Sensors and Actuators B 195 (2014) 692–701

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Optical sensor for pH monitoring using a layer-by-layer deposition technique emphasizing enhanced stability and re-usability

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ARTICLE INFO

Article history:
Received 17 November 2013
Received in revised form 17 January 2014
Accepted 21 January 2014
Available online 29 January 2014

Keywords:
Stabilization
Stable
Layer-by-layer
Sensor
pH optical sensor
Re-usability

ABSTRACT

Stable and reliable operation of an optical sensor for pH monitoring is important for many industrial applications of these types of devices. The layer-by-layer deposition technique is a simple and versatile method used to deposit a sensitive thin film on such an optical fibre-based device but creating a coating which can often be destroyed in use in highly acid or alkali solutions i.e. with very low or very high pH. It is thus important to create stable and durable sensors to meet the needs of users for operation under these extreme environments. The main aim of this study has been to prepare a number of such sensors and compare the performance of three different stabilization approaches used for the development of an effective wavelength-dependent pH-sensitive optical sensor. Techniques such as employing heat treatment, the deposition of two layers of a PAH/SiO_2 (poly(allylamine hydrochloride)/Silica nanoparticle) thin film and the deposition of two layers of APTMS/SiO_2 (3-aminopropyl-trimethoxy silane/Silica nanoparticle) as topping layers have been studied to determine the optimum approach to creating a stable and reliable sensor–one yielding the same value of peak wavelength for a measurement of a known value of pH and to do so repeatedly. An improvement in performance and in shelf-life, stability and re-usability of the sensor has been achieved by the addition of two bilayers of APTMS/SiO_2 in the work carried out and the results of the investigation undertaken are reported.

1. Introduction

In industry today, it is important in many situations to detect a range of chemical and biochemical substances, as well as the measurement of a variety of systems operating parameters. pH is one of the most common analytical measurements needed in both industrial processing and in laboratory research, in which reliable real time sensor data, such as can be obtained from an optical sensor system due to its light weight and non-electrical mode of operation is needed. In order to achieve optical recognition of these parameters using optical fibre-based devices, active indicators such as sensitive films must be immobilized on the distal ends of suitable optical fibres. The layer-by-layer (LbL) technique is one of the deposition methods widely used to coat such thin films on to optical substrates and optical fibres. The LbL technique is used to build up a sufficient thickness of such material on the fibre and is based on the electrostatic attraction between oppositely charged molecules to create the layers and thereby increase the overall coating thickness [1]. The principal advantage of the use of this technique is the ability to create stable deposited thin films with well-organized structure and controlled nanometer thicknesses on substrates of various shapes and sizes [2–7]. Generally, the thin films created by using the LbL technique are stable [2,8], and it is difficult to remove them from a solid substrate. There are two main methods to remove LbL deposited films, should this be needed. First, a solution of high pH can be used which will attack the first polycation layer and destroy the ionic bonds that stabilize the films. A second method is to expose the LbL multilayers to a solution with very high ionic strength, such as 3 M NaCl, under sonication for approximately 2–3 h [9]. Destruction of the layers happens when the coated surface is immersed into the high pH buffer solution. For practical applications, especially those needing continuous monitoring, it is critical to have a pH probe that can give consistent results and survive for as long as possible. However, the destruction of the layers limits the life of the probe and does not make it as suitable for continuous monitoring. A variety of techniques has been proposed to improve the stability of the film and to avoid progressive destruction of the coating. Ionic strength, pH, concentration of the polyion solutions and the presence of a copolymer such as salt affect the LbL assembly, the film thickness

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0925-4005/$ – see front matter
http://dx.doi.org/10.1016/j.snb.2014.01.080

and its stability [2,3]. Heat treatment is also an important process which has been discussed in many works in the literature [10–12] to achieve a higher stability of the thin films and avoid problems with the destruction of the films when they are immersed in buffer solutions of different values of pH [13,14]. However this sort of treatment affects the sensor performance and decreases its sensitivity [14], as well as allowing for a degradation of the indicator dyes used which happens at high temperatures.

The stability of thin films thus generated does depend on the interaction between the layers, such as through the formation and destruction of hydrogen bonds. Hence, the stabilization of the LbL-assembled films via polyamide bond formation was a further method reported in the literature [15–17]. The amine coupling reaction can easily allow a cross-linkage of an amino group to a cationic polyelectrolytes and a carboxyl group on anionic polyelectrolytes via amide bond formation. There is a further report in the literature [18] which focused on the film stability under chlorine treatment as a means to improve the stability of the LbL-assembled nanofilteration membranes in combined high ionic strength conditions and under chlorine treatment. In another approach, the stabilizing of the thin film is achieved by forming siloxane bonds owing to a silane coupling reaction between oppositely charged polyelectrolytes which leads to the crosslinking between the silane groups [18,19]. Egawa et al. demonstrated [20] crosslinking between the sulfonate group in the polyanion and the diazonium ion in polycation due to exposure to UV light. The pH sensor reported in their work could be used to measure solutions of high pH.

An alternative approach is to build up several capping layers using different materials such as nanoparticles to enhance the film stability. Prakash et al. [21] discussed applying nanoparticles to achieve an adequate sensitivity and stability with the modification of the sensors (or biosensors) with nanomaterials such as gold and/or silver nanoparticles [6,22,23], carbon nanomaterials [24,25] and silica nanoparticles [26] and these have shown considerable promise. Putzbach et al. reported that the immobilization of enzymes improves stability of the biosensor discussed [27]. In further work reported in the literature [28], a coating of 5 nm layers of Al or 1 nm layers of EuS (Europium(II) sulfide) was applied as a covering layer to stabilize ultrathin tin films and reduce the diffusion of tin atoms. Abdelghani et al. used long chain alkanethiols to protect a silver film from oxidation and thus increase its stability [23]. Ng et al. employed three different drug stabilization approaches in the study presented in literature [29] through changing the architectures of the films. In their work, in the first approach, a solid dispersion film of the drug and polymer was prepared. A second approach involved coating the surface of a freshly prepared drug thin film with a thin polymer film, whereas for the third approach, the solid substrate surface was modified with a polymer coating prior to the laying of the pure drug thin film on top. A cross comparison of these three stabilization approaches was carried out and it was found that the polymer thin film coatings were more effective for the model drugs tested in their study.

The application of silica nanoparticles (SiO_2) has drawn considerable attention for surface modification, due to its uses as an enhancer for the sensitivity, selectivity and strength of the thin films as well as a its use as a pH indicator in many research situations and in industry [30–35]. In the work published by Lee et al. [36], pH-sensitivity of the nanomaterial thin film chemo-resistor and transistors was tuned by depositing a SiO_2 nanoparticles layer on top of a semiconducting nanomaterial multilayer fabricated by using a LbL self-assembly in which the silica nanoparticles play the role of the charge collector, influencing the conductance of the semiconducting layers of the carbon nanotubes and the indium oxide nanoparticles. Liu et al. also used a silica nanoparticle layer on top of further layers of indium oxide nanoparticles and poly(styrene sulfonate) (PSS) as an insulating layer, in the approach published in Ref. [30]. Selectivity for hydrogen gas was obtained by deposition of a thin film of silica nanoparticles on top of the $SnO_2 \pm Cu/Pt$, in a mixture of the two gases [10].

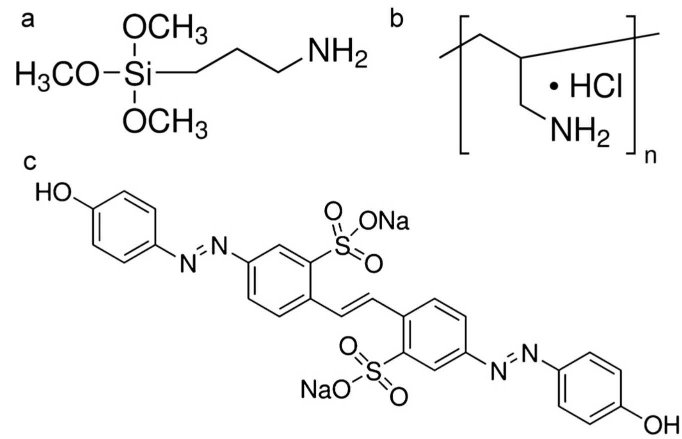

Fig. 1. Chemical structure of (a) APTMS, (b) poly(allylamine) hydrochloride [PAH] and (c) brilliant yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The use of silica nanoparticles can create a very strong thin film if they are used to cover the indicator multilayers. The work presented in this paper thus takes advantage of this and compares and contrasts three different stabilization approaches with the aim of creating a stable pH sensor which is re-usable and stable under storage. In the course of the investigation and optimization of the sensor system developed, aspects of the fabrication process such as heat treatment, the deposition of two layers of PAH/SiO_2 as thin film 'topping' layers and the deposition of two layers of APTMS/SiO_2 as similar 'topping' layers have been investigated and the resulting sensors characterized to determine the best approach to creating a sensor which is stable and reliable in operation: thus giving the same calibration, in terms of the value of the peak wavelength for a particular value of pH, and doing so in a reproducible way. Further aspects which relate to improved sensor performance, such as longer shelf-life, better stability and sensor re-usability after cleaning for a sensor prepared using the LbL technique in this work are considered and reported, showing the value of the approach taken in this research.

2. Materials and methods

2.1. Chemicals

In order to create an effective optical pH sensor, brilliant yellow (BY) was selected as the pH indicator to be used, as discussed in prior work by the authors [37]. This indicator dye was chosen for its wavelength variation and ease of use and it was cross-linked to poly (allylamine hydrochloride) [PAH] with an average molecular weight (MW) ~15,000, supplied by Sigma–Aldrich. PAH is a positively charged molecule and was used as a polycation. 3-Aminopropyl-trimethoxy silane (APTMS) (99%) as a silane coupling agent and SM-30 containing 30 wt% SiO_2 nanoparticles in H_2O as a strength enhancer were used as supplied by Sigma–Aldrich. The structures of these molecules are shown schematically in Fig. 1.

2.2. Procedures

The multilayer coating which was deposited by using a self-assembly, layer-by-layer (LbL) technique was carried out using a glass microscope slides of dimensions 76 × 26 mm, with thickness