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A new silver (I) ions optical sensor based on nanoporous thin films of sol–gel by rose bengal dye

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ABSTRACT

In this work, a new optical sensor was fabricated based on the incorporation of rose bengal (RB) dye as ionophore into the nanopores of thin film prepared through the sol-gel technique which was suitable for the determination of silver (I) ions in aqueous solutions. The prepared thin films were composed of Tetraethoxysilane (TEOS), RB dye, methanol (MeOH), hydrochloric acid and Triton X-100. They were characterized by field emission scanning electron microscopy (FE-SEM) and atomic force microscope (AFM). The results confirmed the uniformity and low roughness of the prepared thin films. Average roughness of thin films was obtained to be about 2.5 nm. After sensing Ag ions, X-ray photoelectron spectroscopy (XPS) was performed to understand the mechanism of interaction of Ag ions with thin film. Leaching of this sensor was investigated and it was found that the proposed sensor is stable over the time without observing any change in its sensitivity. The proposed sensor revealed a maximum peak at 519 nm in its UV-vis spectra corresponding to silver (I) – RB complex with response time of 7 min at pH 7. HNO_3 was found to be the best regenerator reagent for this optical sensor. The constructed sensor displayed a working range for Ag (I) of 3.24×10^{-6}–8.23×10^{-7} mol L^{-1} with a detection limit of 9.8×10^{-8} mol L^{-1}. The optode was tested in real water samples for the determination of Ag^+ ions with good selectivity.

1. Introduction

Optical chemical sensors as powerful analytical devices have been widely used in various places for agricultural, medical diagnostics, environmental and industrial monitoring. They have advantages such as cost-effectiveness, simple to use, rapid response, portability, miniaturization, and being free of dangerous materials [1–8]. In kinds of optical sensors, materials such as copolymeric nanoparticles [9], polymeric matrix like PVC [10], PVA [11,12], sol-gel matrix [13], agarose film [14], ethyl cellulose [15], silica colloidal crystal bead (SCCB) in two different forms [16] and Nanostructured polymers [NSPs] of the order of the nanometer scale [17] may be used where in some colorimetric sensors, molecularly imprinted photonic crystals have been used for visual detection of molecules [18].

The sol-gel process versus organic polymer supports is very interesting for research due to acceptable thermal stability, high abrasion resistivity, transparency in the visible region of electromagnetic waves and negligibility in bulging in aqueous and organic solutions. It is performable technique at room temperature where its product is porous and glassy substrates are commonly used as substrates for optical analyses [19,20]. In this process, porous silicates are synthesized by hydrolyzing alkoxide precursors such as tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS) or an equivalent organometallic alkoxide (such as tetraisopropoxytitanium or triisopropoxyaluminum) in the presence of an acid or base catalyst. In the next step, the condensation of hydroxylated species is carried out until forming an inorganic SiO_2 network [21]. It is essential to control the rate of hydrolysis and condensation because they affect the structure and properties of sol-gel product such as rigidity, average pore size, distribution of pore sizes, specific surface area, surface polarity, ionic conductivity, mass fractal dimension, concentration of silanol groups, and other structural properties of xerogels. The parameters, which may affect the structure and properties of sol-gel include pH, temperature, H_2O: Si molar ratio, solvent and catalyst so that pH and water: silica molar ratio is the most important variables. At high pH, deprotonation and surface charges increase, which therefore cause a delay in step of aggregation and gelation. At low pH conditions, it resembles the polycondensation of organic polymers, which results in dense and low surface area materials and thus an overall decrease in the

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efficiency of sensor occurs. At high H_2O: Si molar ratio, the porosity and specific surface area of silica network increase. At low H_2O: Si molar ratio, alkoxy groups may rarely be hydrolyzed. The approximate water: silica molar ratio of 4 is the best. In acidic media, silica oligomers are more stable than that in basic media because of having higher molecular weight [22].

To develope optical sensors and increase their selectivity, various organic reagents such as dyes [23], enzymes [24] and ligands [25] are immobilized in sol-gel matrix. In addition, materials such as metallic nanoparticles (e.g.Ag and Au-NPs), nonmetals (e.g. Graphene, CdTe quantum dots), metal oxides (e.g. Fe_xO_y NPs) polymeric moieties (e.g. micelles) have been incorporated in polymer hydrogel network, which create synergistic, unique and potentially useful effect in developing soft tactile-sensing devices [26].

Immobilization of the modifiers in the silica network, has been typically carried out using three methods of impregnation, covalent binding, and chemical doping. Impregnation method includes physical or chemical adsorption between surface of applied glass substrate and immobilized species. In second method, chemical bond is formed between surface silanol groups and organic reagents. The sol-gel process completion results in some shapes such as monolith blocks, spherical monodispersion, fibers and films. The films are the most helpful forms for optical sensors because of short diffusion pathways in such thin layers. Adhesion of films to the support such as glass slide is accomplished in some forms such as plate spreading, dip coating and spin coating. Ions- and molecules-selective reagent and pH indicators are encapsulated in these thin films for the detection and determination of ions, molecules or pH [9,17,18,27–34].

Meanwhile, sol-gel-based designed ion-selective optical sensors have been used for the detection and determination silver (I). Ag metal and its components are widely used in macroscale and nanoscale. Silver in macroscale is applied in automobile industry, brazing, battery etc. Moreover, silver is used in nanoscale in photography, biomedical science, imaging, sensors and as antibacterial, antifungal applications [35–43]. Recently, the synthesis of silver nanoparticles has been developed in various methods [44–46]. Although silver is one of the most applicable metals, it is one of the most hazardous metal pollutants when it is released into water, waste water, soil, air, and even food by different sources [47–49]. The silver ion at concentration higher than 1.6 $nmol{\cdot}L^{-1}$ in water is toxic to numerous fishes, microorganisms. It is also dangerous to human if its concentration is higher than 0.9 $mmol\,L^{-1}$ [50–53]. Accordingly, human health is in risk because Ag^+ may cause DNA damage via the complex formation between Ag^+ and polynucleotide [54,55]. Moreover, Ag^+ ions are able to bind to various metabolites and sulfhydryl enzymes, which causes the deactivation of enzymes and thus harm the human health [52,56].

Therefore, the detection of silver ions is highly important and essential that may be carried out by various methods including atomic absorption spectrometry [57], fluorescence [58,59] and electrochemical technique [60] which are expensive and time- and reagent-consuming while UV–vis spectroscopy is more advantageous [61,62]. In this work, rose bengal dye (See Fig. 1 for its chemical structure) as ionophore was entrapped in sol-gel matrix, for the detection of Ag (I) ions with suitable selectivity and without leaching in aqueous solution. This optical sensor was constructed by coating the obtained gel on a glass plate by dip coating method.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS), absolute methanol (MeOH), hydrochloric acid, sodium hydroxide and Triton X-100 as a nonionic surfactant were obtained from Merck (Darmstadt, Germany). Rose bengal was purchased from Sigma–Aldrich (USA). Silver nitrate, copper (II) nitrate and the other nitrate salts used here were purchased from Merck. The stoke solutions were prepared by dissolving nitrate salts in deionized water in certain volume. Sodium dihydrogen phosphate and sodium hydrogen phosphate were used for the preparation of phosphate buffer solution. Glass slides were cut out into 0.7 cm × 4 cm pieces.

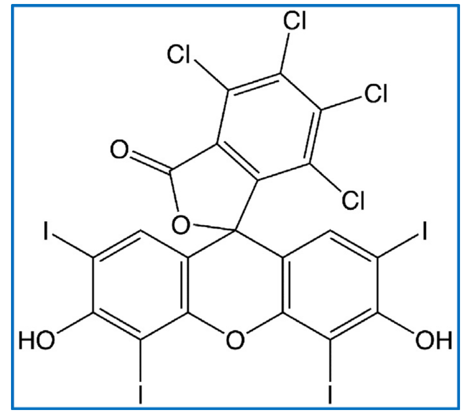

Fig. 1. Chemical structure of rose bengal.

2.2. Instrumentation

The pH measurements were performed by pH/Ion meter model 686 (Metrohm, Switzerland Swiss) and spectroscopic measurements were carried out by UV–vis spectrophotometer (Perkin Elmer Lambda 25). The glass slides were placed in a quartz cuvette and all absorption experiments were accomplished in a batch method at room temperature. Atomic force microscopy (AFM) image of membrane was provided by WITec, Japan (WITec K.K., Kawasaki-shi Kanagawa). The morphology of membrane surface was characterized using field emission scanning electron microscopy (FE-SEM: Sigma, Zeiss).

2.3. Preparation of sol–gel matrix as thin film

2 ml of TEOS and MeOH were stirred for 30 min. Because alkoxysilanes are not miscible with water, 645 μL of H_2O, Triton X-100 (10 drops), 1 ml of rose bengal were dissolved in MeOH (100 mg/L) and 0.5 ml of HCl (0.3 $mol\,L^{-1}$) was added drop by drop in the above mixture, followed by stirring for 5 h at room temperature to obtain a homogeneous solution. The obtained solution was remained in glass vial for 24 h in dark at room temperature to obtain a more viscous solution. The glass slides (0.7 cm × 4 cm), as solid supports, were treated with concentrated HNO_3 for two hours. Then they were washed several times with methanol and deionized water followed by drying in oven at 100 °C for one hour. The glass slides were coated with viscous solution by dip coating method and aged for about two weeks to enable them to form a smooth and even membrane. These slides were heated in oven at 40 °C, stored in suitable place and used whenever needed.

3. Results and discussion

3.1. Study of varying some experimental parameters on film preparation

One of the most important properties of thin film membrane fabricated by sol-gel method is leaching of indicator when immersed in analyte solution. Therefore, a good membrane has