Sensors and Actuators A 238 (2016) 8–18

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Sol–gel based fiber optic pH nanosensor: Structural and sensing properties

Shumaila Islam[a], Noriah Bidin[a,*], Saira Riaz[b], Ganesan Krishnan[a,c], Shahzad Naseem[b]

[a] Laser Centre, Ibnu-Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
[b] Centre of Excellence in Solid State Physics, University of the Punjab, Lahore, Pakistan
[c] Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, Skudai 81310, Malaysia

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form 2 December 2015
Accepted 2 December 2015
Available online 4 December 2015

Keywords:
Sol–gel method
Fiber optic
Encapsulated indicators
pH sensing
Silica–titania

ABSTRACT

Evanescent wave absorption based PCS (plastic clad silica) fiber optic pH sensor is constructed by encapsulation of indicator dyes in the heterogeneous inorganic hybrid silica–titania nanomatrix in the presence of cetyl trimethyl ammonium bromide (CTAB) surfactant by sol–gel method. A nanoporous multilayers (triple layer and six layers) of silica–titania hybrid is deposited on 5 cm uncladed middle portion of the fiber by dip-coating sol–gel technique. The CTAB surfactant expressively improved the host matrix structure and enhanced its porosity. Thermally stable, adhesive and smooth thin nanocladding has been examined using microscopic and thermal analysis. Indicators encapsulated nanomatrices are highly sensitive to pH and show optical output signals in terms of intensity. Therefore, it provides confirmation that interactions between the host matrix and pH-indicator molecules are in good assistance. Furthermore, experimental findings reveal that the sensing species are probably better encapsulated in the matrix and show no leaching of sensing molecules. The prepared nanosensors exhibit a much faster response time because of the material to be sensed diffuses faster into the triple-layer sensors <2 s. These pH sensors are found to have 60 days (2 months) age stability and high reproducibility. A repeatable response over a wide range of pH values between 3 and 11 is obtained.

1. Introduction

Modern society has attracted considerable attention towards the exploitation of advanced chemical detection systems. Optical sensors relying on the various optical detection principles such as absorbance, reflectance, luminescence, fluorescence and excitations as a mode of transduction have proven to be highly effective in this regard [1–4]. The development of optical pH sensors has gained attraction because in several scientific research studies and industrial applications conventional pH glass electrodes are considered unsuitable such as in chemical, biomedical, clinical and in environmental areas [5]. Moreover, optic fiber pH sensors can be implemented in all sorts of risky and hazardous environments such as deep-water analysis. Optical sensing would be most advantageous due to the feasibility of miniaturization, associated with exciting possibilities for remote sensing and in-situ measurement. Other reasons for the development of optical pH sensors include the lack of requirement of a reference sensor, resistance from electrical interference and improvements in electrical safety concerning clinical applications [2,6]. Hence, there is numerous efforts that have been focused towards the development of fiber optic pH sensors, in which pH indicator is physically and chemically immobilized into a polymer matrix [7–9]. Some of these are summarized in Table 1. Furthermore, San, Dantan, Dong, and Werner developed the pH chemical sensors by using the uncladed surface of the fiber which was coated with a material and was used as a sensing region for corrosion detection [10–13]. Zaggout studied different dyes for sensing such as methyl orange [14], thymol phtalein [15] and *a*-naphtholphthalein [16]. These pH-indicator dyes physically get entrapped in the inorganic matrix by sol–gel method. Goicoechea [17] fabricated evanescent wave optical fiber pH sensors using layer-by-layer (LbL) electrostatic self-assembly technique. However, one major problem associated with many of these studies is leaching. Moreover, leaching of indicator leads to reduce fluorescence and absorption properties with loss of dye sensitivity, which makes impractical long-term use of the sensors [18]. However, monitoring the changes in intensity based signals can often be inconvenient or unreliable due to limitations in

* Corresponding author. Fax: +60 75566162.
E-mail addresses: shumaium@yahoo.com (S. Islam), noriah@utm.my, noriah.utm@gmail.com (N. Bidin), saira_cssp@yahoo.com (S. Riaz), kganesan34@yahoo.com (G. Krishnan), shahzad_naseem@yahoo.com (S. Naseem).

http://dx.doi.org/10.1016/j.sna.2015.12.003
0924-4247/

Table 1
pH indicators with response time.

pH Indicator	pH range	Response time	Ref.
Bromophenol blue	3.0–8.0	20–40 s	[28,29]
Bromophenol blue	4.0–7.5	5 s	[30]
Phenol red	7.5–11.5		
Cresol red	6.5–11.0		
Bromophenol blue	5.0–7.0	10 s	[4]
Bromophenol blue	2.0–12.0	15–150 s	[31]
Thymol blue	8.0–12.0	5 s	[32]
Methyl red	8.0–14.0	1 min	[33]
α-Naphtholphthalein	4.0–11.0	1 min	[34]
Bromopyrogallol red	2.3–9.4	1 min	[35]
Bromophenol blue	3–5	1–2 min	[36]
Phenol red	7–8.5		
Bromothymol blue	8–10		

stability and reproducibility of the sensing material as a direct result of changes in the concentration of dyes due to leaching effects from encapsulating matrices. Basically, cracks are responsible for leaching and appear due to shrinkage of the densifying film and are responsible for reduction in the effective coupling of the evanescent field. Therefore, sensitivity of the device has been reduced. To solve this problem, the stability of host matrix silica–titania and sensitivity of the surrounding environment are linked with a combination of optical fibers and materials, this provides a prospect for the sensor assembly with high sensitivity and possibly a precise response to identify and mark the ions. Furthermore, the physical dimensions of mesostructure's matrix can be decreased by sol–gel processing parameters. By sol–gel technique, high densification can be achieved, at low temperatures which allows for fine tuning of the final product's chemical and physical make-up [19–22]. The main advantage to choose the hybrid silica–titania matrix is their porous nature which easily introduces the various functional groups or encapsulations of sensing elements. Most attractiveness belongs to their physical characteristics (e.g. pore size, shape and surface area) and physicochemical properties such as purity, density and refractive index. Moreover, the encapsulation of indicators into sol–gel based multilayer nanomatrix reduces the decomposition, cracks and leaching of indicators [18,23,24]. The activity of entrapped compounds into a gel matrix remain accessible to external reagents by diffusion through the porous matrix, so it is possible to couple optics and natural process to make photonic devices and detectors. Encapsulation of indicators within the solid matrix gel offers many advantages over conventionally dissolved procedures [10,25,26] such as they allow continued sensing without contamination and are easy for concentration measurements with species detections. It gives good adhesive property with direct coating on glass and silica fibers without the use of additional membrane. Choices of the indicator to stimulate the behavior of the sensor, such as its mechanical stability, selectivity, suitability for reagent immobilization, permeability of the analyte and response time [27]. Some indicators were summarized with response time in Table 1. For broad dynamic pH range and fast response purpose, in this work, mixture of pH sensitive indicators namely bromophenol blue ($C_{19}H_{10}Br_4O_5S$), phenol red ($C_{19}H_{14}O_5S$), cresol red ($C_{21}H_{17}NaO_5S$) and phenolphthalein ($C_{20}H_{14}O_4$) were chosen and encapsulated within inorganic heterogeneous silica-titania matrix and have been investigated as fast and stable pH nanosensor. The resulting gel-network exhibits homogeneous, a mesoscale level porosity coating with full stability and quick response time. Moreover, sol–gel based multiple coatings were applied on fiber optic in two manners i.e. triple layer and six layers at room temperature with appropriate aging time and were characterized for the nanocoating hybrid material for pH sensors, especially in terms of species selectivity. The use of sol–gel assisted hybrid as a nanomatrix for pH sensing has not yet been published in the literature. These hybrid silica–titania have also been deposited for other sensor types such as corrosion sensors and gas sensors. However, the choice of silica–titania nanomatrices encapsulated with four indicators has not been deposited on PCS fibre optic pH sensors. Three layers and six layer coatings were deposited to sense the chemical species in different pH media and a change in wavelength of the transmission band has been observed. Overall, this work has been aimed at fabricating and characterizing PCS fibre optic pH nanosensors leading to low cost, chemically selective, reversible sensors which are stable under ambient conditions.

2. Experimental work

2.1. Sol formation

Hybrid nanomatrices were prepared from the precursor solution of TEOS, titanium tetra-isopropoxide, ethanol, propanol and nitric acid, doped with 0.05% molar concentrations of the dyes and 0.5 M surfactant CTAB. The used dyes were: bromophenol blue ($C_{19}H_{10}Br_4O_5S$), phenol red ($C_{19}H_{14}O_5S$), cresol red ($C_{21}H_{17}NaO_5S$) and phenolphthalein ($C_{20}H_{14}O_4$). The dye's concentration 0.05 M was selected since there was no response observed at lower concentrations and stability was not found at higher concentrations. Therefore, the concentration of surfactant and indicators was varied in order to prepare the sensing films with high porosity without leaching. Composite coatings prepared with a mole ratio of 1:1 and with co-indicators' ratio 0.05 M were found to be the best in terms of uniformity, stability and response. In this procedure, both precursors, TEOS and TIPP, were simultaneously hydrolyzed and subsequently condensed to form the multi-component heterogeneous sol–gel. The hybrid silica–titania with 1:1 M ratio solution was stirred for several hours until colloidal suspension of particles was obtained. The details of synthesis of silica and titania sol of the two precursors, i.e. tetraethylorthosilicate and titanium isopropoxide, can be found in our previous paper [37]. The synthesis procedure is shown in Fig. 1. Moreover, 2 ml of 0.5 M CTAB and 5 ml of 0.05 M co-indicators were added in the resulting sol and stirred for 1 h at 80 °C temperature. The resulting sol remains fluid for up to several months and can be used to coat slides or fibers at any time after the gel has been prepared.

2.2. Preparation of pH sensors

In order to fabricate the pH sensor, before coating, 35 cm long PCS optical fiber 1012 μm core diameter ($NA = 0.37 \pm 0.02$) with 5 cm decladed region was washed with HNO_3 for 10 min and rinsed several times with de-ionized water. Both ends of the fiber were polished carefully in order to ensure the constancy in the coupling behavior of the launched light into the fiber during the detection measurement. This cleaning procedure with HNO_3 produces hydroxyl groups on the surface that assist in bonding of the gel [38]. For 2–3 μm thickness, the fiber was coated three and six times by sol–gel technique (manually dip coating) at room temperature. An interface exists between different layers which supports the sensing mechanism. These fibers were then kept for several days for the homogeneity and stabilization of dyes in the host matrix that helps reduce leaching of the dye molecules. Most of the solvent gets evaporated during the aging process, leaving a very viscous film on the coated side. The dried coatings were then washed with water to remove the excess and unbound dye [39]. No cracking or peeling of the gel was observed in fiber A (triple layer coated). However, fiber B (six layers coated) shows some flaking of coated gel as shown in Fig. 2 (inset). The coated region is again dried at room temperature to produce a tough, inert and highly adhesive coating (Fig. 2).