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Sol–gel based phenolphthalein encapsulated heterogeneous silica–titania optochemical pH nanosensor

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

[a] Laser Centre, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, Skudai 81310, Johor, Malaysia
[b] Centre of Excellence in Solid State Physics, University of the Punjab, QAC, Lahore 54590, Pakistan

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ABSTRACT

Thermally stable phenolphthalein encapsulated silica–titania nanomatrix is fabricated by sol–gel method for optochemical pH sensing. The particle size ~56–121 nm is obtained with average surface roughness of 3.95 nm after the encapsulation of dye which is highly appropriate for optical and sensing applications. High surface area value ~218 m^2/g, pore volume of 0.16 cm^3/g and pore diameter of 31.49 Å is obtained after encapsulation. Furthermore, the sensor response is optimized at pH 10. Fast response time 1–2 s, sensitivity with good reproducibility identify that the fabricated optochemical nanosensor is challenging for the detection of pH at room temperature.

Introduction

Prevention of environmental ecological damage can be hardly imagined without the use of sensors. Therefore, a new and exciting area of research and development within the large field of sensing is the optochemical sensors which have not been envisioned in the last two decades. In recent years, progress in the development and utilization of optochemical nanosensors has been made because of their small size and exceptional structural, optical, mechanical, catalytic and magnetic properties of nanoparticles that further widen the optical nanosensing field. Optochemical nanosensor applications include the detection of bioterrorist threats, food industry, security, explosive detection to prevent the ecological environmental damage and many more [1]. However, modification to optochemical nanosensors requires new materials and approaches to create nanosized structures, and new techniques for their integration in complex environments. The controlled synthesis of nanostructured materials can improve sensitivity of the sensors because of their anomalous surface-to-volume ratio. Therefore, sol–gel wet chemical technique is quite attractive to prepare nanomaterials by polycondensation of different precursors in liquid [2–6]. The fabricated nanomaterials can be used as a host matrix to encapsulate the sensitive dyes. When organic dyes are encapsulated in the matrix, applications such as heterogeneous catalysis and sensing are possible. In heterogeneous matrix, heteroatoms (silica and titania) can broaden the potentials of interesting characteristics. Mostly, silica–titania composite compared with pure titania has high thermal stability, improved dispersibility in solvents and good mechanical strength. Furthermore, in heterogeneous silica–titania nanomatrix, refractive index can be easily controlled by the addition of titania. Titania shows high binding capacity due to its surface area in hybrid form. By adding a surface active agent in the sol, surface tension of the sol can be reduced, the rise of particles of polymerizing gel can be enforced and the inward tension can be decreased. In this way, we can obtain heterogeneous nanocomposites of high porosity and of low refractive index which gives better sensing performance [7,8]. Furthermore, the evanescent wave principle has been utilized for the detection of pH change of fluorescent pH indicator phenolphthalein entrapped in heterogeneous silica–titania porous nanomatrix associated with fiber optic. Recently, optical fiber has evolved into sensors because of its small size, fast detection, multiplexing and remote sensing capability, immunization to electromagnetic interference; reference electrode is not needed and most advantageous benefit is that the optical spectroscopy can be performed on sites inaccessible to conventional spectroscopy and over long distances [9]. Specifically, this principle can offer the accuracy and distribution of sensing. Furthermore, the fiber optic pH sensor benevolences numerous advantages over the commercial pH meters such as portability, lightweight and low cost. In the literature, different efforts about the use of films sensitive to pH changes on optical fibres [3,10–13], and encapsulation of phenolphthalein within silica framework have been reported

* Corresponding author. Tel.: +60 197340740.
E-mail addresses: shumaium@yahoo.com (S. Islam), noriah@utm.my (N. Bidin), Saira_cssp@yahoo.com (S. Riaz), shahzad_naseem@yahoo.com (S. Naseem).

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[14–16]. However, to the best of our knowledge no literature on silica–titania mesoporous nanomatrix encapsulated with phenolphthalein for optical pH sensing has been reported so far. We report here the synthesis and characterization of silica–titania host matrix encapsulated with guest phenolphthalein dye for optical sensing purpose. Moreover, a key challenge in the processing of the sensor is to achieve homogeneous surface and a defect-free structure that gives better sensing performance of the device. The fabricated material was deposited on planar or fiber substrates with the aim of determining the absorption changes of the phenolphthalein within acidic and basic regime. The prepared nanosensors exhibit a much faster response time without leaching/cracking. A fiber optic pH sensor was found to have a good stability and high reproducibility. A linear response over a wide range of pH values 3–10 was obtained.

Experimental

Synthesis of the sols

In this multi-step synthesis process, the sol A (SiO_2) was prepared by optimizing 2.5 ml of tetraethylorthosilicate, TEOS [98% Aldrich] that was mixed with 15 ml ethanol (EtOH) that contained mixture of water (H_2O) and nitric acid (HNO_3) [65% Merck]. The whole mixture was stirred for 2 h at 70 °C. The molar ratios were TEOS: EtOH: H_2O: HNO_3—0. 5:3.0:3.0:0.3. The pH of the solution was kept below 1.5 to maintain the viscosity. Sol B (TiO_2) was obtained in two steps. In the first step, 5 ml of titanium(IV) isopropoxide [97% Aldrich] was mixed into 10 ml isopropanol (Grade GC, 99.7%). In the second step, 10 ml propanol was added to the mixture of water and HNO_3. The molar ratio for tetraisopropylorthotitanate: propanol: H_2O:HNO_3 of final sol was 1.0:4.0:1.0:0.5. The solution was stirred for 2 h at 100 °C to get a stable sol. The final product was a mild yellow gelatinous. To prepare encapsulated indicators stable matrix, the two sols A and B were mixed in 1:1 volume ratio of silica–titania sol. 2 ml of 0.5 M concentration of phenolphthalein ($C_{20}H_{14}O_4$) and 1 ml of 0.5 M concentration of Cetyl Trimethyl Ammonium Bromide (CTAB) solution were mixed into a mixture of the two sols. This mixture was stirred and heated at 80 °C for 1 h to ensure proper combination of the constituents. After mixing, the sol turned whitish in color. Then the mixed sol was left for several days for appropriate aging cycles to increase viscosity of the solution and removal of volatile components at room temperature.

pH sensor preparation

For uniform and adhesive coatings, the glass slides were thoroughly cleaned with acetone for 15 min and propanol for 10 min in an ultrasonic bath in separate runs to remove any adsorbed gases or contaminants and then dried at room temperature [4]. Prepared sol was deposited on cleaned glass substrates by spin coating at a rate 3000 rpm for 30 s. The coating was done at room temperature. Solvent evaporation, accompanied by further condensation reactions, resulted in deposition of a solid thin film on the substrate. The overall outline of the synthesis and coating is shown in Fig. 1. In the case of sensors, before coating, 35 cm long PCS optical fibers (15 μm core diameter) with the 5 cm

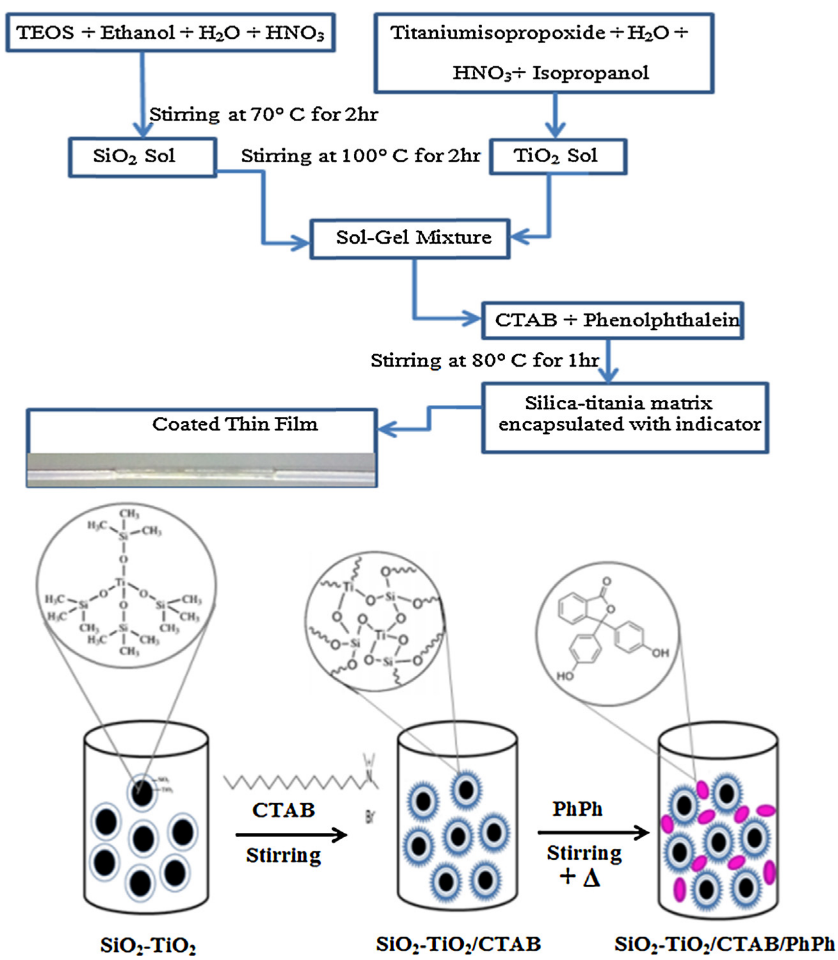

Fig. 1. Overall outline of the synthesis and coating.