Coated Sol-Gel Thin Films of some pH- Indicators, preparation and Characterization

تحضير أفلام رقيقة بطريقة الصل - جل لبعض كواشف الرقم الهيدروجيني ودراسة خصائصها

Submitted by
Ahmed I. El-Basioni

 Supervised By
Prof. Nizam M. El-Ashgar  
Analytical Chemistry  
The Islamic University of Gaza

Prof. Issa M. El-Nahhal  
Inorganic Chemistry  
Al-Azhar University-Gaza

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Dedication

To prisoners of freedom ..................
To our martyrs blood.......... 
To Palestine, land and people ........
To my parents and families ........
To my wife and my children......
To my brothers and my sister .......
To my teachers and supervisors ......
To the Islamic university of Gaza ............
To all who helped me .............
I dedicate this modest research and hope to obtain pride
Acknowledgement

This dissertation would not have been possible without the guidance and the help of several people generously who, in one way or another, contributed and extended their valuable assistance in the preparation and completion of this study. So I would like to thank: My supervisors, Prof. Nizam M. El-Ashqar and Prof. Issa M. El-Nahhal for encouragement, supervision and support from the beginning to the end that helped me to develop better understanding of the subject.

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Chemistry department at the Islamic university of Gaza.
All my teachers ……..
My parents ……..
My brothers and my sister ……….
My wife ………
My friends ……………

Finally, all my acknowledgment is devoted to those who supported me in any respect during the completion of the research.

The Researcher
Ahmed I. Al Basioni
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Abstract

Transparent sol-gel thin films immobilized with bromocresol purple (BCP) and bromocresol green (BCG) pH-sensitive indicators were made via the acid catalyzed sol-gel reaction of tetraethylorthosilicate in presence of (BCP) or (BCG) indicators. Different surfactants include; cationic cetyl trimethyl ammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS) and nonionic Triton X-100 (TX-100) were used to improve the mesostructure of the host material and to increase its porosity. With the exception of BCP in presence of SDS; the BCP and BCG thin films show similar behavior in presence of surfactants as their free counterparts in aqueous solution with very small shifts in the wavelength's of absorption. The color change behavior of the immobilized bromocresol purple indicator affected significantly and show three absorption bands in presence of SDS at ($\lambda_{\text{max}}$=435 nm, , $\lambda_{\text{max}}$=535 nm and $\lambda_{\text{max}}$=595 nm) comparing with its free counterpart in aqueous solution, while only two absorption bands were observed in case of other surfactants for both BCP and BCG thin films. Both BCP and BCG retain their structures during the sol-gel reactions in terms of response to pH. Different parameters include concentration of indicators and surfactants, temperature, number of layers, response time, life time and number of measurements were investigated. The pKa values of the different prepared BCP and BCG immobilized thin films were determined. The BCP and BCG thin films sensor showed stability, reversibility, repeatability, reproducibility, fast response and long life time behavior. Lowest leaching of BCP and BCG indicators was showed when thin films were dried at 80 $^\circ$C. Stability of the indicators thin films was observed up to ten month life time. The indicator thin films show very fast response.
Construction of multi-layer sol-gel film enabled higher indicator lading and improve signal sensitivity.
The electrostatic attraction between indicators molecules, surfactants and silica host matrix enhanced the accommodation of indicators molecules and improve their stability and preserve sensitivity. The polarized light microscopy indicated that the bromocresol purple and bromocresol green molecules were distributed uniformly within the host silica network especially in presence of surfactants.
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<td>BCP</td>
<td>Bromocresol Purple</td>
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<td>CSD</td>
<td>Chemical Solution Deposition</td>
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<td>CTAB</td>
<td>Cetyl trimethyl ammonium bromide</td>
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<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>EtOH</td>
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<td>ISFET</td>
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Chapter 1

Introduction
1- Introduction.

Silica based materials are the most ancient and widely used inorganic materials known to man. Likewise, silica (SiO$_2$) is a very common metal oxide material in daily life. The chemical inertness and rigid structure of this material has promoted its extensive usage over a very long period of time and has led to the development of various applications, which include corrosion protection and chromatographic applications [1-3]. The porosity of the silica based materials also allows wide applications such as immobilization and catalysis [4-6].

In the last decades sol–gel chemistry has played a major role in preparation of silica based hybrid materials by bridging organic and inorganic in coupling [7]. The attractive characteristics of these materials with electrochemical science is now in progress [7–8]. Preparation of sol-gel matrices doped with some chemically and biologically active molecules is a promise route to chemical solid-state sensors [7-9]. Sol-gel matrices appear as a very important technique for immobilization, entrapment, encapsulation for large variety of materials such as organic, inorganic, and bimolecules [10-11].

A wide variety of organic molecules and complexes have been proved as dopants sensing purposes [12]. The low temperature of the sol-gel method, porosity of material formed and high surface area of host matrix favors the use of a wide range of organic dyes. The entrapment of pH sensitive dyes into such inorganic host porous materials using sol-gel processing has received considerable attention over the past few years [13-14]. The entrapped pH-sensitive materials often retain their activity and functionality to a large extent. The porosity of sol-gel matrices allows diffusion of active material and reactants. Through these reactions, the pH-sensitive materials posses sensing ability to detect the pH of solutions. The pH indicators were chemically or physically immobilized into a solid support [15-16]. Silica is considered as one of the best
solid substrate used to host the pH indicators. Subsequently, active pH sensitive molecules are added to the sol medium, and as the inorganic three-dimensional network develops the active material and the residue solvents are expelled from the growing network and finally trapped into network cages [17-18]. A relatively long period of time e.g. few weeks, can then cause solvent evaporation to obtain active-molecules doped, transparent and dried matrix [19]. Surfactants were used considerably in recent years to form mesostructures of silica matrix and so high porosity silica was obtained that host sensing molecules efficiently [20]. Recently sol-gel thin films was useful to immobilize many active molecules such as inorganic clusters, porphyrins, photochromic and laser dyes, rare earth complexes, bioactive molecules, etc, that were mainly obtained for sensing purposes [18-22].

There are three techniques of indicator immobilization in sol-gel include 1) impregnation, 2) covalent binding, 3) chemical doping [23]. Many pH-sensing materials immobilized into solid supports have been reported. The effects of the silica matrix and presence of surfactants on the pH response and $pK_a$ were well documented for many pH-sensitive doped systems.

1.1 Sol – Gel Method.

The sol-gel process, also known as chemical solution deposition, is a wet-chemical technique widely used in the fields of material science and ceramic engendering. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers [25]. Typical precursor are metal alkoxides such as tetraethoxysilane (TEOS), which undergoes various forms of hydrolysis and polycondensation reactions.
1.2 Sol - Gel Technology.

The sol-gel technique is one of the most promising tools in material science. The versatility of this method allows designing desired materials at low temperatures, alternatively to conventional methods for manufacturing glass and other products.

Sol-gel produced oxides are used in numerous applications, such as coatings and thin films in electronic or optical components and devices. Sol-gel monoliths and coatings have been investigated as matrices for catalysts, optical filters or as biosensors in diagnostic applications [26]. In addition to sensors development many investigations have been conducted on the use of sol-gel matrices for entrapment of laser dyes, proteins, enzymes, microbial cells and porous membranes [27]. Sol-gel processes offers advantages such as low processing temperature with high homogeneity and purity of the material enabling preparation of hybrid materials and incorporation of drug substances or even cells [28]. A large number of materials (proteins, hydrogen peroxidase, indicators, and oxides), that retain their activity and stay in the matrix, have been incorporated into silica xerogel matrix through moulding.

1.3 Sol – Gel Process.

Generally, it is a process concerning transition of a system of Metal alkoxides from liquid 'sol' (the colloidal suspension of particles) into solid 'gel' [29]. There are three steps for sol-gel processing (Scheme 1); the first method is gelation of colloidal particles, the second is the hydrolysis and poly condensation reactions of alkoxide precursor followed by hypercritical drying, while the third method is similar to the second one: the only difference is in the drying process, which takes place at ambient temperatures. Metal alkoxides are very famous precursors; as soon as they are exposed to water they are hydrolyzed. The partially hydrolyzed alkoxide molecules react with each other
or with the un-hydrolyzed ones to undergo a condensation reaction and form a cross-linked matrix liberating water or alcohol [18].

**Hydrolysis:**

\[
\begin{align*}
\text{CH}_3\text{O} &-\text{Si}-\text{OCH}_3 + 4\text{H}_2\text{O} \rightarrow \text{OH}-\text{Si}-\text{OH} + 4\text{CH}_3\text{OH} \\
\end{align*}
\]

**Condensation:**

\[
\begin{align*}
\text{OH} &-\text{Si}-\text{OH} + \text{OH} &-\text{Si}-\text{OH} \rightarrow \text{OH} &-\text{Si}-\text{O}-\text{Si}-\text{OH} + \text{H}_2\text{O} \\
\end{align*}
\]

**Further Condensation:**

\[
\begin{align*}
\text{HO} &-\text{Si}-\text{O}-\text{Si}-\text{OH} + 6\text{Si(OH)}_4 \rightarrow \\
\text{HO} &-\text{Si}-\text{OH} &-\text{Si}-\text{OH} + 6\text{OH}_2 \\
\end{align*}
\]

Scheme 1 (the three steps for sol-gel processing)
1.3.1 Factors Affecting the Structure of Sol-Gel Processed Silica Xerogel.

A porous and amorphous structure is one of the most characteristic features of sol-gel derived silica xerogel. Reactivity of the matrix, due to free hydroxyl groups, is the other typical property of silica xerogel. The microstructure of silica xerogel can be controlled by changing the water/alkoxide molar ratio, the catalyst type or concentration, by consolidating /sintering the silica xerogel by heat treatment or by using alkyl-substituted alkoxides or other additives.

A- Water/alkoxide molar ratio.

The water/alkoxide molar ratio \(r\) has significant effect on the silica xerogel microstructure [31]. When the water/alkoxide molar ratio is low, alcohol condensation is dominating and gelation time is longer, leading to more microporous materials. Gels made from higher water content sol \([r > 4]\) have shown more coarse microstructure than gels made from lower water content sols \([r < 4]\) [32]. However, when the water/alkoxide ratio is more than 10, the microstructure was only slightly dependent on water content. The gels made from lower water content sols have more unreacted alkoxy ligands than those from higher water content sol and therefore form more linear chain-like structures [25]. At higher water concentration, more branched polymers are formed. Fiber drawing is possible from sols made at low water/TEOS ratio and low pH [31].

B- Catalyst.

The effect of pH on the pore structure and morphology has been extensively studied [31]. Changes in solution pH alter the relative rates of hydrolysis and condensation, yielding products ranging from weakly
branched to particulate silica sols [31]. Polymerization process is divided into three approximate pH domains: pH < 2, pH 2-7 and pH > 7 [20]. The pH = 7 appears as a boundary because the silica solubility and dissolution rates are maximized at or above pH = 7. The kinetics and growth mechanisms of the reaction depend on the pH value of the solution. With acidic pH, repulsive forces between particles are low and particles collide and form continuous networks leading to gels. Above pH = 7 particle growth is mainly dependent on the temperature and particles of more than 100 nm in diameter can be formed (particulate s) [25]. Above pH = 7 particles are negatively charged and they repel each other and no aggregation of particles occurs. [31].

1.4 Sol Gel Applications.

The materials formed under sol-gel technology have found numerous applications in various fields, such as the glass industry, ceramics, and thin films, different biological and chemical sensors. There are some inherent features of sol-gel materials that make them a promising tool for sensing applications [33].

1.4.1 Coating Applications.

Various materials may be coated with liquid sol-gel hydrolizate, such as (indicators, enzymes, oxides, proteins, bacteria etc ……), thus changing their characteristics [34–35], preventing corrosion [36], improving biocompatibility [37], changing sensitivity or electrical insulating properties [38]. The sol-gel coatings properties are the subject of many examinations [39–40].
1.4.2 Bioactive Sol-gel Materials.

The sol-gel technique is a versatile method for embedding and immobilizing bioactive compounds within an inorganic oxide matrix and/or the preparation of new bioactive coatings [41]. The sol-gel matrices can be transparent, inert, non-toxic, thermally stable, and forms stable coatings on such varied substrates as polymer foils, paper, tissue, metal or wood. Oily and high viscosity substances of pharmaceutical interest can also be incorporated without problems.

1.4.3 Medical and Environmental Sensors

1.4.3.1 Sol-gel Optodes for Fiberoptic Sensors.

Construction of the optode for optical biosensor requires immobilization of sensitive compounds in the host matrix. There are several methods enabling molecules entrapment. One can use gels, polymers, various meshes and membranes [42].

1.4.3.2 Biosensors.

The biosensors may be constructed from silicate sol-gels with encapsulated of enzymes and proteins. These systems can detect biologically relevant analytes like O$_2$, CO, NO, glucose and oxalate. For biorecognition of specific compounds, enzymes and metalloproteines may be used. The recognition of dissolved oxygen is possible with use of hemoglobin and myoglobin. Myoglobin can also bind CO, and sol-gel with entrapped myoglobin can be used as the sensor for CO by taking advantages of the changes in the absorption spectrum due to protein (CO interaction) [43].

1.4.3.3 Gas Sensors.

Sol-gel porous materials may be exploited for construction of gas sensors. The specially designed porous networks of SnO$_2$ nanoparticles for an
optical detection of gaseous CO was proposed [44]. The Japanese scientists tested the fiber optic carbon dioxide sensor [45], prepared by dip-coating method. The sol-gel film containing indicator dye, thymol blue, was deposited on unclad fiber and The fiber optic NO$_2$ sensors based upon dye encapsulation in the silica sol-gel [46].

1.4.3.4. Metal Sensors and pH Sensors.

Various agents sensitive to selected analytes may be immobilized in monolithic xerogel blocks. By monitoring of the characteristic color changes in the doped materials, it is possible to detect the metal cations (Fe$^{2+}$, Al$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$), the inorganic anions e.g. SO$_2$, the organic analysts (e.g. orthophenanthroline), pH changes [47].

The TEOS based sol-gel films doped with bromophenolblue and eriochrome cyanine served for measuring pH (from 3 to 8) and detection of Cu$^{2+}$ in solutions. The sol-gel entrapment of xylenol orange (XO) provided optical sensing films selective and sensitive to bismuth(III), with low leaching characteristics, fast response, and long life time [48]. Detection of heavy metals with porphyrine sol-gel sensor is possible, as well [49]. A dual-transducer approach based on sol-gel optical sensors was proposed to measure acid and salt concentrations in concentrated aqueous and HCl solutions [50,51]. Various other constructions of sol-gel based pH sensors are described [52–53].

The pH optical fiber sensor without any pH-sensitive dye was also described [54]. Porous silica layer made by the sol gel method was cladded onto optical fiber core and was exploited as the optical transducer. Acid-base properties of silica surface caused that the surface charge of silica changed with pH of the solution.
1.4.3.5 Pesticides, Herbicides, and Insecticides Sensors.

The sol gel coated infrared optical sensors enable reproducible detection of organophosphates down to the sub-ppm concentration range [55].

1.5 Sol Gel Advantages.

1- Its reaction can be controlled easily by chemical methods.

2- It allows to introduce a permanent organic groups to form inorganic – organic hybrid materials [56].

3- The process takes place at low temperature [57].

4- High porous material prepared.

5- The matrix is chemically inert and low poisoning [34].

6- It has exultant optical low intrinsic fluorescence [58].

7- The process provides good flexibility during polymerization steps [59].

8- Ability to be functionalized before or after polymerization.

9- The major advantage of sol- gel materials is in formation of thin films of extremely small layer heights in the nanometer range. These thin layers are produced by spin coating or dip coating methods [59].

1.6 Sol- gel Disadvantages.

1- Long processing time.

3- Large shrinkage during process.

3- At high pH value Si-O-Si bond is breaking [61].

1.7 Immobilization and Encapsulation.

Entrapment of cells in a gel matrix of alginates is the most popular system of immobilization [62]. The terms immobilization and encapsulation were used interchangeably in most reported literature.
While encapsulation is the process of forming a continuous coating around an inner matrix that is wholly contained within the capsule wall as a core of encapsulated material, immobilization refers to the trapping of material within or throughout a matrix. A small percentage of immobilized material may be exposed at the surface, while this is not the case for encapsulated material [63]. Microencapsulation helps to separate a core material from its environment until it is released. It protects the unstable core from its environment, thereby improving its stability, extends the core’s shelf life and provides a sustained and controlled release. The structure formed by the micro-encapsulation agent around the core substance is known as the wall. The properties of the wall system are designed to protect the core and to release it at controlled rates under specific conditions while allowing small molecules to pass in and out of the membrane. The capsules may range from submicron to several millimeters in size and can be of different shapes [64], compared to immobilization entrapment techniques.

1.8 Immobilization Techniques.

Immobilization can take place according to three main techniques: impregnation technique; chemical immobilization by covalent binding to pre-activated matrices and chemical doping.[65]. For each technique, different methods can be selected. There is no single technique displaying the best results, with different authors usually opting for thmost familiar one.

1.8.1 Impregnation Technique.

Impregnation technique can be performed by physical adsorption, chemisorption or electrostatic bonding of reagents onto the porous
support. It is carried out by exposing the porous support to a concentrated solution of the reagent and evaporates the solvent. Impregnation can be used for organic and inorganic matrices. However, the attachment of the reagent to the support is weak [58].

1.8.2 Chemical Immobilization by Covalent Binding to Pre-activated Matrices.

This immobilization technique is a direct chemical bonding of organic reagents to silica supports. This type of immobilization is highly specific and each case has its own conditions and precursors [58].

1.8.3 Chemical Doping.

This technique is more popular due to its simplicity and generality as a large variety of anions, cations, redox species and microorganisms have been successfully immobilized in silica matrices. The chemical Doping is an intermediate between the impregnation and the covalent bonding techniques and including spine coating and dip coating [63].

1.9 Immobilization Methodologies of Chemical Compounds.

There are two main types of immobilization:

1.9.1 Physical Immobilization

The physical immobilization of material on an inert matrix can be done by using different inert matrices such as starch gel, polycrylamide gel and silicon rubber [66]. The physical immobilization technique is very simple and virtually applicable to all systems in comparison to the grafting method [67]. The only problem associated with physical immobilization is the leaching of template, which is a major factor in the control of pore size.
There are two types of physical immobilization can be explained:

**A- Microencapsulation.**

It is physical phenomenon in which template molecules are entrapped by polymer chains the reactant and product can readily diffuse through the microcapsule [68].

**B- Adsorption.**

It is simple method resulting from hydrogen bonding or hydrophobic or by electrons interaction, for example protein can be adsorbed on glass or silica gel [66].

**1.9.2 Chemical immobilization.**

It is not an easy method, resulting from covalent bond for example flexible cross- linked organosilicon thin films formed by initiated chemical vapor deposition [69].

**1.10. Thin Film Technique.**

A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Electronics semiconductor devices and optical coating are the main applications benefiting from thin film construction [70].

**1.10.1 Deposition of Thin Film.**

The deposition techniques play a very important role to achieve desired film properties since the deposition of the same material by different deposition methods leads to different coating properties.

"Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometer. Deposition techniques fall into
two broad categories, depending on whether the process is primarily chemical or physical.

1.10.1.1 Chemical Deposition.

A fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer. An everyday example is the formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, deposition happens on every surface, with little regard to direction; thin films from chemical deposition techniques tend to be conformal rather than directional.

1.10.1.2 Chemical Deposition Types.

A - Chemical Solution Deposition (CSD) uses a liquid precursor, usually a solution of organometallic powders dissolved in an organic solvent. This is a relatively inexpensive, simple thin film process that is able to produce stoichiometrically accurate crystalline phases [71].

B - Chemical Vapor Deposition (CVD) generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited [71]. In the case of MOCVD (Metal-Organic Chemical Vapor Deposition), an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas.

C - Plasma Enhanced Chemical Vapor Deposition (PECVD) uses an ionized vapor, or plasma as a precursor. Unlike the soot example above, commercial PECVD relies on electromagnetic means (electric current, microwave excitation), rather than a chemical reaction, to produce a plasma [72,73].
1.10.2 Physical Deposition.

Physical deposition uses mechanical or thermodynamic means to produce a thin film of solid. An everyday example is the formation of frost. Since most engineering materials are held together by relatively high energies, and chemical reactions are not used to store these energies, commercial physical deposition systems tend to require a low-pressure vapor environment to function properly; most can be classified as:

A- Physical Vapor Deposition (PVD).

The material to be deposited is placed in an energetic, entropic environment, so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer [74]. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal [74].

1.11. Spin Coating Technique:

A process in which solution is spread evenly over a surface using centripetal force [75].

1.11.1 Spin Coating Properties [74,75].

A- Spin coating will result in a relatively uniform thin film of a specific thickness.
B- Spin coating is an important way of creating thin films in the microelectronics industry.

1.11.2 Spin Coating Process Theory.

Spin coating has been used for several decades for the application of thin films.
A typical process involves depositing a small puddle of a fluid resin onto
the center of a substrate and then spinning the substrate at high speed.
The speed of the spin coater helps us to control the thickness of the films.
The potential application of these thin films is to develop optical sensors
as they are transparent in the visible region. These sensors are employed
for detection of metal ions, monitoring of pH and in several other fields.

1.11.3 Spin coating stages [77].

Stage 1: This stage started by pouring a filtered coating solution on the
substrate. The solution should wet the surface completely during this
stage.

Stage 2: The second stage started when the substrate is accelerated up to
desired rotation speed. During this rotation spiral vortices are formed as a
result of the twisting motion caused by the inertia of the top of the fluid
layer while the substrate below rotates faster and faster.

Stage 3: In this stage the substrate is spinning at constant rate and fluid
viscous forces dominate the fluid thinning behavior.

Stage 4: The last stage occurs when the solvent evaporation dominates
the coating thinning. At this point, the coating transformed into a gel.

1.11.4 Spin Coating Advantages [78].

1. A small quantity of fluid is used for large substrates.
2. The process is very rapid.
3. It used for multilayer thin film.
4. All commercial equipment is available.
1.11.5 Spin Coating Disadvantages [78].

1. It is really good for circular substrate.
2. Requires stringent solvent properties.
3. Difficult to keep clean.
4. Large substrates are difficult to coated uniformly.

1.12 Dip Coating Method.

Dip coating is a process where a clean substrate is immersed in a liquid and then withdrawn at a given speed with control temperature and atmospheric conditions. The environmental conditions affect the quality of the coating. The dip-coating methods, which may be divided in five stages: immersion, start-up, deposition, evaporation and drainage [79]. Dip coating can also be made by lifting the substrate from the coating solution or by lowering the solutions, a process in which the substrate remains at rest and the liquid level of the solution is lowered by draining [79].

In the dip-coating method the substrate is slowly dipped into and withdrawn from a tank containing the sol, with a uniform velocity, in order to obtain a uniform coating.

1.12.1 Advantages of Dip Coating Method [78].

1- Good method to prepare thin films with high optical quality.
2- Any size and shape of sample can be coated on both sides in one step at room temperature.
3- It is a simple method.
4- Keep contamination at a minimum.
5- Not too sensitive to solvent or solutions properties.
6- Does not require vacuum.
1.12.2 Disadvantages of dip coating method [78].

1- Large amount of solutions is required.

2- It is not a good method for multilayer systems.

3- Both sides are coated which made complications if only one side needs coating.

1.13 pH Indicators.

pH indicators are frequently weak acids or bases which is used in titrations in analytical experiments to determine the extent of a chemical reaction. Because of the subjective determination of color, pH indicators are susceptible to imprecise readings. In this study two indicators will be entrapped within a spin coated thin films.

1.13.1 Bromocresol Green.

Bromocresol Green (BCG) (Scheme 2) is a dye of the tryphynylmethane family (triarylmethyl dyes). It is a yellowish gray crystalline powder which is soluble in water and alcohol [80-81]. BCG used as a pH indicator and as tracking dyes for DNA electrophoresis. It can be used in its free acid form (light brown solid), or as a sodium salt (dark green solid).
Scheme 2 (Bromocresol Green structure)

IUPAC name: 4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9\(\lambda\)6-thiabicyclo[4.3.0]nona- 1,3,5- trien-7-yl]

Molecular Formula : C\(_{21}\)H\(_{14}\)Br\(_4\)O\(_5\)S

Molecular Weight: 698.01 g mol\(^{-1}\)

In aqueous solutions both solids ionize to give the mono anionic form (yellow), that further deprotonates at higher pH to give the dianionic form (blue), which is stabilized by resonance (Scheme 3). The pKa of this reaction is 4.8 and the pH range for color change is 3.8 - 5.4 [81].

Scheme 3 (resonance form for stabilized BCG)
1.13.2 Bromcresol Purple.

Bromocresol Purple (BCP) or 5',5"-dibromo-o-cresolsulfophthalein, (Scheme 4) is a pinkish gray crystalline powder which is insoluble in water and soluble in alcohol [81]. (BCP) is a pH indicator used in medical laboratories to determination serum albumin. It is also used as an addition to acid stop baths used in photographic processing as an indicator that the bath has reached neutral pH and needs to be replaced.

![Scheme 4 (Bromocresol purple structure)](image)

**IUPAC Name:** 5,5'-Dibromo-o-cresolsulfonphthalein

**Molecular Formula:** C\textsubscript{21}H\textsubscript{16}Br\textsubscript{2}O\textsubscript{5}S

**Molecular Weight:** 540.22 g/mol

Bromocresol purple is stabilized by resonance (Scheme 5). The \( p_{ka} \) of this indicator reaction is 6.2 and pH range for color change is 5.2 - 6.8 [81].
1.14 Surfactants.

Surfactants are compounds that lower the surface tension of a liquid, allowing easier spreading, and lowering of the interfacial between two phases [82]. These molecules contain both hydrophobic and hydrophilic regions. The hydrophobic region has weak interactions with the solvent and is poorly dissolved in that solvent; conversely, the hydrophilic region has strong interactions with the solvent and prefers to dissolve in it. The hydrophobic region of a surfactant is typically composed of one or more hydrocarbon chains that are either linear or branched [83]. This portion of the surfactant has a weak interaction (in the form of dispersion forces and hydrogen bonding) with water molecules in an aqueous environment.

The hydrophilic region of a surfactant is often called a head group; head groups can be classified as cationic, anionic, nonionic, or zwitterionic. Anionic surfactants have negatively charged head groups when dissolved in water, and cationic surfactants have positively charged
head groups. The head group of nonionic surfactants possesses no charge but is polar; The nonionic surfactant head group is often based on a short polyoxyethylene chain, -(C2H4O)x-. Zwitterionic surfactants have both positively and negatively charged portions on the head group; depending on the pH of the solution, they can act as cationic, anionic, or nonionic molecules. The polar or ionic head group of a surfactant has strong interactions with water molecules, including dipole-dipole and ion-dipole interactions that cause the head group to be hydrophilic.

Surfactants and their characteristic adsorption at gas, liquid, and solid interfaces have been widely investigated. An interface is defined as a boundary between two phases; the boundary is present because of the difference in certain properties between the phases. The common types of interfaces include: gas-liquid, gas-solid, liquid-liquid, liquid-solid, and solid-solid [84]. Three types of surfactants used in this study will be discussed.

1.14.1 Sodium Dodecyl Sulfate (SDS).

Sodium dodecyl sulfate (SDS) is an anionic surfactant (Scheme 6) used in many cleaning and hygiene products. The molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphilic properties required of a detergent. [85].

![Scheme 6 (Sodium dodecyl sulfate structure)](image)

The actual structure of SDS: CₙH₂ₙ₊₁SO₄Na (n=12)
SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues. For example, it is found in higher concentrations with industrial products including engine degreasers, floor cleaners, and car wash soaps.

1.13.2 Cetyl Trimethyl Ammonium Bromide (CTAB)

CTAB is called cetrimonium bromide, \((\text{C}_{16}\text{H}_{33})\text{N}((\text{CH}_{3})_{3}\text{Br})\) is one of the components of antisepetic cetrimide (Scheme 7) [85]. CTAB is usually used as a cationic surfactant and can be used as a phase-transfer catalyst under conditions, which avoid emulsions.

\[
\text{CTAB structure}
\]

**Scheme 7 (CTAB structure)**

1.13.3 Triton X-100

Triton X-100 \((\text{C}_{14}\text{H}_{22}\text{O}((\text{C}_{2}\text{H}_{4}\text{O})_{n})\) is a non ionic surfactant which has a hydrophilic polyethylene oxide group and a hydrocarbon lipophilic or hydrophobic group [87] (Scheme 8). It is used in almost every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents.
Polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether, octyl phenol ethoxylate,

**Scheme 8 (Triton X-100 structure)**
chapter 2

experimental
2. Experimental.

2.1. Chemicals and Reagents.

All starting materials were purchased either from Merck or Aldrich as listed in Table 2.1, and used as received without further purification.

<table>
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<tr>
<th>Chemicals</th>
<th>Symbol</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetraethylorthosilicate (TEOS)</td>
<td>(C₂H₅O)₄Si</td>
<td>Aldrich</td>
</tr>
<tr>
<td>bromocresol purple (BCP)</td>
<td>C₂₁H₁₆Br₂O₅S</td>
<td>Merck</td>
</tr>
<tr>
<td>bromocresol green (BCG)</td>
<td>C₂₁H₁₄Br₄O₅S</td>
<td>Merck</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>CH₃(CH₂)₁₁OSO₃Na</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Cetyl trimethyl ammonium bromide (CTAB)</td>
<td>(C₁₆H₃₃)N(CH₃)₃Br</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Triton X-100 (TX-100)</td>
<td>(C₁₄H₂₂O(C₂H₄O)n</td>
<td>Aldrich</td>
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<tr>
<td></td>
<td>(n= 9-10)</td>
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<tr>
<td>Sodium hydroxide (NaOH)</td>
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<td>Merck</td>
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<tr>
<td>Absolute ethanol (EtOH)</td>
<td>C₂H₅OH</td>
<td>Merck</td>
</tr>
</tbody>
</table>

2.2 Synthesis of Materials.

2.2.1 Preparation of Hydrolyzed TEOS.

A mixture of 2.5 ml of absolute MeOH, 0.5 ml of 0.1M of HCl and 2.5 ml of distilled water were added to 5 ml of TEOS under stirring. The obtained solution was kept under stirring at room temperature until a homogeneous clear solution was obtained. The solution was aged at least for 24 hours before used in the coating process. The hydrolyzed TEOS solution was used as a host matrix for the indicators.
2.2.2 Preparation of Indicators.

Indicator solutions of different concentrations (0.00001M, 0.0001M, 0.001M, 0.01M and 0.05 M) of bromocresol purple (BCP) and bromocresol green (BCG) were prepared using absolute EtOH as solvent.

2.2.3 Preparation of Surfactants.

Surfactants solutions of different concentrations (0.00001M, 0.0001M, 0.001M, 0.01M and 0.05M) of Cetyl trimethyl ammonium bromide (CTAB), Sodium dodecyl sulfate (SDS) and Triton X-100 (TX-100) were prepared by using absolute ETOH as solvent.

2.3.1 Blank Solutions.

Two different blank solutions of TEOS and TEOS/surfactants were prepared by TEOS only or by mixing TEOS and surfactants (CTAB, SDS, or TX-100) using 2:1 v/v respectively.

2.3.2 Sample Solutions.

Two types of sample solutions containing an indicator with and without surfactant were prepared. The first type sample solution (surfactant free) was prepared by mixing 1ml of blank hydrolyzed TEOS solution and 1ml of bromocresol purple (BCP) or bromocresol green (BCG). The other type solution was prepared by mixing 1ml of hydrolyzed blank solution of TEOS, 0.5ml (surfactant) of CTAB or SDS or TX-100 and 1ml of bromocresol purple (BCP) or bromocresol green (BCG).
2.3.3 Preparation of Silica-immobilized Thin Films.

2.3.3.1 Substrate Cleaning.

Glass microscope slides (2.5cm * 0.8cm * 1.0mm) were activated by concentrated H₂SO₄ for 24 hours, then washed with distilled water and ethanol. The surface was finally rubbed with cleaning paper.

2.3.3.2 Spin Coating Method.

All thin films layers prepared in this work were made by spinning three drops of the solutions onto a clean glass slide. The coating process was performed using the spin coater machine at 1900 rpm spinning speed for 25 seconds period time. To obtain multilayer's of thin films a subsequent spin coating method was performed after gradually oven drying of the previous layer at 40 °C for 24 hours, then dried at 80 °C for another 48 hours.

2.3.3.3 Drying and Heat Treatment.

The wet coated film layers were dried at 40 °C for 24 hours, then dried at 80 °C for another 48 hours.

2.4 Characterization Methods.

The coated slides were placed along the wall of the sample cell and washed several times with distilled water. The washes were collected to examine leaching percentage of the film.

2.4.1 UV \ VIS Spectrophotometer.

The optical absorption of the coating solutions and the deposited thin films were obtained by using a single beam Genesys 10 UV Scanning
Spectrophotometer in the range (190 – 1100 nm) of automatically rotation. Coated slides were placed along the wall of the sample cell and exposed to different pH solutions (1 – 13.5). The pH value was measured by using (AD 1020) pH meter.

2.4.2 Polarization Light Microscopy.

The surface morphology of the films were characterized by using a Zeiss Standards – polarization microscope model BX50 equipped with an Olympus Dp-100 camera attachment.

2.4.3 Film Thickness Measurement.

The thickness of the coated thin film was measured using ellipsometry technique which is a well known technique for thin film characterization. Ellipsometry is a very sensitive optical technique for the study of optical properties of thin films. It is based on the measurement of the change in the light polarization state after reflection from the sample. Ellipsometry has received an increasing interest [88-91] because of several reasons: it is nondestructive technique, has an outstanding sensitivity to minute interfacial changes, can be used for in-situ measurements, can be operated at different wavelengths and under multiple angles of incidence.
2.5 ml water
0.5 mL HCl (0.1M)
2.5 mL methanol

Adding to 5 ml of TEOS drop wise

Mixing by stirring for 1 hour

Hydrolyzed TEOS
(waiting for 24 h before use)

Spin coating with 1900 rpm for 25 sec

Single layer of wet film

Drying for 24 h at 40°C followed by drying at 80°C for another 24 h

Film characterization
- measuring thickness
- UV/Vis

Indicators or surfactant can be added

Scheme 2.1: Flow Chart of Coating
chapter 3

results and
discussion for

immobilized BCP
3.1 Synthesis of Sol-gel BCP pH indicator Thin Film.

Glass slides have been coated with bromocresol purple (BCP) pH-indicator through spin coating process. The substrate was spinned at a controlled speed (1900 rpm) where the sol was spread onto the substrate.

Different factors are considered: the porosity and monolithity of the silica thin film including amount of solvent, catalyst concentration, amount of added ingredients e.g. ionic surfactants CTAB, SDS and non-ionic surfactant TX-100.

3.2 UV/Vis Spectra of free and Silica-immobilized BCP Thin Film.

The electronic spectrum of the free BCP shows two absorption bands at 433 nm and 591 nm (λ<sub>max</sub>) respectively due to π-π* and n-π* transitions. The electronic spectra for the free BCP, Silica-immobilized BCP thin film and BCP/SDS thin film at the range 300-700 nm, are given in (Fig. 3.1). The spectrum of the Silica-immobilized BCP thin film exhibits an absorption peak at 440 nm with a red shift of about 7 nm compared with the free BCP. This implies that the BCP molecules are probably physically interacted into the silica network (Scheme 3.1). The spectrum for the Silica-immobilized BCP/SDS thin film shows stronger absorption band at 435 nm, than that of the Silica-immobilized BCP thin film without surfactant (Fig. 3.1). The reason for this behavior is that the presence of SDS has modified the silica network structure and may increase its porosity and therefore increase the surface area.

Scheme 3.1 : synthesis of Silica-immobilized BCP thin film
3.3 Effect of BCP Concentration.

Different concentrations of BCP (0.00001M, 0.0001, 0.001, 0.01, 0.05 M) in presence of (0.05 M SDS) were used to investigate the effect of increasing indicator concentration on absorption capacity of the film. It is found that the absorbance increases with increasing BCP concentration and reach its maximum at 0.05 M (Fig. 3.2). This implies that, the binding sites available for the indicator increasing with increasing indicator concentration. Solution of BCP concentration higher than 0.05 M do not formed clear films and lead to cracking in the films.
3.4 Effect of Surfactants Concentration.

Different concentrations of SDS or CTAB or T-X 100 (0.00001M-0.05M) trapped with BCP (0.05M), were prepared and examined versus the absorbance at $\lambda_{\text{max}} = 430$-$435$ nm (Figs. 3.3a-c). It is found that the absorbance is in general increased with increasing concentration of surfactants, and reaches its maximum at 0.05 M for all surfactants used. The rate of increasing absorbance is dependent on the surfactant concentration. These results imply that the number of binding sites available for the surfactants increases with its concentration. Surfactant concentration that higher than 0.05 M, lead to cracking in the films.
Fig. 3.3a: Absorption spectra of Silica-immobilized BCP/SDS thin film at different concentrations of SDS and constant BCP concentration ($5 \times 10^{-2}$ M):
(a) 0.00001 M (b) 0.0001 M (c) 0.001M (d) 0.01 M (e) 0.05 M

Fig. 3.3b: Absorption spectra of Silica-immobilized BCP/CTAB thin film at different concentrations of CTAB and constant BCP concentration ($5 \times 10^{-2}$ M):
(a) 0.00001 M (b) 0.0001 M (c) 0.001M (d) 0.01 M (e) 0.05 M CTAB
Fig. 3.3c: Absorption spectra of Silica-immobilized BCP/TX-100 thin film at different concentrations of TX-100 and constant BCP concentration (5*10^{-2} M):-
(a) 0.00001 M  (b) 0.0001 M  (c) 0.001 M  (d) 0.01 M  (e) 0.05 M

3.5 Comparison Between Surfactants.

The electronic spectra of the Silica-immobilized BCP thin films in the presence of different surfactants are given in (Fig 3.4). Three different surfactants were used to examine their effect on the absorbance of BCP. Generally the absorbance has increased in the presence of surfactants. This is probably due to modification of silica structure and increasing of the porosity, and therefore increasing the host capacity of the silica network for loaded BCP. It is observed that SDS surfactant shows the most significant change were highest absorbance was observed.
Fig. 3.4: Absorption spectra of Silica- immobilized BCP thin film in presence of different surfactants: (a) Surfactant free (440nm) (b) TX-100 (432nm) (c) CTAB (430nm) (d) SDS (435 nm)

3.6 UV/ Vis Spectra of BCP versus pH.

3.6.1 Spectrum of Free BCP versus pH.

The UV/ Vis absorption spectrum of free BCP ($5 \times 10^{-5}$) treated with different pH solutions (pH=1-14) is shown in Fig 3.5. Two absorption bands at 433 and 590 nm were clearly observed, the bands are correspond to, acidic (yellow), neutral and basic (purple) colors respectively (Scheme 3.2). when pH is increasing in the range of pH 1-5.5 (acidic medium) only one absorption band occurs at 433 nm without significant changes of absorbance. At pH $>$ 5.5 the absorption band at 433nm was decreased and a new absorption band at 590 nm was developed, with the presence of an isosbestic point at 490 nm. This is probably corresponds to a change from the neutral HIn to the basic form In$^-$.  

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3.6.1.1 The pKa Values of Free BCP.

BCP is a weak acid and stabilizes by resonance form (Scheme 3.2).

Scheme 3.2: two resonance form for BCP In

The pKa value of free BCP was calculated from the relationship between absorbance and pH, and was found 6.21 (Fig 3.6). This value was consistent with reported values [92].
3.6.2 UV/Vis Spectra of Silica-immobilized BCP Thin Film versus pH

When BCP thin film was treated with different pH solutions, the film suffered from significant leaching of dye, this may be refer to very weak interaction between BCP and silica network. Different surfactants (SDS, CTAB and TX–100) were added to obtain stable BCP thin films.

3.6.2.1 UV/Vis Spectra of Silica-immobilized BCP/SDS Thin Film versus pH.

There are three absorption bands for the immobilized BCP/SDS thin films at 435 (neutral), 535 (acidic) and 595 nm (basic) were observed when the immobilized BCP/SDS thin films were treated with different pH solutions (pH 1-13.5) correspond to neutral form, acidic form and basic form respectively (Schem 3.3). Two indicating transitions were clearly observed as shown in Fig. 3.7 with the presence of two coincided isosbestic points at 493 nm. The first transition is probably due

Fig 3.6: pka value of free BCP.
to equilibrium between acidic form (red color) and neutral form (yellow color). The second transition was probably due to the equilibrium between the neutral form (yellow color) and basic form (purple color) form. There were, two absorption bands were observed (535 and 435 nm) at pH 1-4.5 as shown in (Fig 3.8). It is obvious that the peak at 535 nm corresponds to the acidic form (pH 1-4.5) which was decreased significantly as the pH increased of the whereas the peak at 435 nm of the neutral form was increased. When the pH increases > 10.5, the absorbance of the peak at 435 nm was decreased and a new absorption at 595 nm was developed and reach its maximum at pH 13.5 (Fig. 3.10). The spectra of the immobilized BCP thin film have a new peak appeared at 535 nm at pH 1-4.5 (acidic medium) which is not found in case of free BCP in solution (Scheme 3.4).

Scheme 3.3: Three resonance form expected for Silica-immobilized BCP/SDS thin film (neutral, basic and acidic medium).
Scheme 3.4: expected forms for the Silica-immobilized BCP/SDS thin film in (neutral, acidic, and basic)

Fig. 3.7: Absorption spectra of Silica-immobilized BCP/SDS thin film at different pH values (1-13.5).
Fig. 3.8: Absorption spectra of Silica-immobilized BCP/SDS thin film at pH 1-4.5.

Fig. 3.10: Absorption spectra of Silica-immobilized BCP/SDS thin film at pH 10-13.
3.6.2.1 pKa Values of Silica-immobilized BCP/SDS Thin Film with PH (1-13.5).

The pKa$_1$ and pka$_2$ values for the BCP/SDS thin film were calculated from the relationship between absorbance versus pH (1-13.5). These values were found; 2.75 and 9.85 respectively as shown in Fig 3.11a&b. pKa1 for the immobilized BCP/SDS thin film was found 2.75 at acidic medium (Fig. 3.11a). This can be explained, that in acidic medium, there were perhaps electrostatic forces between protonated HBCP$^+$ and anionic SDS surfactant as shown in Scheme 3.4. The increases of pKa$_2$ value from 6.21 for the free BCP to 9.85 for the BCP/SDS thin film (Fig. 3.11b) is probably that in basic medium, deprotonation of the silanols and ($\equiv$S$-$O$^-$) species was formed and (BCP$^-$) anion is more favorable as shown in Scheme 3.4. In neutral medium it is expected that a hydrogen bonding species ($\equiv$Si-OH$\cdots$BCP) is probably formed as shown in Scheme 3.4.

Fig.3. 11a: pka$_1$ value of Silica-immobilized BCP/SDS thin film at pH (1-6).
Fig. 3. 11b: pka₂ value of Silica-immobilized BCP/SDS thin film at pH (8-13).

3.6.3 Spectra of Silica-immobilized BCP/CTAB Thin Film versus pH.

The absorption spectra of the immobilized BCP/CTAB thin film treated with different pH solutions (pH = 1-13.5) is shown in Fig 3.12. Two absorption bands were clearly observed due to, neutral and acidic form (yellow color), and basic form (purple color) which occurs at 430 and 595 nm respectively. Only one transition was observed (from neutral form to basic form) upon pH change from 1 to 13.5, with the presence of an isosbestic point at 495 nm. At pH range 1-8, a strong specific band occurs at 430 nm without significant changes of absorbance. at pH >8, the absorption band at 430 nm is decreased and a new peak was developed at 595 nm. This corresponds to a change from the neutral form to the basic form as shown in Scheme 3.5. The intensity of the peak at 595 nm is increased with an increasing pH of the solutions.
Scheme 3.5: two forms expected for the Silica-immobilized BCP/CTAB thin film in (neutral, acidic and basic)

3.6.3.1 pKa Values of Silica-immobilized BCP/CTAB Thin Film.

pKa value of the immobilized BCP/CTAB thin film was calculated from the relationship between absorbance versus pH as shown in Fig 3.13. This value was 6.9 which is higher than that of the free BCP (pKa=6.21) due to the electrostatic force between (BCP⁻) and cationic (CTAB) which favors the anionic hydrophilic species of BCP as given in Scheme 3.5.

Fig. 3.12: Absorption spectra of Silica-immobilized BCP/CTAB thin film at different pH values (1-13.5).
3.6.4 UV/Vis Spectra of Silica-immobilized BCP/ TX-100 Thin Film versus pH.

The absorption spectra of the immobilized BCP/TX-100 thin film treated with different pH solutions (pH=1-13.5) is shown in Fig 3.14. Two absorption bands were clearly observed at 432 and 593 nm due to, neutral and acidic form (yellow color), and basic form (purple color) respectively. An indicating transition was observed (from neutral form to basic form) upon treatment of pH from 1 to 13.5, with the presence of an isosbestic point at 492 nm. At pH 1-7 a strong specific band occurs at 432 nm without significant changes of absorbance. At pH > 7, the absorption band at 432 nm is start to decrease its intensity and a new band was developed at 593 nm and reached its maximum at pH 13.5 (Fig.3.14). This corresponds to a change from the neutral form to the basic form as shown in Scheme 3.7.
Fig. 3.14: Absorption spectra of Silica-immobilized BCP/CTAB thin film at different pH values.

Schem 3.6: Two forms expected for the Silica-immobilized BCP/TX-100 thin film in (neutral, acidic, and basic)

3.6.4.1 pKa values of Silica-immobilized BCP/TX-100 Thin Film.

The pKa value of the immobilized BCP/TX-100 was calculated from the relationship between absorbance versus pH as shown in Fig. 3.15. This value was 5.19 which is lower than that of the free BCP
(pKa=6.21) due to the weak electrostatic force between BCP and neutral TX-100 as given in Scheme 3.5.

![Graph showing pH vs. pKa](image)

**Fig. 3.15: pKa value of Silica-immobilized BCP/TX-100 thin film at pH (1-13.5)**

### 3.7 Effect of Temperature:

The immobilized BCP/SDS thin films have been dried at different temperatures (25-90 °C). It was found that highest absorption occurred for samples dried at 80 °C (Fig 3.16). This can be explained that, most of the physically absorbed water and alcohol molecules were evaporated from the pores of silica matrix when the films dried at 80 °C. This allows BCP to accommodate well within the silica pores and strongly interacted within the silica matrix. At temperatures higher than 80 °C the absorption decreases this can be due to cracking of the film.
3.8 Leaching study for immobilized BCP thin films

It is found that the lowest leaching of BCP molecules from the immobilized BCP thin films was observed when SDS surfactant was used (Fig 3.17) and dried at 80 °C (Table 3.1). This is because of the strong electrostatic force between the BCP molecules and the anionic SDS surfactant. It was found that the leaching percentage of BCP from the silica matrix thin film arranged in the following order (Table 3.1):

SDS < CTAB < TX-100 < Free of surfactant
Table 3.1: Effect of surfactant type on % Leaching of BCP at pH 7.

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>% Leaching of BCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCP Thin Film</td>
<td>36.60%</td>
</tr>
<tr>
<td>BCP/TX -100 Thin Film</td>
<td>17.30%</td>
</tr>
<tr>
<td>BCP/CTAB Thin Film</td>
<td>12.20%</td>
</tr>
<tr>
<td>BCP/SDS Thin Film</td>
<td>2.10%</td>
</tr>
</tbody>
</table>

Fig 3.17: leaching measurements of BCP at pH 7 for (a) immobilized of BCP/SDS thin film (b) immobilized of BCP/CTAB thin film (c) immobilized of BCP/TX-100 thin film (d) immobilized of BCP thin film.

The effect of temperature on leaching of BCP molecules from immobilized BCP/SDS thin films was studied and the results are given in Fig. 3.18. It is shown that as temperature increases, the amount of BCP decreases up to 80 °C after this temperature the thin film become less stable and so BCP molecules leached out.
Figure 3.18: Effect of temperature on leaching of immobilized BCP/SDS thin films at pH 7:- (d) 90°C, (a) 80°C, (b) 70°C, (c) 60°C, (e) 40°C, (f) 25°C.

3.9 Reversibility of the Silica-immobilized BCP/SDS Thin film:

The immobilized BCP/SDS thin films were act as reversible sensors for pH changes forward and backward. The spectra were obtained at pH 1-13 in the range from 300 nm to 700 nm, with response time of 20 minutes for both forward and reverse paths (Fig 3.19 a,b).

Fig. 19a: Forward electronic spectra of Silica-immobilized BCP/SDS thin film at pH 1-13.
3.10 Repeatability of Silica-immobilized BCP/SDS Thin Film Sensor:

Ten cycles measurements using immobilized BCP/SDS thin film were conducted. The cycles were repeated within 24 hours to check the repeating stability. It is found that the absorbance after each measurement remains almost unchanged over the pH range 1-13. Absorbance measurement was performed at 435 nm (pH 1-10) and at 595 nm (pH 11-13). Figure 3.20 shows the absorbance versus number of measurements at pH 7. The absorbance is nearly constant. The standard deviation and % relative standard deviations of 10 repeated measurements at pH 7 within 24 hours are 0.002 and 0.36 respectively. Similar results were observed for repeating measurements at pH range 1-13. The standard deviation and percentage relative standard deviation ranges for ten measurements were zero - 0.036 and zero -5.45 respectively (Table 3.2). This provide an evidence that the immobilized BCP/SDS thin film can be used as a good sensor without degradation during repeated measurements at pH range (1-13)
Table 3.2: Repeatability of Silica-immobilized BCP/SDS Thin film.

<table>
<thead>
<tr>
<th>pH</th>
<th>Number of measurements</th>
<th>SD</th>
<th>%RSD</th>
</tr>
</thead>
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<tr>
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<td>10</td>
<td>0.0055</td>
<td>1.37</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.0150</td>
<td>3.33</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
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<td>3.78</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.0140</td>
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</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.0080</td>
<td>1.34</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>0.0020</td>
<td>0.36</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.0110</td>
<td>2.09</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0.0017</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.0054</td>
<td>1.12</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>0.0012</td>
<td>0.19</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>0.0270</td>
<td>4.46</td>
</tr>
</tbody>
</table>

Fig. 3.20: Electronic spectra of Silica-immobilized BCP/SDS for ten measurements at pH 7.
3.11 Reproducibility of the Silica-immobilized BCP/ SDS Thin Film Sensor.

Seven independent preparations of the immobilized BCP/SDS thin film were performed using the same method of preparation and tested. Figure 3.21 shows the absorbance of 7 different prepared films at 435 nm in water (pH 6.5). Results given in Fig 3.21 showed good agreement for all the prepared thin films.

![Fig3. 21: Electronic spectra of seven different Silica-immobilized BCP/SDS thin films at pH 7.](image)

3.11 Response Time.

The relation between absorbance and time for immobilized BCP/SDS thin film at $\lambda_{\text{max}} = 435$ nm is given in Figure 3.22. It is observed that the thin film is highly sensitive to color change. This explained by the availability of BCP molecules for the active pH ingredients and immobilization of BCP within the porous silica matrix in presence of surfactant molecules does not diminish the activity of BCP molecules.
3.12 Effect of Interferences and Life time on Thin Film Stability.

The immobilized BCP/SDS thin film was immersed in different solutions of 1M concentration including: hydrochloric acid, acetic acid, ammonium hydroxide, sodium carbonate, potassium chloride and sodium hydroxide, then washed with water and neutralized at pH 7 (Fig. 3.23.) The UV/Vis spectra showed that the film is stable for measurement in different types of solutions.

Fig. 3.22: Relation between absorbance of Silica-immobilized BCP/SDS Thin film and time.

Fig. 3.23: Electronic spectra of Silica-immobilized BCP/SDS thin film at pH 7 after immersed in 1M of different aqueous solutions: (a) 1 M KCL (b) 1M HCl (c) 1 M CH₃COOH (d) 1 M Na₂CO₃ (e) 1 M NH₄OH (f) 1 M NaOH
The lifetime of immobilized BCP/SDS thin film was also studied at six months time period. Almost no leaching or change in response was shown for these films (Fig. 3.24). So these films are considered to be very stable at different conditions include interference ions or long time periods (Table 3.3).

Fig. 3.24: Spectra of Silica-immobilized BCP /SDS for six months time period measured at pH.

Table 3.3 : The lifetime of immobilized BCP/SDS thin film at six months

<table>
<thead>
<tr>
<th>No. of Weeks</th>
<th>Abs (435nm)</th>
<th>Number of Weeks</th>
<th>Abs (435nm)</th>
<th>Number of Weeks</th>
<th>Abs (435nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5781</td>
<td>9</td>
<td>0.5777</td>
<td>17</td>
<td>0.5776</td>
</tr>
<tr>
<td>2</td>
<td>0.5781</td>
<td>10</td>
<td>0.5777</td>
<td>18</td>
<td>0.5775</td>
</tr>
<tr>
<td>3</td>
<td>0.5781</td>
<td>11</td>
<td>0.5777</td>
<td>19</td>
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</tr>
<tr>
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<td>12</td>
<td>0.5777</td>
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</tr>
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<td>13</td>
<td>0.5777</td>
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<td>0.5775</td>
</tr>
<tr>
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<td>14</td>
<td>0.5776</td>
<td>22</td>
<td>0.5775</td>
</tr>
<tr>
<td>7</td>
<td>0.5778</td>
<td>15</td>
<td>0.5776</td>
<td>23</td>
<td>0.5775</td>
</tr>
<tr>
<td>8</td>
<td>0.5778</td>
<td>16</td>
<td>0.5776</td>
<td>24</td>
<td>0.5775</td>
</tr>
</tbody>
</table>
3.13 Effect of Multilayer Thin Film Coating.

Coating of the glass slides with multilayer of silica immobilized with BCP/SDS at the same conditions was performed (Fig 3.25). It is obvious that the absorbance of the immobilized BCP/SDS thin film increases as the number of layers increase. The percentages of signal increment were 34.3% and 67.7% for double and triple layers compared with single layer.

![Electronic spectra of multilayer Silica-immobilized BCP/SDS thin film measured at pH 7: (a) single layer thin film. (b) double layer thin film. (c) Triple layer thin film.](image)

**Fig 3.25**: Electronic spectra of multilayer Silica-immobilized BCP/SDS thin film measured at pH 7: (a) single layer thin film. (b) double layer thin film. (c) Triple layer thin film.

3.14 Effect of Multilayer Thin Film on BCP Leaching.

After washing the thin films with distilled water. It is found that single layer of immobilized BCP/SDS thin film showed lower leaching than both double and triple layers (Fig.3.26). The leaching percentages were; 2.1%, 5.6% and 13.4% for single, double and triple layer, respectively. The order of leaching is arranged as follows: Single layer < Double layer < Triple layer.
Fig. 3.26: Electronic spectra of leached BCP from multilayer of immobilized BCP/SDS thin films: (a) single layer leaching. (b) double layer leaching. (c) Triple layer leaching.

3.15 Film Thickness Measurement.

The thickness of the single layer thin film was measured using ellipsometry technique which is a well known technique in thin film characterization. Ellipsometry is a very sensitive optical technique for the study of optical properties of thin films. It is based on the measurement of the change in the light polarization state after reflection from a sample [88-91]. Figure 3.27 shows the measured ellipsometric parameters \( \psi \) and \( \Delta \) as a function of the wavelength in the range 300 nm – 750 nm. TF Companion version 3.4, Thin films measurement and data analysis software, (Semicon Soft) was used to invert the ellipsometric parameters and to calculate the film thickness. The thickness of immobilized BCP/SDS single layer thin film is found to be about 140 nm ± 10 nm.
Fig 3.27: Measured ellipsometric parameters $\psi$ and $\Delta$ as a function of the wavelength in the range 300 nm – 750 nm.
3.16. Polarized Light Microscopy

Several photographs for thin films of free silica, immobilized BCP and immobilized BCP/SDS in order to examine the nature of interaction between BCP, silica and surfactants. Photograph 3.28a and 3.28b involve the free silica and immobilized BCP respectively. From these photographs, it is clear that the particle size distribution is wider in the free silica, while in presence of BCP, the modified particles become more uniform and smaller in size. In the presence of SDS surfactant from the photograph of immobilized BCP/SDS, it is shown that there is an increase in the number of particles than the free immobilized BCP. Also, the size of the particles becomes smaller and more uniform. This behavior is due to the interaction of surfactant with BCP molecules through electrostatic interaction. This was supported by the increase of absorption intensities of the band at 435 nm (Fig. 3.2) as the hydrophobic part of surfactant participate in the acceleration of the association of the particles which lead to increase its stability.

Fig. 3.28a: PLM photograph of the sol–gel silica free thin film.
Fig 3.28 b: PLM photograph of Silica-immobilized BCP thin film.

Fig. 3.28c: PLM photograph of the Silica-immobilized BCP/SDS thin film.
3.17 Conclusion.

The immobilized BCP thin films (single, double and triple) were prepared by deposited thin films with sol containing hydrolyzed TEOS and BCP in the presence of SDS, CTAB, and TX-100 surfactants onto a substrate. The immobilized BCP/SDS thin films were dried at 80 °C which show the least leaching. The best film of BCP was prepared in the presence of SDS surfactant which probably attributed to strong interaction between SDS and BCP indicator. Three color changes; red color (acidic form), yellow color (neutral form) and purple color (basic form) was observed in case of immobilized BCP/SDS corresponding to three different forms of the immobilized BCP/SDS sensor. In the presence CTAB or TX-100 two color changes; yellow color (neutral and acidic form) and purple color (basic form) were observed. The immobilized sensors showed high reproducibility, sensing, repeatability, reversibility and aging stability. The pKa of the immobilized BCP was calculated, which showed a significant shift compared with the free BCP in aqueous solution. PLM studies showed a uniform distribution of particles with a significant modification of size particles for the immobilized BCP in presence of surfactants comparing with the free immobilized BCP.
Chapter 4

Results and discussion for immobilized BCG
4.1 Synthesis of Silica-immobilized BCG Thin Film.

The glass slides have been coated with bromocresol green (BCG) through spin coating process. The substrate was spinned at a controlled speed at (1900 rpm) were the sol spread onto the substrate. Different factors are considered: the porosity and monolithity of the silica thin film including amount of solvent, catalyst concentration, amount of added ingredients e.g. ionic surfactants CTAB, SDS and non-ionic surfactant TX-100.

4.2 UV/Vis Spectra of the Free and Silica-immobilized BCG Thin Film.

The electronic spectrum of the free BCG shows two absorption bands at 444 nm and 616 nm (λ max) due to π- π* and n -π* transitions. The electronic spectra for the free BCG, immobilized BCG thin film and immobilized BCG /SDS thin film at the range 300-700 nm, are given in Fig. 4.1. The spectrum of the immobilized BCG exhibits an absorption peak at 441 nm which is slightly different than that of solution counterpart which occurs at 445 nm. The shift of about 4 nm of the BCG thin film compared with the free BCG implies that the BCG molecules are physically interacted into the silica network (schem4.1). The spectrum for immobilized BCG/SDS thin film shows stronger absorption band at 446 nm, than that of the immobilized BCG thin film without surfactant (Fig 4.1). The reason for this behavior is that the presence of SDS has modified the silica network structure and may increase its porosity and therefore increase the surface area.

Scheme 4.1: synthesis of Silica-immobilized BCG thin film
Fig. 4.1: Absorption spectra of: (a) Silica-immobilized BCG thin film   (b) Silica-immobilized BCG /SDS thin film  (c) free BCG

4.3 Dependence of BCG Concentration.

Different concentrations of BCG (0.00001M, 0.0001, 0.001, 0.01, 0.05 M) in presence of (SDS 0.05 M) were used to investigate the effect of increasing concentration of BCG indicator on absorption capacity of the films. It is found that the absorbance increases with increasing concentration of added BCG and reach its maximum at 0.05 M (Fig. 3.2). This implies that, the binding site for indicator increases with increasing indicator concentration.
Fig. 4.2: Absorption spectra of Silica-immobilized BCG/SDS thin film at different concentrations of BCG and constant concentration SDS (5*10^{-2} M):-(a) 0.00001 M. (b) 0.001 (c) 0.001 M (d) 0.01 M (e) 0.05 M.

4.4 Effect of Surfactants Concentration.

Different concentrations of surfactant (SDS, CTAB or T-X 100) (0.00001M- 0.05M) for the immobilized (0.05M BCG ), were prepared and examined versus the absorbance at $\lambda_{\text{max}}$= 438-446 nm (Figs. 4.3a-c). It is found that the absorbance is in general increased with increasing concentration of surfactant involved and reaches its maximum at 0.05 M for all surfactants used. The rate of increasing absorbance is dependent on the type of surfactant used. These results imply that the number of binding sites available for the surfactant increases with concentration. Surfactant concentration that higher than 0.05 M, lead to cracking in the films.
Fig. 4.3a: Absorption spectra of Silica-immobilized BCG/SDS thin film at different concentrations of SDS and BCG ($5 \times 10^{-2}$ M):- (a) 0.00001 M (b) 0.0001 M (c) 0.001 M (d) 0.01 M (e) 0.05 M

Fig. 4.3b: Absorption spectra of Silica-immobilized BCG/CTAB thin film at different concentrations of CTAB and BCG ($5 \times 10^{-2}$ M):- (a) 0.00001 M (b) 0.0001 M (c) 0.001 M (d) 0.01 M (e) 0.05 M
Fig. 4.3c: Absorption spectra of Silica-immobilized BCG/TX-100 thin film at different concentrations of TX-100 and BCG (5*10^-2 M):- (a) 0.00001 M (b) 0.0001 M (c) 0.001 M (d) 0.01 M (e) 0.05 M

4.5 Nature of Surfactants.

The electronic spectra of the immobilized BCG thin films in the presence of different surfactants are given in (Fig 4.4). Three different surfactants were used to examine their effect on the absorbance of BCG. Generally, the absorbance has increased in the presence of surfactants. This is probably due to modification of silica structure and increasing of the porosity, and therefore increasing the host capacity of the silica network for loaded BCG. It is observed that SDS surfactant have the most significant change were highest absorbance was observed.
Fig. 4.4: Absorption spectra of Silica-immobilized BCP thin film in presence of different surfactant: (a) surfactant free (445nm) (b) CTAB(438nm) (c) TX-100(445nm) (d) SDS(446 nm).

4.6 UV/Vis Spectra.

4.6.1 UV/Vis Spectra of free BCG versus pH.

The UV-Vis absorption spectrum of free BCG (3.2*10^{-5}M) treated with different pH solutions (pH=1-13) is shown in Fig.4.5. Two absorption bands at 444 and 616 nm were clearly observed. These bands correspond to acidic form (yellow color), and basic form (blue color) respectively (Scheme 4.2). When the pH is increased in the range of (pH 1-4.5) (acidic medium) only one absorption band occurs at 444 nm without significant changes of absorbance. At pH > 4.5 as the acidity of the solution decreases the absorption band at 444 nm was diminished and a new absorption band at 616 nm was developed with the presence of an isosbestic point at 512 nm. This is probably corresponds to a change from the acidic form HIn^+ to the basic form In^- of BCG.
4.6.1.1 pKa Value of Free BCG.

BCG is a weak acid and stabilizes by resonance form (Scheme 4.2)

The pKa value of free BCG was calculated from the relationship between absorbance and pH which found 4.7 (Fig 4.6). This value was consistent with reported values [93].
4.6.2 UV/Vis Spectra of Silica- immobilized BCG thin film versus pH.

When BCG thin film was treated with different pH solutions, the film suffered from significant leaching of dye, this may be refer to very weak interaction between BCG molecules and silica network. Different surfactants (SDS, CTAB and TX – 100) were added to obtain stable BCG thin films.

4.6.3 UV/Vis Spectra of Silica- immobilized BCG/SDS Thin Film versus pH.

The absorption spectra of the immobilized BCG/SDS thin film treated with different pH solutions (pH=1-13) are shown in Fig 4.7. Two absorption bands were clearly observed due to equilibrium between acidic form (yellow color) and basic form (blue color), which occurs at 446 and 614 nm respectively. Only one transition was observed (from acidic form to basic form) upon pH changes from 1 to 12.5 with the presence of an isosbestic point at 509 nm. At pH range 1-6.5, a strong
specific band was occurs at 446 nm. At pH >7 the absorbance of the peak at 446 nm is decreased and a new peak was developed at 614 nm. This corresponds to a change from the acidic form (HBCG⁺) to the basic form (BCG⁻) as shown in Scheme 4.3. The intensity of the peak at 614 nm is increased with an increasing pH of the solutions.

Fig. 4.7: Absorption spectra of Silica-immobilized BCG/SDS thin film at different pH values (1-12.5).

Figure 4.9 immobilized BCG/SDS with pH (1-12.5) 4.6.3.1 pKa Value of Silica-immobilized BCG/SDS Thin Film.

The pKa value of the immobilized BCG/SDS thin film was calculated from the relationship between absorbance versus pH as shown in Fig 4.8. This value was 4.17 which is lower than that of the free BCG (pKa=4.7) due to the electrostatic force between (BCG⁺) and anionic SDS which favors the cationic hydrophilic species of BCG as given in Scheme 4.3.
Scheme 4.3: expected forms for the Silica-immobilized BCG/SDS thin film in acidic, and basic medium.

Fig. 4.8: pKa value of Silica-immobilized BCG/SDS thin film.

pKa = 4.17

Abs

0.32
0.34
0.36
0.38
0.40
0.42
0.44
0.46

1 2 3 4 5 6 7

Fig. 4.8: pKa value of Silica-immobilized BCG/SDS thin film.
4.6.4 UV/Vis Spectra of Silica- immobilized BCG /CTAB Thin Film versus pH.

The absorption spectra of the immobilized BCG/CTAB thin film treated with different pH solutions (pH=1-12.5) are shown in Fig 4.9. Two absorption bands were clearly observed due to, acidic form (yellow color), and basic form (blue color) which occurs at 438 and 619 nm respectively. Only one transition was observed (from acidic form to basic form) upon pH change from 1 to 12.5, With the presence of an isosbestic point 515 nm, due to the acid base equilibrium of the two forms of BCG. At pH range 1-6, a strong specific band occurs at 438 nm without significant changes of absorbance. At pH > 6, the absorbance of the peak at 438 nm is decreased and a new peak was developed at 619 nm. This corresponds to a change from the acidic form to the basic form.

![Absorption spectra of Silica-immobilized BCG/CTAB thin film at different pH values (1-12.5).](image)

Fig. 4.9: Absorption spectra of Silica-immobilized BCG/CTAB thin film at different pH values (1-12.5).
4.6.4.1 pKa value of Silica- immobilized BCG/CTAB Thin Film.

The pKa value of immobilized BCG/CTAB thin film was calculated from the relationship between absorbance versus pH as shown in Fig 4.8. This value was 5.94 which is higher than that of the free BCG (pKa=4.7) due to the electrostatic force between (BCG\textsuperscript{+}) and cationic CTAB as given in Scheme 4.4.

Scheme 4.4 expected forms for the Silica- immobilized BCG/SDS thin film in acidic, and basic medium.

![Scheme 4.4 expected forms](image)

Fig. 4.10: pKa value of BCG/CTAB thin film at pH (1-6) 4.6.5 UV/Vis Spectra of Silica- immobilized BCG/TX-100 thin film versus pH.
The absorption spectra of the immobilized BCG/ TX-100 thin film treated with different pH solutions (pH=1-12.5) are shown in Fig 4.9. Two absorption bands were clearly observed due to, acidic form (yellow color ), and basic form (blue color ) which occurs at 445 and 620 nm respectively. Only one transition was observed (from acidic form to basic form) upon pH change from 1to12.5, with the presence of an isosbestic point 510 nm, due to the acid base equilibrium of the two forms of BCG. At pH range 1-6, a strong specific band occurs at 445 nm without significant changes of absorbance. At pH > 6, the absorbance of the peak at 445 nm is decreased and a new peak was developed at 620 nm. This corresponds to a change from the acidic form to the basic form as shown in Scheme 4.5.

Fig. 4.11: Absorption spectra of Silica- immobilized BCG/TX-100 thin film at different pH values (1-12.5).
4.6.5.1 pKa Value of Silica- immobilized BCG/TX-100 Thin Film.

The pKa value of the immobilized BCG/ TX-100 thin film was calculated from the relationship between absorbance versus pH as shown in Fig 4.8. This value was 4.62 which is near than that of the free BCG (pKa=4.12).

Scheme 4.5: expected forms for the Silica- immobilized BCG/SDS thin film in acidic, and basic medium.

Fig. 4.12: pKa value of Silica- immobilized BCG/TX-100 thin film at pH (1-6).
4.7 Effect of Temperature.

The immobilized BCG /SDS thin films have been dried at different temperatures (25-90 °C). It was found that the highest absorption occurred for samples dried at 80 °C (Fig 4.13). This can be explained that, most of the physically absorbed water and alcohol molecules were evaporated from the pores of silica matrix when the films dried at 80 °C. This allows BCG to be accommodated well within the silica pores and strongly interacted within the silica matrix. At temperatures higher than 80 °C the absorption decreases this can be due to decomposition of SDS surfactant and so the thin film started cracking.

![Chart: Fig 4.13: Effect of temperature on immobilized BCG/SDS thin film:- (a) 25 °C (b) 40 °C (c) 60 °C (d) 70 °C (e) 80 °C (f) 90 °C.]

4.8 Leaching study of Silica-immobilized BCG thin films.

It is found that lowest leaching of BCG molecules from thin films was observed when SDS surfactant was used (Fig. 4.14) and dried these films at 80 °C ( Table 4.1). The reason for this is that in case of SDS a strong interaction between the BCG molecules and the anionic SDS surfactant takes place. It was found that the leaching percentage of BCG from thin film silica matrix arranged in the following order (table 4.1):

SDS < <TX-100 < CTAB < Free of surfactant
Table 4.1: Effect of surfactant type on % leaching of BCG at pH 7.

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>% Leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immobilized BCG</td>
<td>36.70%</td>
</tr>
<tr>
<td>Immobilized BCG/CTAB</td>
<td>22.50%</td>
</tr>
<tr>
<td>Immobilized BCG/TX -100</td>
<td>14.40%</td>
</tr>
<tr>
<td>immobilized BCG/SDS</td>
<td>8.65%</td>
</tr>
</tbody>
</table>

Fig. 4.14: measurements leaching of BCG at pH 6 for :
- (a) immobilized BCG/SDS thin film
- (b) immobilized BCG/TX-100 thin film
- (c) immobilized BCG/CTAB thin film
- (d) immobilized BCG thin film

The effect of temperature on leaching of BCG molecules from immobilized BCG/SDS thin films was studied and results are given in (Fig. 4.15). It is shown that as temperature increases, the amount of BCG decreases up to 80 °C after this temperature the thin film become less stable and so BCG molecules leached out.
Fig. 4.15: Effect of temperature on leaching of immobilized BCG/SDS thin film at pH 6:-(a) 80°C (b) 70°C (c) 90°C (d) 60°C (e) 40°C (f) 25°C.

4.9 Reversibility of the BCG Thin Film Sensor.

The immobilized BCG/SDS thin film were act as reversible sensors for pH changes as forward and backward activities. The spectra were obtained at pH 1-12.5 in the range from 300 nm to 700 nm, with response time of 20 minutes for both forward and reverse paths (Fig. 4.16 a, b)

Fig. 4.16a: Forward electronic spectra of immobilized BCG/SDS thin film at pH 1-12.5.
Fig. 4.16 b: Backward electronic spectra of immobilized BCP/SDS thin film at pH 1-12.5.

4.10 Repeatability of Silica- immobilized BCG /SDS Thin Film .

Repeatability of BCS sensor was studied by conducting ten cycles measurement using immobilized BCG/SDS thin film. The cycles were repeated within 24 hours to check stability of the BCG pH sensor on repeating measurements. It is found that the absorbance after each measurement remains almost unchanged over the pH range 1-12. Absorbance of the repeatability measurements was performed at 446 nm (pH 1-7) and at 614 nm (pH 8-12). Figure 4.17 shows the absorbance of 10 measurements at pH 7. The absorbance is nearly constant. The standard deviation and % relative standard deviations of the ten repeated measurements at pH 7 within 24 hours were 0.0006 and 0.17 respectively. Similar results were observed for repeating measurements at pH range 1-12. The standard deviation and percentage relative standard deviation ranges for ten repeated measurements for different pH values were zero - 0.07 and zero - 8.2 respectively (Table 4.2). This promises that immobilized BCG/SDS thin films can be used as a good pH sensor without degradation during repeated measurements at pH range 1-12.
Table 4.2: Repeatability of Silica-immobilized BCG thin film sensor

<table>
<thead>
<tr>
<th>pH</th>
<th>Number of measurements</th>
<th>SD</th>
<th>%RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.0012</td>
<td>0.33</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.0017</td>
<td>0.47</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.0005</td>
<td>0.13</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.0004</td>
<td>0.11</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.00052</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>0.0006</td>
<td>0.17</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.0009</td>
<td>0.25</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0.0025</td>
<td>0.76</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.0094</td>
<td>1.8</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>0.04</td>
<td>7.4</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>0.07</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Figure 4.17: Electronic spectra of Silica-immobilized BCG/SDS for ten measurements at pH 7.
4.11 Reproducibility of the Silica-immobilized BCG/SDS Thin Film.

Seven independent preparations of immobilized BCG/SDS thin films were performed using the same method of preparation and tested. Figure 4.18 shows the absorbance of 7 different prepared films at 435 nm in water (pH 6.5). Results given in Fig 3.18 showed good agreement for all the prepared thin films.

![Figure 4.18: Electronic spectra of seven different Silica-immobilized BCG/SDS thin films at pH 6.5.](image)

4.12 Response Time.

The relation between absorbance and time for immobilized BCG/SDS thin film at $\lambda_{\text{max}} = 446$ nm is given in Figure 4.19. It is observed that the thin film is highly sensitive to color change. This explained by the availability of BCG molecules for the active pH ingredients and immobilization of BCG within the porous silica matrix in presence of surfactant molecules does not diminish the activity of BCG molecules.
4.13: Effect of Interferences and Life Time on Thin Film Stability.

The immobilized BCG/SDS thin film was immersed in different solutions of 1M concentration including: hydrochloric acid, acetic acid, ammonium hydroxide, sodium carbonate, potassium chloride and sodium hydroxide, then washed with water and neutralized at pH 7 (Fig. 4.20) The UV/Vis spectra showed that the film is stable for measurement different type of solutions.

Fig. 4.20: Spectra of silica-immobilized BCG/SDS thin film at pH 6 after immersed in 1M of different solutions: 1 M KCL, 1M HCl, 1 M CH₃COOH, 1 M Na₂CO₃, 1 M NH₄OH and 1 M NaOH
The lifetime of immobilized BCG/SDS thin film was also studied at six months time period. Almost no leaching or change in response was shown for these films. So these films are considered to be very stable at different conditions include interference ions or long time periods (Table 4.3).

**Table 4.3: The lifetime of Silica-immobilized BCG/SDS thin film at six months**

<table>
<thead>
<tr>
<th>Number of Weeks</th>
<th>Abs (446nm)</th>
<th>Numbers of Weeks</th>
<th>Abs (446nm)</th>
<th>Numbers of Weeks</th>
<th>Abs. (446nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3884</td>
<td>9</td>
<td>0.3881</td>
<td>17</td>
<td>0.3880</td>
</tr>
<tr>
<td>2</td>
<td>0.3884</td>
<td>10</td>
<td>0.3881</td>
<td>18</td>
<td>0.3880</td>
</tr>
<tr>
<td>3</td>
<td>0.3884</td>
<td>11</td>
<td>0.3881</td>
<td>19</td>
<td>0.3880</td>
</tr>
<tr>
<td>4</td>
<td>0.3882</td>
<td>12</td>
<td>0.3881</td>
<td>20</td>
<td>0.3880</td>
</tr>
<tr>
<td>5</td>
<td>0.3882</td>
<td>13</td>
<td>0.3881</td>
<td>21</td>
<td>0.3878</td>
</tr>
<tr>
<td>6</td>
<td>0.3882</td>
<td>14</td>
<td>0.3881</td>
<td>22</td>
<td>0.3878</td>
</tr>
<tr>
<td>7</td>
<td>0.3882</td>
<td>15</td>
<td>0.3880</td>
<td>23</td>
<td>0.3878</td>
</tr>
<tr>
<td>8</td>
<td>0.3882</td>
<td>16</td>
<td>0.3880</td>
<td>24</td>
<td>0.3878</td>
</tr>
</tbody>
</table>

**4.14 Effect of Multilayer Thin Film Coating.**

Coating of the glass slides with double layer of silica immobilized with BCG/SDS at the same conditions was performed (Fig.4.21). It is obvious that the absorbance of the immobilized BCG/SDS thin film double layer is more than single layer. The percentage of signal increment of duple layers was 45.3% compared with single layer. In case of triple layer thin film, the film suffered from leaching and the preparation of triple layer thin film was failed.
Fig. 4.21: Electronic spectra of single and double layers of Silica-immobilized BCG/SDS thin film: (a) single layer thin film, (b) double layer thin film.

4.15 Effect of Multilayer Thin Film on BCG Leaching.

After washing the thin films with distilled water. It is found that single layer of immobilized BCP/SDS thin film showed lower leaching than double and layers (Fig. 4.22).

Fig. 4.22: Single and double layers leaching of Silica-immobilized BCG/SDS thin film at pH 6: (a) single layer leaching, (b) double layer leaching.
4.16: Film Thickness Measurement.

The thickness of the single layer thin film was measured using ellipsometry technique which is a well known technique in thin film characterization [88-91]. Figure 4.23 shows the measured ellipsometric parameters $\psi$ and $\Delta$ as a function of the wavelength in the range 300 nm – 750 nm. TF Companion version 3.4, Thin films measurement and data analysis software, (semicon Soft) was used to invert the ellipsometric parameters and to calculate the film thickness. The thickness of immobilized BCG film is found to be about 125 nm ± 10 nm.

\[ \begin{align*}
\psi & \text{(deg)} \\
\Delta & \text{(deg)}
\end{align*} \]

\[ \begin{align*}
\text{Wavelength (nm)} & \text{ (nm)} \\
\text{Wavelength (nm)} & \text{ (nm)}
\end{align*} \]

**Fig 4.23:** Measured ellipsometric parameters $\psi$ and $\Delta$ as a function of the wavelength in the range 300 nm – 750 nm.
4.17 Polarized Light Microscopy.

Several photographs were taken by crossed polarized light microscope for thin films of free silica, immobilized BCG, immobilized and immobilized BCG/SDS, in order to examine the nature of interaction between BCG, silica and surfactants. Photograph 4.24a and 4.24b involve the free silica and immobilized BCG thin film respectively. From these photographs, it is clear that the particle size distribution is wider in the free silica, while in presence of BCG, the modified particles become more uniform and smaller in size. The effect of different surfactants on the modification and distribution of the particles were also observed. Photograph 4.24c, of immobilized BCG/SDS thin film. From photograph, it is shown that there is an increase in the number of particles than the free BCG thin film. Also, the size of the particles becomes smaller and more uniform. This behavior is due to the interaction of surfactant with BCG molecules through electrostatic interaction. This was supported by the increase of absorption intensities of the band at 441 nm (Fig. 4.1) as the hydrophobic part of surfactant participate in the acceleration of the association of the particles which lead to increase its stability. This was really obvious when SDS surfactant was added has direct effect on improvement and modification of the particles than other surfactants.
Fig 4.24,a: PLM photograph of sol-gel silica free.

Fig 4.24,b: PLM photograph of Silica-immobilized BCG thin film.
Fig 4.24,c: PLM photograph of Silica-immobilized BCG/SDS thin film.
4.18 Conclusion

The immobilized BCG thin films (single and double layers) were prepared by deposited thin films of sol containing hydrolyzed TEOS and BCG in the presence of SDS, CTAB, and TX-100 surfactants onto a substrate. The immobilized BCG thin films were dried at 80 °C which exhibit the least leaching. The best film of BCG was prepared in the presence of SDS surfactant which probably due to strong interaction between SDS, BCG and silica precursor. Two forms, acidic form (yellow color) and basic form (blue color) was observed for the immobilized BCG/SDS, CTAB and TX-100 corresponding to two different forms of immobilized BCG/surfactants sensor. The thin films sensors showed high reproducibility, sensing, repeatability reversibility and aging stability. The pKa of the BCG thin film was calculated, which showed a significant shift compared with the free BCP in aqueous solution. PLM studies showed a uniform distribution of particles with a significant modification of size particles for the BCG thin film in presence of surfactants comparing with the free BCG thin film.
Conclusion

Spin coating method used to prepare transparent sol-gel thin films immobilized with bromocresol purple (BCP) and bromocresol green (BCG) pH-sensitive indicators were made via the acid catalyzed sol-gel reaction of tetraethylorthosilicate in presence of (BCP) or (BCG) indicators. Different surfactants include; cationic cetyl trimethyl ammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS) and nonionic Triton X-100 (TX-100) were used to improve the mesostructure of the host material and to increase its porosity. With the exception of BCP in presence of SDS which is the best surfactant,. The immobilized BCP and BCG thin films show similar behavior in presence of surfactants as their free counterparts in aqueous solution with very small shifts in the wavelength's of absorption. The color change behavior of the immobilized bromocrersol purple indicator affected significantly and show three absorption bands in presence of SDS at( $\lambda_{\text{max}}$=435 nm, $\lambda_{\text{max}}$=535 nm and $\lambda_{\text{max}}$=595 nm) comparing with its free counterpart in aqueous solution, while only two absorption bands were observed in case of other surfactants for both BCP and BCG thin films. Both BCP and BCG retain their structures during the sol-gel reactions in terms of response to pH. Different parameters include concentration of indicators and surfactants, temperature, number of layers, response time, life time and number of measurements were investigated. The pKa values of the different prepared BCP and BCG immobilized thin films were determined. The BCP and BCG thin films sensor showed stability, reversibility at pH from (1.13), repeatability, reproducibility, fast response and long life time behavior. Lowest leaching of BCP and BCG indicators was showed when thin films were dried at 80 °C. Stability of the indicators thin films was observed up to ten month life time. The indicator thin films show very fast response.
Construction of multi-layer sol-gel film enabled higher indicator lading and improve signal sensitivity.

The electrostatic attraction between indicators molecules, surfactants and silica host matrix enhanced the accommodation of indicators molecules and improve their stability and preserve sensitivity. The polarized light microscopy indicated that the bromocresol purple and bromocresol green molecules were distributed uniformly within the host silica network especially in presence of surfactants. The silica immobilized BCP/SDS and BCG/SDS thin films thickness's were calculated from ellipsometry technique which were 140 nm for immobilized BCP/SDS and 125nm for immobilized BCG/SDS thin films.
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كما تم دراسة قيم ثوابت التفكك الحمضي للكاشفين $K_a$، المثبتين في افلام السليكا الرقيقة.

من خلال الدراسة تبين أن الافلام الرقيقة الشفافة المحتوية على كلا من الكاشفين اظهرت ثباتاً وانعكاسية، ودقة، وسرعة استجابة مع الزمن وفترة عمر طويلة. كما وجد أن كلا من الكاشفين لا ينفصلان عن الافلام عند التسخين عند درجة حرارة 80 درجة مئوية.

كما أن الافلام المحتوية على الكاشفين اظهرت استقراراً لأكثر من عشرة أشهر. كما ان لها قدرة سريعة للاستجابة لدرجة حموضة الوسط. كما تم التمكن من تحضير أكثر من طبقة من الافلام حيث تحسن حساسية الكواشف وواشارة الامتصاص. وقد وجد أن هناك تجاذب الكتروستاتيكي بين جزيئات الكاشف وكل من السيرفاكتنت و شبكة السليكا والتي ساعدت على استيعاب جزيئات الكواشف خلالها وكذلك ثباتها والحفاظ على حساسيتها. وقد بين تصوير الافلام باستخدام المجهر الضوئي المستقطب بأن كل من كاشفي BCP و BCG اندمجت بصورة متجانسة ومنتظمة خلال شبكة السليكا خصوصاً في وجود المواد النشطة سطحياً.
الملخص

تم تحضير أفلام رقيقة شفافة من مادة السيليكا بطريقة الصل-جل. وقد تم دمج كواشف رقم الهيدروجيني خلال هذه الأفلام (البرومو كريزول البنفسجي (BCP) و (البرومو كريزول الأخضر (BCG) حسب حضرت الأفلام من خلال تفاعل التحلل المائي لمادة رباعي الأيثوكسي سيلان (TEOS) في وسط حمضي (HCl) كعامل حفز.

وقد تم استخدام مجموعة من المواد ذات الفعالية السطحية (Surfactants) والتي شملت النوع (TX-) والذي يحمل شحنة سلبية كإكستنشن (SDS) والنوع الذي يحمل شحنة موجبة (CTAB)، والمعتدل (TX-100) وذلك لاختبار مدى قدرتها على تخزين الكيماوي الناتج من السيليكا والمضاف إليها الكاشف الهيدروجيني من حيث تحسن التركيب الشبكي الداخلي وزيادة عدد المسامات، والاستيعاب الجيد للمواد الفعالة خلال شبكة السيليكا.

من خلال الدراسة تبين أن الكواشف المدمجة في أفلام السيليكا الرقيقة وفًي وجود الانواع الثلاثة من المواد النشطة سطحيا تسلك سلوكا مشابهًا للكاشف الحرة في محلولها المائية مع إزاحة قليلة في الطول الموجي الذي تم الامتصاص عنه وذلك عند التحليل باستخدام جهاز التحليل السطحي (UV/Vis Spectrophotometer) حيث وجدت منطقتين لامتصاص وظهور لونان فقط، باستثناء كاشف البروموكريزول البنفسجي (BCP) في وجود SDS، حيث وجدت ثلاثة مناطق لامتصاص للفيلم المحضر وهي في الوسط المتعادل عند الطول الموجي (435 nm) حيث اللون الأصفر وفي الوسط الحمضي عند الطول الموجي (535 nm) حيث اللون الأحمر أما الامتصاص الثالث كان عند الطول الموجي (591 nm) وذلك في الوسط القاعدي حيث اللون الأرجواني.

كلا النوعين من الكاشفين BCP وBCG احتفظا بالتركيب الكيميائي لهما خلال عملية تحضير الأفلام الرقيقة باستخدام طريقة الصل-جل حيث ظهر ذلك باستجابتها للرقم الهيدروجيني. ولقد تم دراسة مجموعة من العوامل التي تؤثر على الأفلام سواء التي حضرت باستخدام الكاشف BCG أو التي حضرت باستخدام الكاشف BCP والتي شملت كلاً من درجة الحموضة (pH) ، تركيز كل من الكاشف والمواد النشطة سطحيا ، درجة الحرارة ، عدد الطبقات ، زمن الاستجابة (Response Time) ، الانتعاسية (Reversibility) ، والاستعاب (Repeatability) التي تعرض لها الفلم.