

UNIVERSITI TEKNOLOGI MARA

**DEVELOPMENT OF SOL-GEL-
DERIVED TiO₂ THIN FILMS AS pH-
SENSITIVE ELECTRODES FOR
EGFET-BASED SOIL pH SENSOR**

MUHAMMAD ALHADI BIN ZULKEFLE

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ABSTRACT

pH measurement is one of the most important parameters in a wide range of applications. Conventional glass-based pH electrodes are fragile and require internal electrolyte to operate, limiting its usage in soil's pH detection. In contrast, extended gate field effect transistor (EGFET) pH sensor does not suffer from these drawbacks and is more flexible in terms of sensing electrode (SE) or sensing membrane selection. The performance of the EGFET pH sensor would be highly dependent on the SE chosen. Compared to other pH-sensitive materials, titanium dioxide (TiO_2) is compelling considering its low cost, abundance, and ease of fabrication. Common fabrication methods for TiO_2 include sputtering and thermal chemical vapor deposition (TCVD) which require high vacuum and high temperature, respectively. On the other hand, the sol-gel-based method does not need high vacuum or high temperature during deposition, making the process easier and lower in cost. The focus of this study is to investigate a suitable sol-gel-based fabrication technique for the production of TiO_2 thin film as pH-sensitive electrode for EGFET pH sensor. Three techniques were studied namely spin coating, electrospinning, and electrospraying. Based on the results obtained, spin coating produced decent TiO_2 thin films with the optimized spin speed found to be at 3000 rpm which produced a sample with pH sensitivity, linearity, drift, and hysteresis value of 51.40 mV/pH, 0.9984, 12 mV/h and 41 mV, respectively. However, spin coating is not suitable for large-scale production as its fabrication method limits one film per deposition process. Electrospinning shows promising structures as its multiple-layer nanofibers technically should be able to provide a higher surface area to volume ratio, which can enhance the sensing performance compared to the relatively flat thin film produced by spin coating and electrospraying technique. The fibers fabricated using different polymer weight percent and varied flow rate have diameters ranging from 53.25 nm to 699 nm. The electrospun fibers, however, were found to have poor adhesion, mechanically fragile, and easily dissolve in the measuring solution, making it unsuitable for pH measurement. Electrospraying, a method which is rarely explored for its implementation in pH sensing devices, does not require the inclusion of polymer during its fabrication process, as opposed to the electrospinning method. Electrospraying also has greater potential in terms of large-scale production because it can produce multiple films at the same time, in contrast to the spin coating technique. The electrosprayed TiO_2 film shows great pH sensitivity (47.50 mV/pH) and linearity (0.9988) values. The drift of the electrosprayed film was 1.57 mV/pH which was 86.92% better compared to that of the spin-coated film. The pH hysteresis obtained by the electrosprayed film was 24 mV/pH and this shows 41.46% improvement as opposed to the spin-coated sample. Due to its superior pH linearity, drift, and hysteresis performance, electrosprayed TiO_2 film had been chosen to be applied as the sensing electrode for pH measurement in soil solution. Based on the results, it was shown that this study was able to successfully produce a working sol-gel electrospraying-based EGFET soil pH sensor with sensing performance comparable to a commercially available soil pH meter. This provides a basis for future improvement and development of a better EGFET soil pH sensor in terms of performance, cost, feasibility, and high-volume production capability.

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CHAPTER 1

INTRODUCTION

1.1 Research Overview

Rapid technological advancement in modern times has enabled improvement of sensors. One of the most prominent sensing areas is in detecting hydrogen ions to determine pH values of liquid measurand. pH refers to a scale in which concentration of hydrogen ions is measured. pH is an abbreviation of “pondus hydrogenii”, a Latin word that means power of hydrogen [1]. The popularity and necessity of pH sensors is contributed by the fact that the amount of hydrogen ions plays vital roles in many chemical and biological reactions. For example, plant growth is dependent on pH of soil [2] and kidney stones formation also depends on pH level [3].

Several methods and materials can be used to detect and measure pH. Metal oxide for instance, has special chemical characteristics that enable them to interact and sense hydrogen ions available in solutions. This specifically refers to the hydroxyl groups available on the surface of metal oxide that come into existence when the surface gets into contact with water molecules [4].

One of the materials belonging to the metal oxide category is titanium dioxide, TiO_2 . It is an n-type semiconductor with great physical, chemical, electrical and optical properties. Due to this, titanium dioxide has been applied in various applications such as photocatalysis, paints, sunscreen and solar cells [5]-[8]. As a type of metal oxide, titanium dioxide also has hydroxyl groups on its surface so it can be used as pH sensing material. However, the performance of a TiO_2 when measuring pH is greatly dependent on its fabrication process.

There are many fabrication techniques that can be chosen to produce TiO_2 in form of thin film namely thermal chemical vapor deposition (TCVD) [9], sputtering [10], spin coating [11], electrospinning [12] and electrospaying [13] where each method has their own advantage and disadvantages. TCVD can be used to coat irregular shaped objects but require gas and high temperature for the deposition process. Radio frequency sputtering can produce high purity thin film but it needs high vacuum conditions and is very costly.