

ORIGINAL ARTICLE

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Thin film optical BTB pH sensors using sol–gel method in presence of surfactants

Issa M El Nahhal*, Shehata M Zourab, Fawzi S Kodeh and Alaa I Qudaih

Abstract

Bromothymol blue (BTB) thin films were prepared by depositing a thin layer of a solution containing tetraorthosilicate and BTB pH indicator in the presence of surfactants, namely cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, CTAB) or dodecyltrimethylammonium bromide ($C_{18}H_{37}NO$, 69%), $C_{16}H_{35}NO$ (11%), Genaminox LA onto a glass slide substrate. CTAB or GLA surfactants were used to improve the mesostructure of the host material and to increase its porosity. Optical BTB thin films were found to be sensitive against pH and behave as free BTB. This provides evidence for weak interactions between the BTB molecules and the host silica matrix. The effects of the sol mixture on the stability and reproducibility and the colorimetric response to solutions of different pH were examined and pKa values were determined. The BTB thin film sensors showed an advantage over the encapsulated monolithic sensors in which the thin film sensors exhibit a faster response time than the monolithic disks. These pH sensors showed reproducibility and high stability behavior.

Keywords: Bromothymol blue, Optical thin films, pH sensors, Surfactants, Tetraorthosilicate

Background

The sol–gel process is used to immobilize pH indicators in the silica matrix network through hydrolysis and subsequent polycondensation of silicon alkoxide precursors at room temperature (RT). The sol–gel matrix provides a physical and chemical environment host for pH indicators as monolithic disks or thin films with excellent optical properties. Sol–gel technology is convenient to the development of optical pH sensors. It allows low temperature preparation of optically transparent porous thin films with tunable properties. There is a great potential use of the sol–gel glasses encapsulated materials for optical sensing because of their optical transparency and their mechanical and thermal stability. In recent years, an increased research effort has been focused on doped porous sol–gel layers coated on glass in order to perform fiber optical chemical and biochemical sensing [1-5]. The formation of mesostructured silica formed by cooperative self-assembly of silicate and surfactants was used to modify its structures [6,7]. More recently, organic functional groups were introduced in inorganic precursors, and their copolymerization with tetraethylorthosilicate (TEOS) results in inorganic/organic hybrid

materials [8,9]. In addition to using different organically modified precursors, film properties can be tuned with surfactants to have an effect on film morphology and porosity of encapsulated reagents [10,11]. Optimization of the glass composition and the right choice of processing parameters are vital for obtaining high quality films that will retain the required sensing performance characteristics. Three methods were used for immobilization of indicators into sol–gel glasses, including impregnation, covalent binding and chemical doping. In a previous work, chemical doping method was used for the immobilization of bromothymol blue (BTB). The synthetic procedure has been designed to obtain monolithic disks of doped BTB in silica [12,13]. The role of the cationic cetyltrimethylammonium bromide (CTAB) and the zwitterionic dimethyl amino oxide (GLA) surfactants in modification of the polysiloxane structure network was examined [14]. In this work, optically transparent sol–gel thin films containing encapsulated BTB molecules were prepared by depositing a sol mixture containing TEOS, BTB and surfactant onto glass substrate using spin-coating techniques in one-pot synthesis. The immobilized thin film material was prepared by entrapping of BTB molecules in the sol–gel matrices. Matrix morphology was controlled by varying the ratios of sol

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Table 1 Weighing of slides

| Number of layers | Weights of empty slides (g) | Weights of coated slides (g) | Weight difference (g) |
|------------------|-----------------------------|------------------------------|-----------------------|
| Single | 0.516 | 0.532 | 0.016 |
| Double | - | 0.550 | 0.034 |
| Triple | - | 0.560 | 0.044 |

mixtures and the surfactants. The effects of the sol-gel mixture on the stability and homogeneity of the films and colorimetric response to pH solutions were also examined.

Methods

Materials and apparatus

TEOS, BTB, CTAB and GLA were purchased from Sigma-Aldrich Corporation (MO, USA). Hydrochloric acid, sodium hydroxide and absolute ethanol (98%) were purchased from Merck & Co., Inc. (NJ, USA). All chemicals were used as received without further purifications.

Preparation of thin films

The optical BTB thin films were prepared by spin coating (2,000 rpm, 30 s) of the 0.5 ml solution containing 1:1:1 volume ratio of TEOS, BTB and surfactant with molar ratio (1.5, 0.018 and 0.16, respectively) onto glass slide (2.5 cm × 2.5 cm × 1.0 mm). Prior to film deposition, the glass substrate was activated by treating it with concentrated nitric acid for 6 h. After which, slides were washed with distilled water and dried at 100°C and then stored in the darkness at room temperature. Small size slides (1 × 0.5 cm) were cut into small strips. The coated strips were immersed in the cuvettes to perform UV-vis

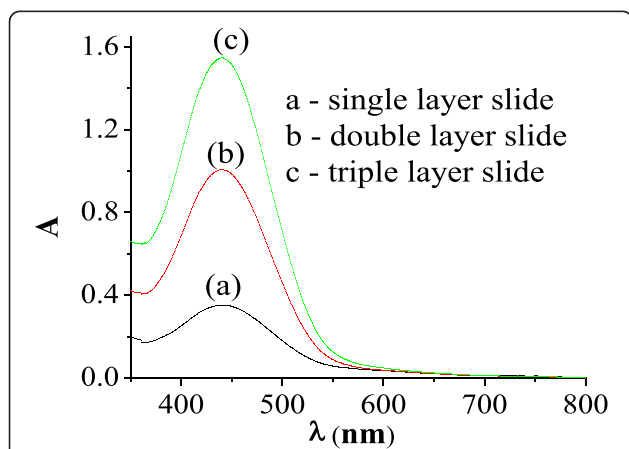


Figure 1 Absorption spectra of immobilized BTB thin film dried at 100°C. (a) Single layer slide, (b) double layer slide and (c) triple layer slide.

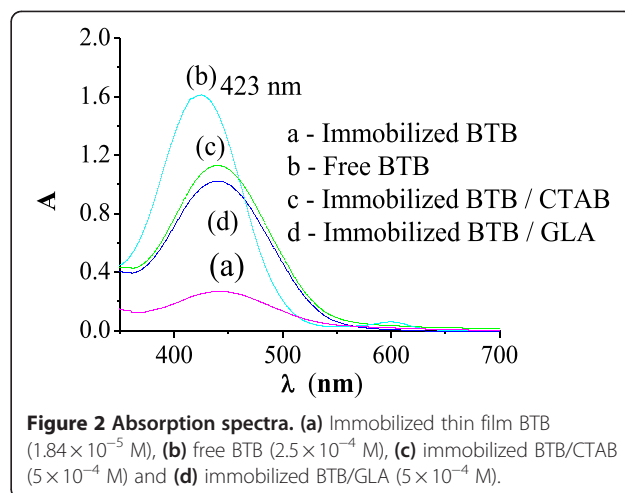


Figure 2 Absorption spectra. (a) Immobilized thin film BTB (1.84×10^{-5} M), (b) free BTB (2.5×10^{-4} M), (c) immobilized BTB/CTAB (5×10^{-4} M) and (d) immobilized BTB/GLA (5×10^{-4} M).

measurements. The obtained wet layer was dried for 5 days at room temperature, then heated for 8 h at 80°C, followed by further heating at 100°C for 5 h. For obtaining multilayers, the spin-coating method was repeated in the single-layered substrate.

UV-vis spectra

The optical absorption of the deposited films was obtained using a UV-vis spectrophotometer, Shimadzu-1601 (Shimadzu Corporation, Tokyo, Japan), in the range of 200 to 800 nm.

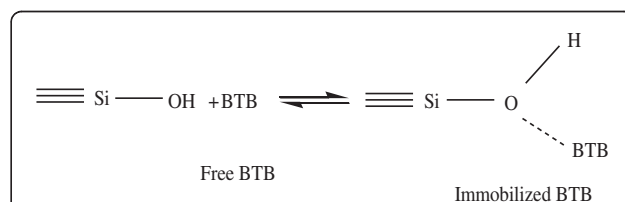
Polarization microscopy

Surface morphology of the films was characterized using a Zeiss standard polarization microscope (PM) model BX 50 (Carl Zeiss AG, Oberkochen, Germany) equipped with an Olympus DP 100 camera (Olympus Imaging America Inc., PA, USA).

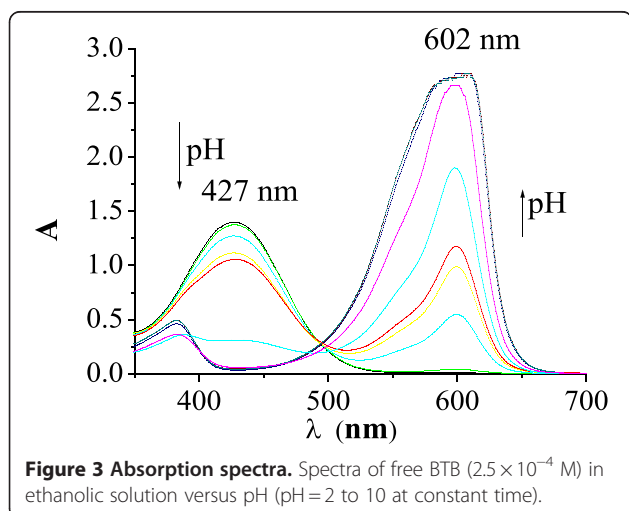
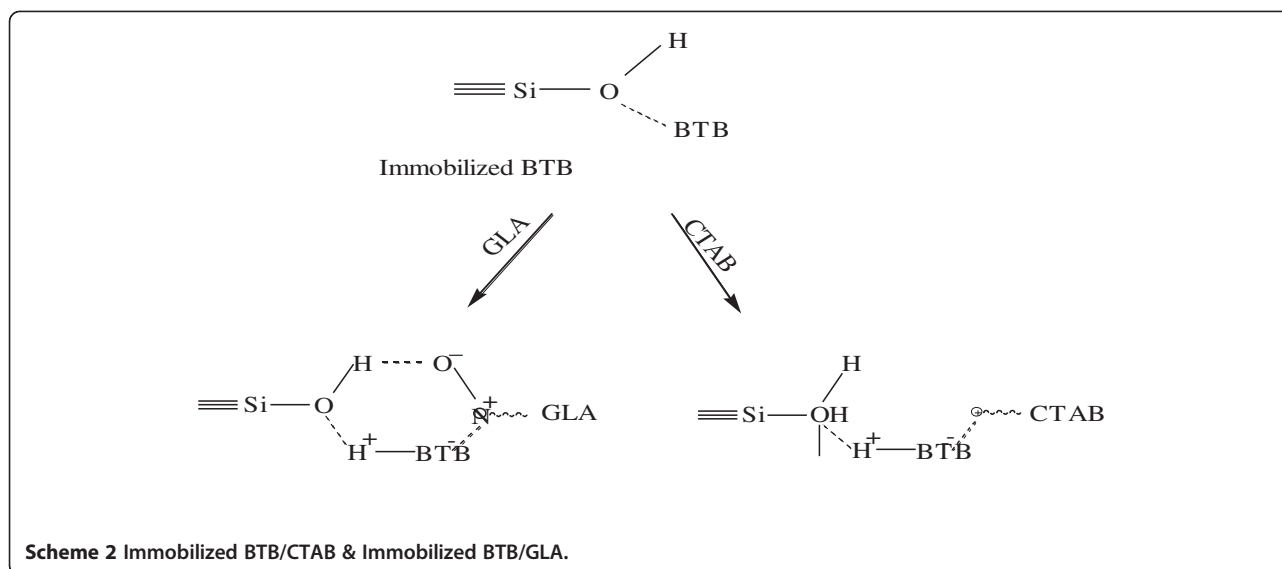
Results and discussion

Synthesis

Optical BTB thin films were obtained by depositing monolayers of a sol containing TEOS, BTB pH-indicator



Scheme 1 Interaction between BTB molecules and silica network.



and a surfactant into a glass side. It is notable that BTB thin films showed no significant leaching of BTB molecules in the presence of GLA surfactant. This is probably due to the physical interactions between BTB molecules and GLA surfactant. Multilayer coating has been

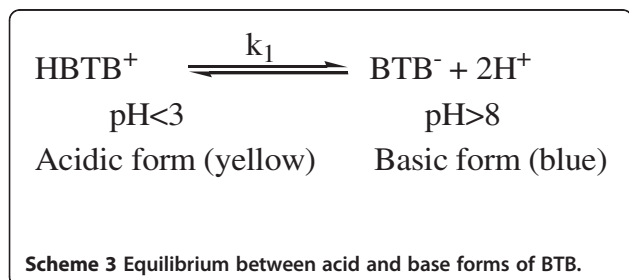


Table 2 pH response ranges and pKa values for free and immobilized BTB

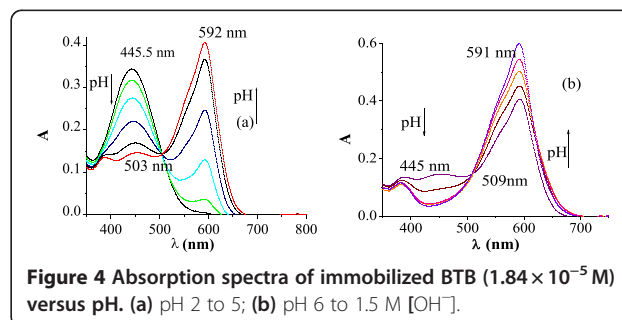
| | pKa ₁ | pKa ₂ | pH response range |
|----------------------|-------------------------|-------------------------|---------------------------|
| Free BTB | 6.60 (7.0) ^a | | 4 to 8 |
| Immobilized BTB | 4.84 (1.6) ^a | 10.8 (9.7) ^b | 3 to 7, 8.5 to 12 |
| Immobilized BTB/CTAB | 4.70 | 11.20 | 3 to 7, 8.5 to 1.5 M [OH] |
| Immobilized BTB/GLA | 4.04 | 11.60 | 3 to 7, 8.5 to 1.5 M [OH] |

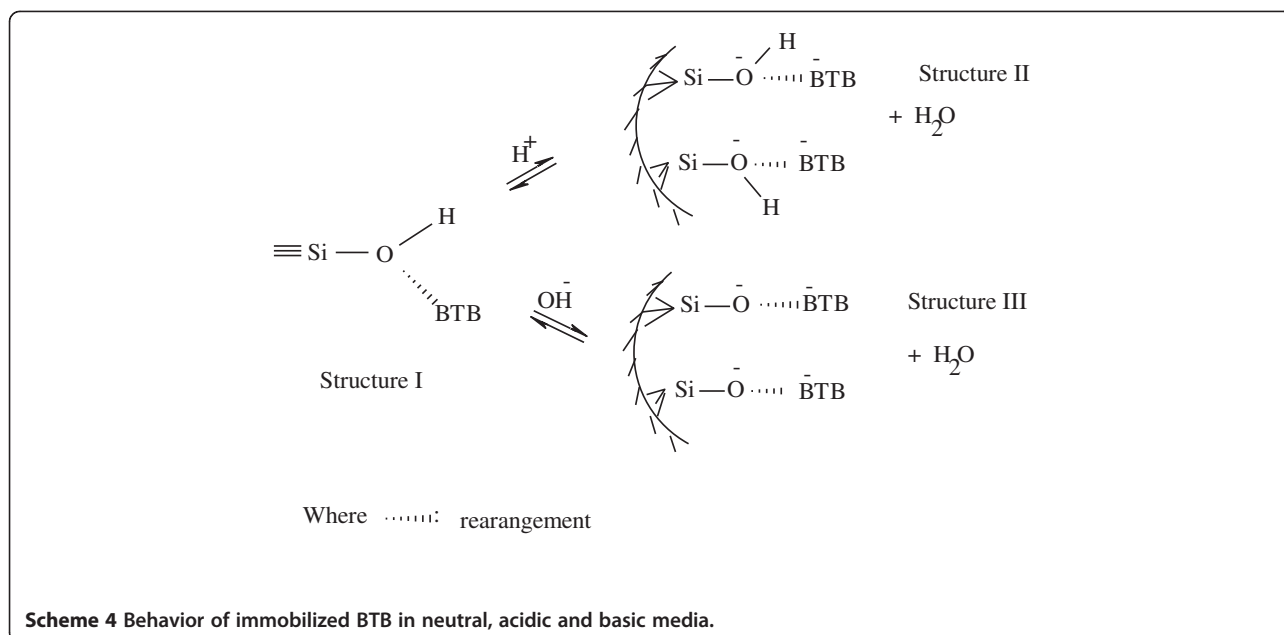
^aReported value in reference [13]; ^breported value in reference [12].

deposited in order to obtain thicker coating thin films by repeating the coating process (spinning, drying and densification). The thickness of the layers increases practically linearly with increasing the number of layers. This has been proved by weighting the slide with and without coating (Table 1). The variation of the absorbance band at 440 nm of the immobilized BTB thin film of different layers is shown in Figure 1. The absorbance increases as the number of layers is increased.

UV-vis spectra

At normal condition, BTB exists in two forms: acid form (yellow color) and base form (blue color) which

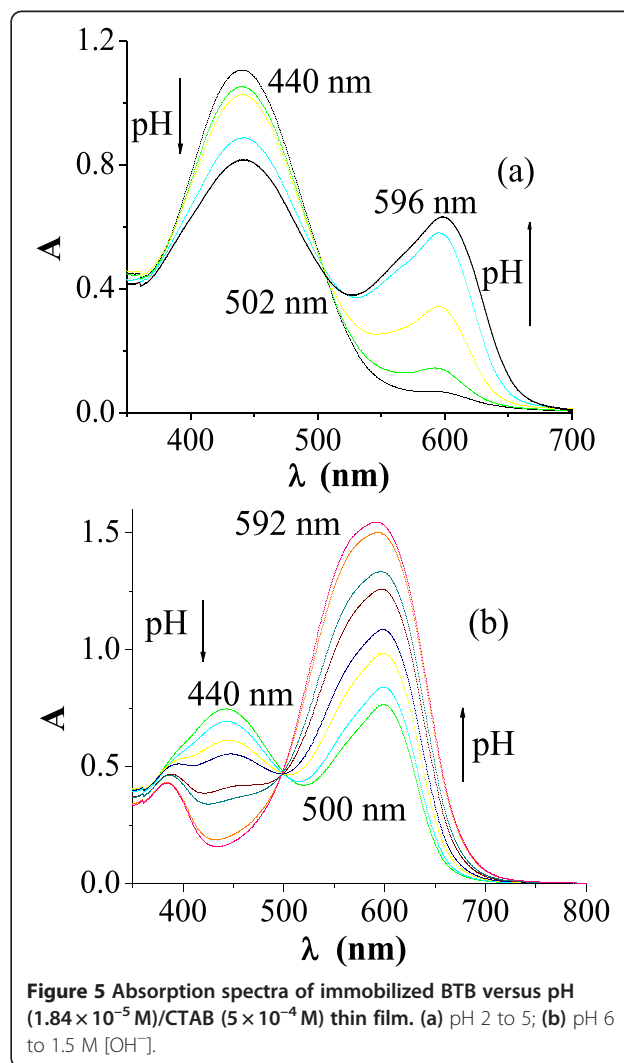


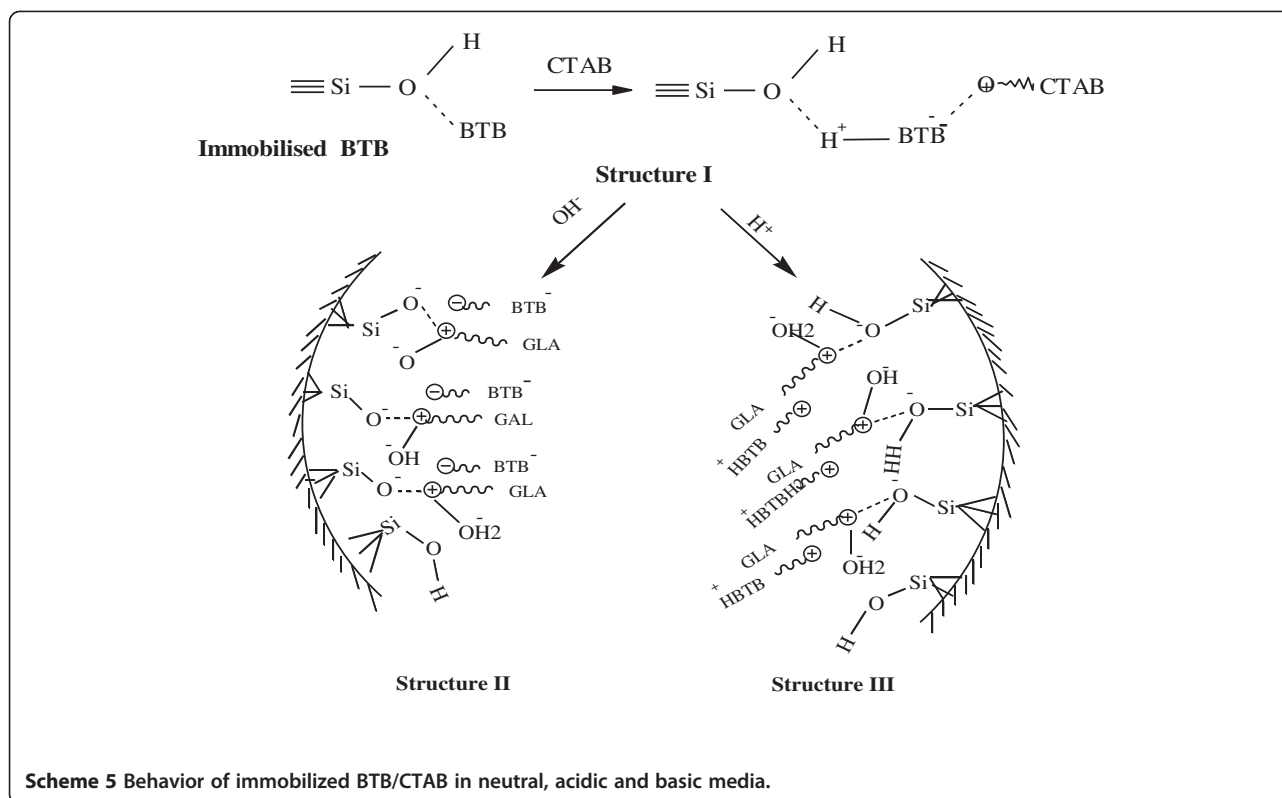


correspond to the two absorption bands at about 423 and 602 nm, respectively. These peaks are due to $\pi-\pi^*$ and $n-\pi^*$ transitions. The absorption spectrum of the free BTB (2.5×10^{-4} M) before exposing to pH effect is almost similar to that of the immobilized BTB (1.84×10^{-5} M) as shown in Figure 2. One absorption band was observed at 423 nm for the free BTB in solution (Figure 2b), whereas an absorption band was observed at 440 nm with a red shift of k 17 nm for the immobilized BTB (Figure 2a). This could be explained as a result of weak physical interaction between BTB molecules and silica network (Scheme 1) [12-15].

The electronic spectrum of the immobilized BTB (Figure 2b) is very similar to that of the immobilized BTB/CTAB (Figure 2c) and the immobilized BTB/GLA (Figure 2d) when CTAB and GLA surfactants were used. They show no significant shift of the absorption band at 440 nm but increase the intensity of peak significantly. The reason for this behavior is that CTAB or GLA surfactants have modified the mesostructure of the BTB thin film material, and therefore, low leaching of the BTB molecules was observed (Scheme 2). This is more pronounced in the case of GLA thin film.

The absorption spectra of the free BTB at different pH values were shown in Figure 3 with the presence of one isosbestic point at 492 nm. Dissociation constant (pK_a) value was found to be 6.6 which is slightly lower from the reported pK_a 7.0 [15] as shown in Scheme 3





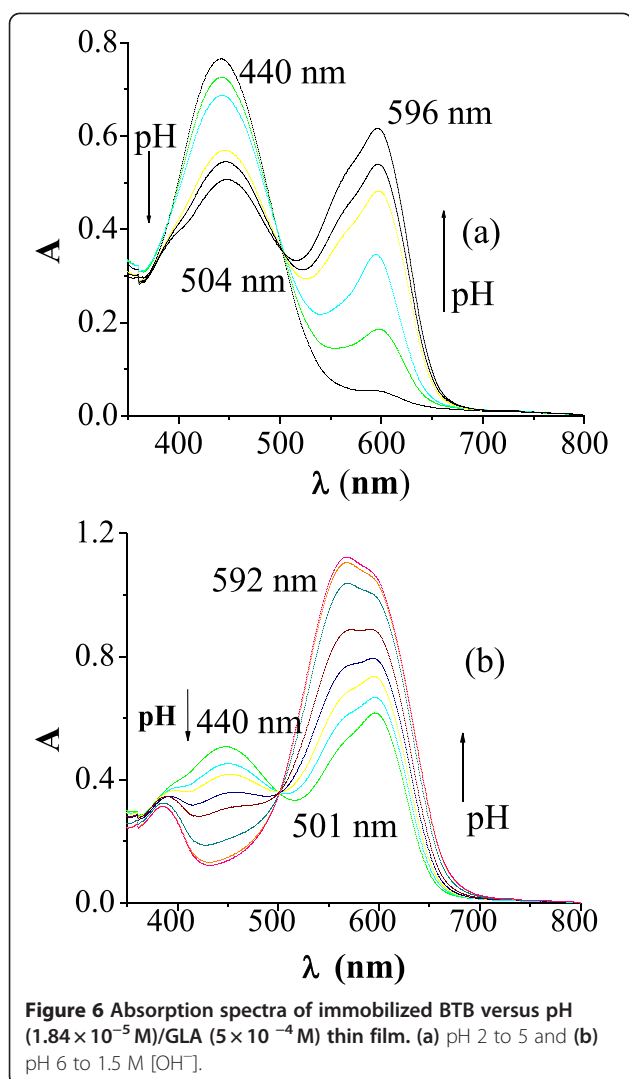
(Table 2). pK_a values were calculated from the titration curves.

When the immobilized BTB is treated with different pH solutions (pH 2 to 12), two indicating transitions for free BTB were clearly shown in Figure 4a,b with the presence of two isosbestic points at 503 and 509 nm, respectively, which are consistent with reported results of similar systems [14,15]. This provides evidence for the presence of two equilibria: the first equilibrium at pH 2 to 7 is between acid and neutral forms of BTB (Figure 4a); the second equilibrium at pH 7 to 12 is between neutral and base forms (Figure 4b). pK_{a1} and pK_{a2} values for the immobilized BTB were found to be 4.84 and 10.8, respectively (Table 2). There was a considerable difference between our pK_a values and the reported ones, in particular, pK_{a1} value (Table 2) [15]. The lower value of pK_{a1} , 4.84, is perhaps due to a weak Van der Waals interaction between protonated (HBTB⁺) and silanol species (Structure II of Scheme 4). The higher value of pK_{a2} , 10.8, is probably that, in basic medium, the anions BTB⁻ are probably involve in weak Van der Waals interactions with silanol ($\equiv \text{Si-O}^-$) species (Structure III of Scheme 4), but in the neutral medium, a hydrogen bonding species ($\equiv \text{Si-OH} \cdots \text{BTB}$) was probably formed as described in Structure I of Scheme 4.

When the immobilized BTB/CTAB were treated with different pH 2 to 1.5 M [OH⁻] solutions, two different

indicating transitions (two equilibria) were also observed (Figure 5a,b), with the presence of isosbestic point for each equilibrium at 502 and 500 nm, respectively. The first transition at pH 2 to 7 was due to the change of yellow color (acid form) to red color (neutral form) (Figure 5a), and the second transition at pH 8 to 1.5 M [OH⁻] was due to the change of red color (neutral form) to blue color (base form) (Figure 5b). In the presence of CTAB, the hydrophobic non-charged BTB molecules are transferred to anionic hydrophilic species and formation of ion pairs between the cationic surfactant CTAB and the anionic species of BTB (Structure I of Scheme 5). In the basic medium, ion pairs between cationic CTAB and BTB anions were formed (Structure II of Scheme 5). There is change of pK_{a2} to more basic in the presence of cationic surfactant CTAB (Table 2). In acidic medium, a weak interaction between the protonated BTB and silanols increases pK_{a1} to more acidic value (Structure III of Scheme 5). This can be explained that the micellar environment favors the anionic hydrophilic species of BTB as given in Scheme 5.

When the immobilized BTB/GLA is treated with different pH 2–1.5 M [OH⁻] solutions, two different indicating transitions (two equilibria) are also observed as given in Figure 6a,b with the presence of an isosbestic point for each equilibrium at 504 and 501 nm, respectively. As the pH increases from 2 to 7, first equilibrium



is accompanied with a change from the yellow color (acid form) to the red color (neutral form) (Figure 6a), and as the pH increases from 8 to 1.5 M [OH⁻], the second equilibrium is accompanied by a change of the red color (neutral form) to the blue color (base form) as shown in Figure 6b. Due to the formation of ion pairs between GLA surfactant and the anionic species of BTB, there was a faster change from the hydrophobic non-charged BTB molecules into the anionic hydrophilic in the presence of GLA species than that in the presence of CTAB. This is probably because of the strong interaction between both positive and negative charges of the zwitterionic surfactant and both BTB species (BTB⁻ and H⁺) as shown in Structure I of Scheme 6. There was a slight change of pK_{a1} to more acidic value and pK_{a2} to more basic value in the presence of GLA (Table 2). The nature of interactions at neutral, basic and acidic media is shown in Scheme 6 (Structures I, II and III).

Effect of temperature

BTB thin films of different layers (single, double and triple) have been dried at different temperatures (RT, 50°C, 80°C and 100°C). It has been found that the highest intensity was observed at 440 nm for samples dried at 100°C (Figure 7). This can be explained that the films dried at 100°C have evaporated most of water and alcohol molecules which are physically absorbed within the silica pores, and therefore, BTB molecules were better accommodated within the silica pores and strongly interacted within the silica matrix.

The effect of leaching

It is found that the lowest leaching of BTB molecules from these films was observed when GLA surfactant was used (Figure 8). The reason for this change is due to strong interaction between cation and anion ends of the zwitterionic surfactant with the anion and the proton species of BTB. It is also found that the lowest leaching was found when these films were dried at higher temperature (Figure 7).

Reversibility of the BTB sensor

BTB thin films act as reversible sensors for the changes of pH, forward and backward as given in Figure 9a,b. The spectra were obtained in the range from 350 to 700 nm; the response time was 20 min in both ways.

Reproducibility of the BTB sensor

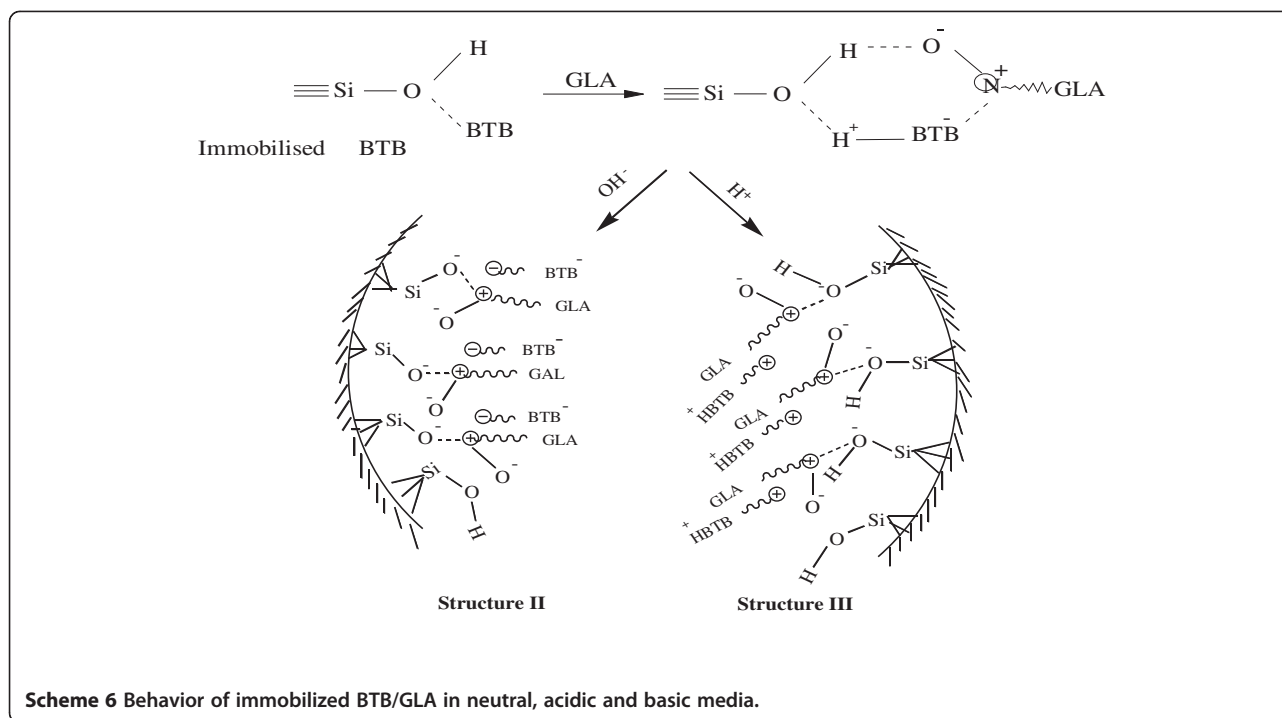
Using a thin film, six-cycle measurements were conducted. The cycles were repeated every 24 h from the previous one to check the intra-week reproducibility. It was found that the absorbance after each measurement over the pH 5 to 9 range gradually decreased and reached a minimum value after 144 h (Table 3). This is probably due to some degradation and significant leaching of BTB species. It is notable that there is no decreasing of absorbance when GLA surfactant was used.

Stability of BTB thin film sensors

To investigate the stability of the sensors, the sol-gel slides were examined after a period of 10 months. After 10 months, the absorbance spectrum of the film was the same. The thickness of the film response has not changed. This may prove that the microstructure of the film is fully stable after a period of 10 months.

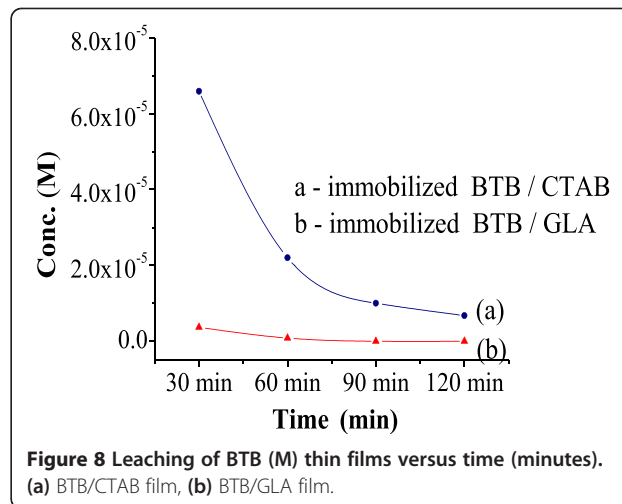
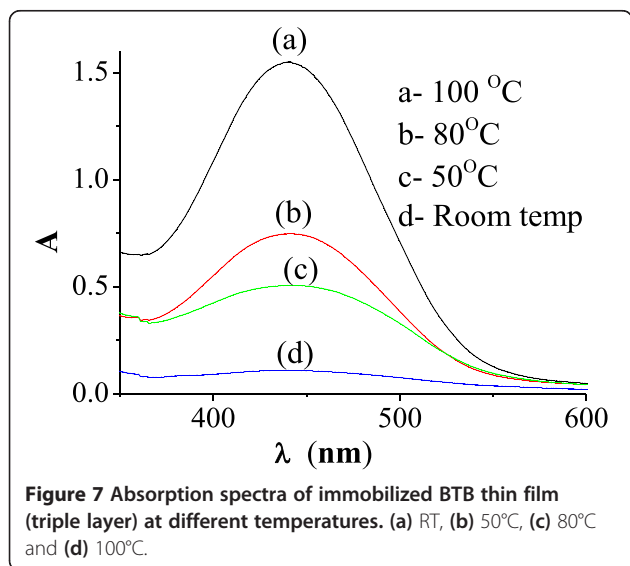
Polarized light microscopy

In order to examine the nature of the interaction between BTB, silica and surfactants, several photographs were taken by crossed polarized light microscope for thin films of free silica, immobilized BTB, immobilized BTB/CTAB and immobilized BTB/GLA. It is clear that the particle size distribution has a wider range in the



free silica (Figure 10a), whereas more uniform and smaller size particles were found for the immobilized BTB (Figure 10b). Large number of particles and more uniform particles were observed when GLA and CTAB were used (Figure 10c,d). This behavior could be attributed to the interaction between the surfactants with BTB molecules through electrostatic interaction. This was also supported by the low leaching of BTB molecules in the presence of surfactants, where the

hydrophobic part of surfactant participates in the acceleration of the association of the particles which lead to increase its stability. From Figure 10d, the GLA surfactant has more effect on the improvement and modification of the particles than CTAB (Figure 10c). This behavior may refer to the chemical structure of GLA. There is a strong interaction between the cation and anion ends of GLA with BTB more than CTAB which has a bulky head group (carry a positive charge). Figure 10d shows a smaller and fine sequence of particles.



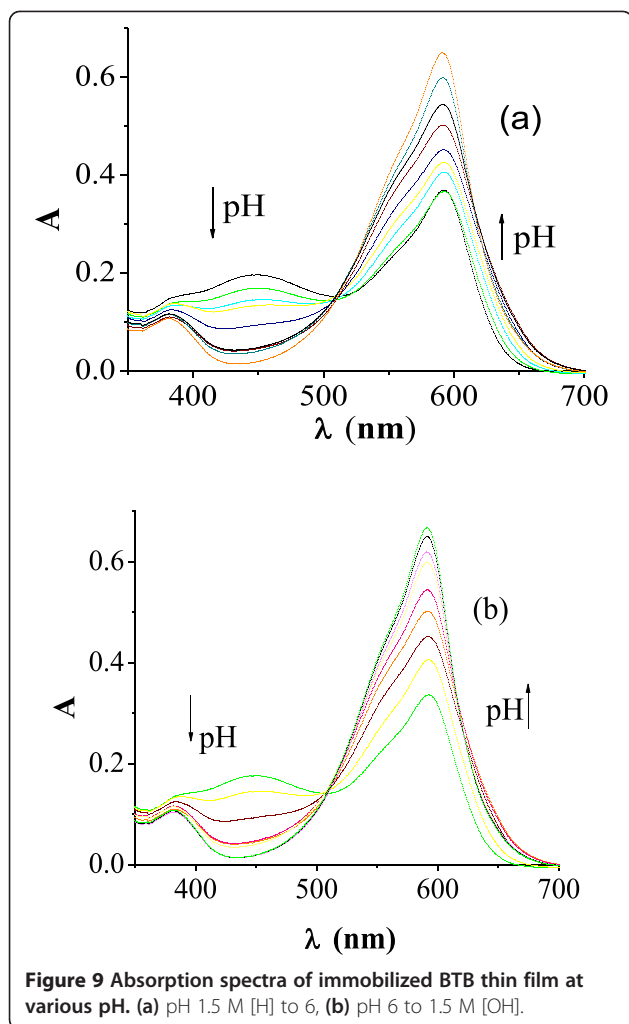
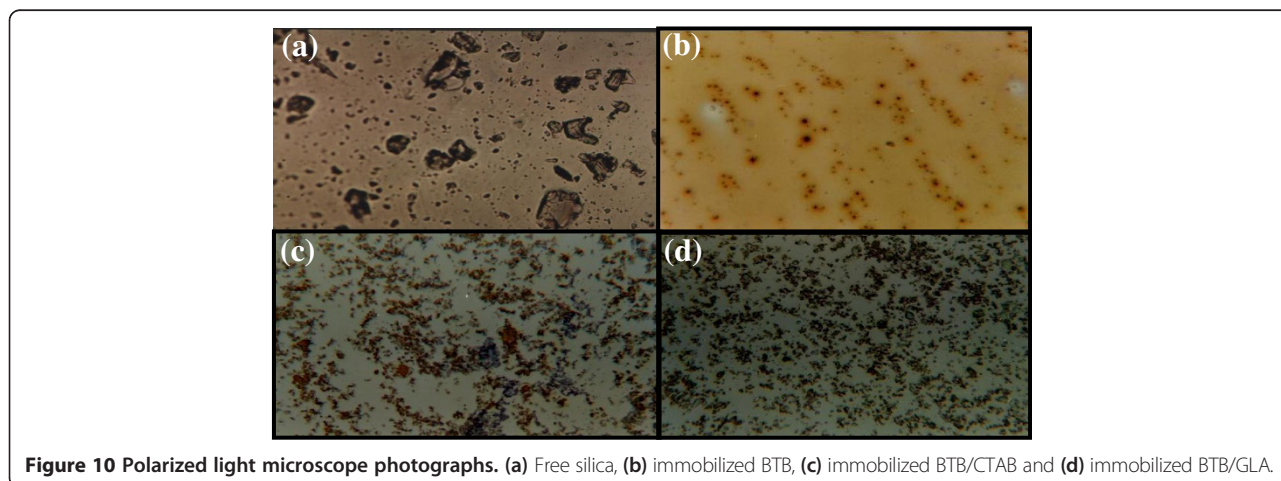


Table 3 Reproducibility of immobilized BTB thin film (single layer) sensors

| Measurement number | Time testing (h) | Absorbance at 592 nm |
|--------------------|------------------|----------------------|
| 1 | 0. | 0.453 |
| 2 | 24 | 0.427 |
| 3 | 48 | 0.415 |
| 4 | 72 | 0.391 |
| 5 | 96 | 0.365 |
| 6 | 120 | 0.334 |
| 7 | 144 | 0.210 |

Conclusion

Three different BTB thin films, immobilized BTB, immobilized BTB/CTAB and immobilized BTB/GLA were prepared by depositing a thin layer of a solution containing TEOS, BTB and CTAB or GLA surfactant onto glass substrate. The lowest leaching of BTB species was obtained when GLA surfactant was used. BTB molecules were properly accommodated within silica network pores when the thin films were heated at 100°C and well interacted when surfactants were used. These sensors were found to be very sensitive for pH change with the presence of two indicating transitions. The presence of surfactants has also improved silica network and increased its surface area.



Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AQ and FK carried out the preparations of coating immobilized BTB thin films and conducted the UV/VIS spectra. IN and SZ participated in the discussions and interpretation of all spectroscopic results. All authors read and approved the final manuscript.

Authors' information

IN was born in Gaza in 1956. He had his PhD degree from Manchester University, UK in 1986. He is a professor of Inorganic Chemistry at Al-Azhar University of Gaza. He has many publications in several topics, especially in immobilized polysiloxane ligands and their applications. SZ was born in Gaza in 1948. He had his PhD degree from Al-Exandria University, Egypt in 1978. He is a professor of Physical Chemistry at Al-Azhar University of Gaza. He has many publications in several topics, especially in colloidal chemistry fields and their applications. FK is a PhD student, and AQ is masters degree student.

Acknowledgments

The authors would like to thank Al-Azhar University of Gaza and the Chemistry Department at AUG for providing their laboratory facilities for completing this research.

Received: 16 March 2011 Accepted: 28 February 2012

Published: 18 July 2012

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doi:10.1186/2228-5326-2-16

Cite this article as: Nahhal et al.: Thin film optical BTB pH sensors using sol-gel method in presence of surfactants. *International Nano Letters* 2012 2:16.

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