen samples were from Messer MG Industries (Morrisville, PA).

### 2.2. Preparation of sol–gel coated slides

The sols were prepared by mixing 4 mL of TEOS ( $1.79 \times 10^{-2}$  mol), 200  $\mu$ L of Ph-triEOS ( $8.29 \times 10^{-4}$  mol) (molar ratio: TEOS: Ph-TriEOS: 21.6: 1), 1.60 mL of 0.1 M of HCl ( $1.6 \times 10^{-3}$  mol), and 20.0 mg of PR ( $5.64 \times 10^{-5}$  mol), 5.0 mL of ethanol (99.9%, v/v) as co-solvent. The mixtures were stirred at room temperature for 20 min. Two-hundred microliters of the sol was placed on a pre-cleaned microscopic slide (7.5 cm  $\times$  2.5 cm  $\times$  1 mm) and then spin cast at 1500 rpm for 30 s. The resulting sol–gel coated glasses were dried and stored at room temperature. Measurements were made at least 2 weeks after the sol–gel have been made to ensure stable gel composition. Smaller sol–gel glass slides (0.9 cm  $\times$  3 cm) were cut from the coated glasses in order to be placed into the standard cuvette or in a flow-cell. The thickness of the sol–gel glass films was

approximately 1  $\mu$ m when measured by scanning electron microscopy.

### 2.3. Optical measurements

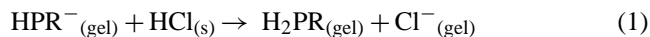
Absorbance measurements were recorded with on a UV–vis single-beam photo-diode array, or on double beam (DU-2, Shimadzu) spectrophotometers. For solution and steady state gaseous responses, the sol–gel coated glass slides were placed in a commercial quartz cell (1 cm  $\times$  1 cm  $\times$  4.4 cm). All quantitative measurements were made at 510 nm with the double beam DU-2. In most of cases, sol–gel coated glass slides were firstly soaked for more than 20 min in a pH 3 buffer to ensure a stable absorbance value before the first measurement was made. For the solution samples, calibration was performed by immersing the sol–gel coated glass slides in a 3 ml sample solution contained in the cuvette; absorbance was taken after 1 min. The spectrophotometer base line was taken by considering zero absorbance of the sol–gel coated glass slides at 700 nm with the double beam spectrophotometer. For the gas phase response, the coated sol–gel glass slides were placed into a flow-cell. The slides were used dry under room temperature and humidity (60–70%). All measurements and pre-calibration operations were carried out under room conditions ( $\sim 23$  °C).

Phenol red stock solution was prepared by dissolving 10.0 mg of phenol red in 100 mL of de-ionized water. Measuring solutions at various acid concentrations were prepared by mixing the stock solution with 2 M Na<sub>2</sub>SO<sub>4</sub> and the acids in a 0.2:1:1 ratio. Absorption spectra of phenol red solutions were taken in a standard cuvette at room temperature.

## 3. Results and discussion

### 3.1. Response principle

The phenol red solution can turn to orange red when mixed with solutions of high concentrated strong acids. Similarly, the above described PR-doped sol–gel coated glass slides also change color from yellow to orange red when exposed to concentrated strong acid solutions of HCl or gaseous HCl. The color change in the sol–gel could be reflected in the following equilibrium:



where HPR<sup>−</sup> indicates monoprotic acid form and H<sub>2</sub>PR the neutral form of phenol red. HCl(s) indicates the concentration of HCl in the solution or gas sample. The reaction equilibrium constant is dependent on the concentration of the acid in the sample. The gel absorbance (*A*) would be depending on the dye concentration and the position of the protonation equilibrium. By using relative absorbance  $\alpha$  [29] to represent the fraction of total phenol red concentration (*C<sub>T</sub>*) in the protonated form (*[C]*),  $\alpha$  can be related to the absorbance values

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