Structural and Ph Sensing Properties of Spin-Coated Tio$_2$ Thin Films with Varied Sol-Gel Concentration and with Different Composite Bilayer Configuration

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***Abstract*—Sol-gel spin coated titanium dioxide (TiO_2) was applied as the sensing membrane for extended gate field effect transistor (EGFET) pH sensor. The molarity of the TiO_2 sol-gel was manipulated to study its influence on the film pH sensing capability. In this study, the sol-gel solution concentration was varied from 0.2 M to 1.0 M. It was observed that an increase in molarity used would results in the decrease of pH sensitivity of the TiO_2 thin film, in which, the highest pH sensitivity (42.60 mV/pH) was obtained from the film deposited using the lowest concentration. As sol-gel concentration becomes higher, the films becomes thicker, deteriorating its pH sensing performance. FESEM images showed that the variation of the sol-gel concentration influenced the surface morphology. XRD results obtained confirmed the anatase phase existence in all TiO_2 samples, excluding that of 0.2 M sample that was amorphous with no peaks. Besides that, composite bilayer sensing structure obtained by incorporating ZnO with TiO_2 thin film can produce sensing membrane with higher pH sensitivity than a pure TiO_2 sensing membrane. The sensitivity value for TiO_2/ZnO and ZnO/TiO_2 composite bilayer samples are 57.1 mV/pH and 46.9 mV/pH respectively.**

***Index Terms*—composite bilayer, EGFET, pH sensor, sol-gel concentration, titanium dioxide**

I. Introduction

PH has been one of the most common electrochemical measurements for its importance in numerous chemical and biological reactions [1]. For a material to be used as pH sensitive membrane, it must possessed several characteristics such as chemically stable [2], does not corrode [3] and non-toxic [4].

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More importantly, the material must be able to interact with hydrogen (hydronium) ions in solutions with high sensitivity. Titanium dioxide (TiO_2) meets those criteria and hence can act as pH sensing membrane.

TiO_2 is a type of metal oxide with three common crystallographic phase; anatase, rutile and brookite [5]. Brookite has orthorhombic crystal system and is the least common [6] compared to both metastable anatase (tetragonal) and thermodynamically stable rutile (tetragonal) [7]. TiO_2 is also an n-type semiconductor with wide band gap [8] between 3.0 eV to (rutile) and 3.2 eV (anatase) [9]. Owing to its unique chemical, physical, optical and electrical properties, TiO_2 had been widely used for various purposes such as sunscreen [10] and pigments [11] and also implemented in many applications like for photocatalysis [12] and sensors [13-14].

A wide variety of methods are available to synthesis TiO_2 thin films. Some examples include but not limited to sputtering [15], chemical vapor deposition [16], spray pyrolysis [17] and sol-gel spin coating [18]. Comparing the methods, sol-gel spin coating is the more desirable deposition technique because of its low deposition temperature, flexibility of material manipulation, relatively lower in cost, excellent final film properties and simplicity in handling.

Solid-state sensing like TiO_2 thin film is more preferable for pH sensing compared to glass-liquid-based pH sensor because of the brittleness [19], arduous maintenance [20] and miniaturization limitation of the latter [21]. Extended gate field effect transistor (EGFET) sensor structure was introduced in 1983 [22] as alternative to its predecessor ion sensitive field effect transistor (ISFET) [23] and had since been used in pH sensing area [24-25]. In this paper, both TiO_2 and EGFET were integrated with a readout interface circuit (ROIC) to act as a working pH sensor.

There are some other studies reported in literatures discussing capabilities of TiO_2 as membrane for pH sensor with modifications made on the parameters such as annealing temperature [26] and time [27]. However, specific investigation on influence of increasing sol-gel spin coated TiO_2 concentration towards its pH sensitivity using EGFET configuration are scarcely available or almost non-existent.

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Thus this paper concentrates on varying the TiO_2 sol-gel molarity to study its effects on pH sensing properties as well as to its physical characteristics.

Another metal oxide that had been used as pH sensing membrane for EGFET pH sensor is zinc oxide, ZnO. Like TiO_2, ZnO possessed good chemical stability and can be prepared using similar deposition techniques. Although single layer ZnO and single layer TiO_2 had both being used to measure pH of solutions, the combination of both materials in the form of composite bilayer structure as pH sensing membrane is rarely studied. Therefore this work also investigate the influence of integrating TiO_2 with ZnO towards its pH sensitivity.

II. Experimental Details

TiO_2 sol-gel was produced by mixing different chemicals of different purposes. Titanium (IV) isopropoxide (TTIP) ($Ti[OCH(CH_3)_2]_4$, Sigma-Aldrich, 97%) as precursor, deionized (DI) water (H_2O, Milli-Q Advantage A10) as water source, absolute ethanol (C_2H_5OH, SYSTERM, 99.8%) as solvent, glacial acetic acid (GAA) (CH_3COOH, Friendemann Schmidt, 99.8%) as stabilizer and Triton X-100 ($C_{34}H_{62}O_{11}$, R&M Chemicals, 98%) as surfactant.

Initially two solutions in two different bottles were made. Solution A contains TTIP (1.5 ml), GAA (2.5 ml) and absolute ethanol (23 ml) while solution B contains Triton X-100 (0.05 ml), DI water (0.2 ml) and absolute ethanol (23 ml). Both solutions were stir at room temperature using magnetic stirrer for one hour before being mixed together. The mixture was then continued to be stirred for one more hour. Then 10 drops of the TiO_2 sol-gel was dropped on indium tin oxide (ITO) substrate and spun using spin coating technique. The spinning speed and spinning time during deposition process was 3000 rpm and 60 seconds respectively. After that, the produced TiO_2 film was dried at temperature of 200 °C for 10 minutes. To further improve crystallinity of the film, post-deposition annealing process was performed using temperature of 400 °C for duration of 30 minutes.

The steps were repeated but with variation on precursor volume used to produce samples with different concentration of 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M. To produce composite bilayer samples, a layer of ZnO was added either on top of TiO_2 surface (forming TiO_2/ZnO composite bilayer film) or at the bottom of the TiO_2 layer (forming ZnO/TiO_2 bilayer film). The deposition procedure of the ZnO layer was similar to the TiO_2 layer but the recipe used to prepare the ZnO sol-gel is different. For ZnO sol-gel, the precursor, zinc acetate was first magnetically stirred with monoethanolamine and 2-methoxyethanol for 3 hours at temperature of 80 °C. Then at room temperature, the stirring process was continued for another 24 hours.

All the fabricated films were then tested for their pH sensing properties by first connecting them to copper wires. Then the copper wires were connected to gate of a metal oxide semiconductor field effect transistor (MOSFET), forming EGFET structure. The MOSFET is a component of a readout interfacing circuit (ROIC) with constant voltage constant current [28]. The ROIC was connected to a multimeter for the output. The overall measurement setup for EGFET pH sensor is illustrated in Fig. 1.

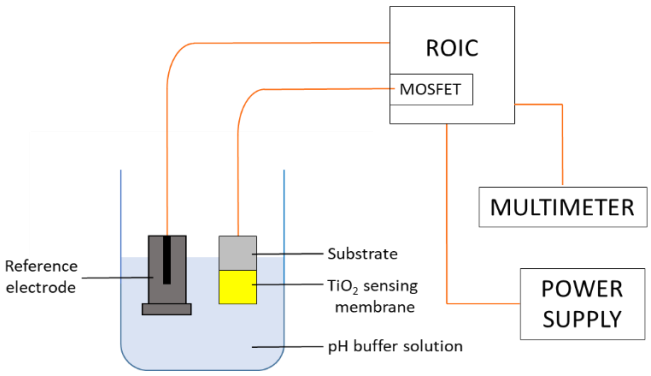
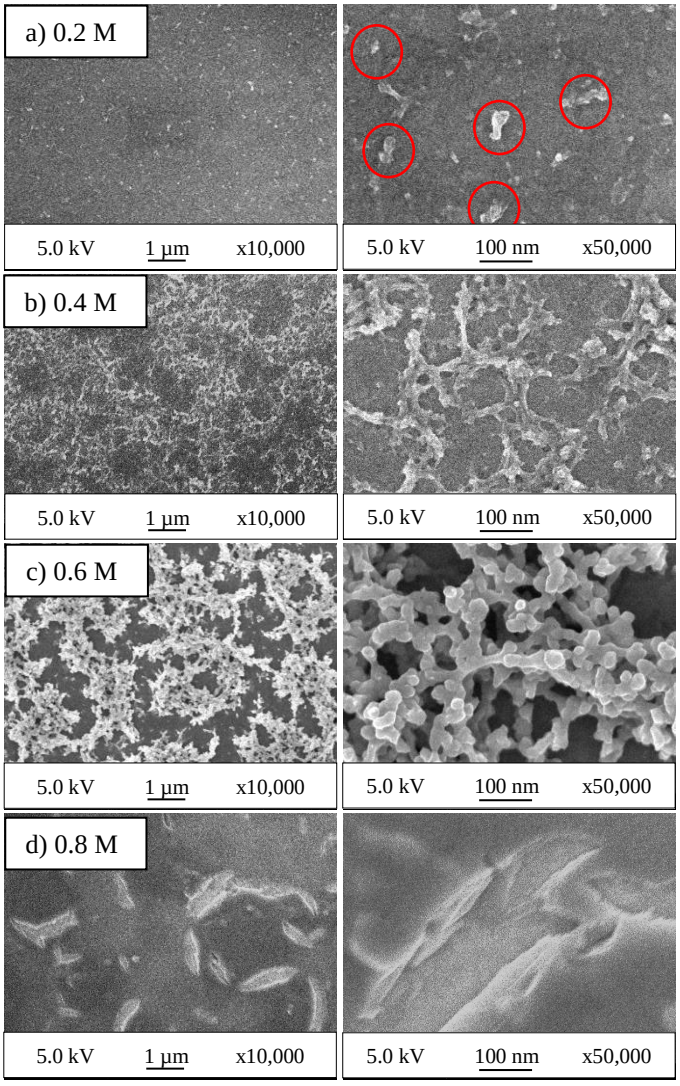


Fig. 1. Schematic diagram of pH measurement setup of EGFET pH sensor

III. Results & Discussion

The fabricated TiO_2 thin films were then characterized for its physical properties, namely surface morphology and crystalline quality. Using field emission scanning electron microscopy (FESEM), the surface morphology images were obtained and shown in Fig. 2.



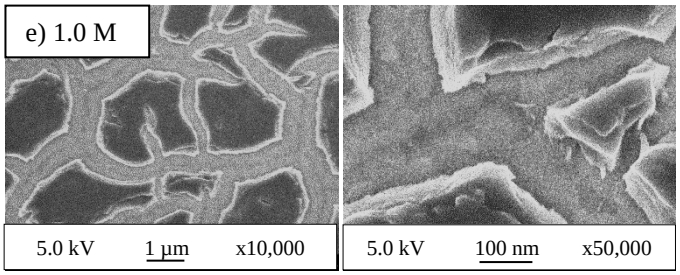


Fig. 2. FESEM images of TiO_2 samples a) 0.2 M b) 0.4 M c) 0.6 M d) 0.8 M and e) 1.0 M (left images x10k magnification, right images x50k magnification)

For the TiO_2 film fabricated using lowest sol-gel concentration of 0.2 M, the TiO_2 was uniformly distributed throughout the film but there are no significant structural growth can be clearly seen. However, upon closer observation using bigger magnification of x50,000, there are several small, randomly shaped particles (marked by the circles). At higher concentration of 0.4 M, the particles that was previously seen in 0.2 M sample seems to have grown into larger particles and are connected with each other, forming branching networks of TiO_2 structure. 0.6 M sample exhibits a more distinct structural growth. It is a structure formed from countless of irregularly rounded or sphered particles bonded to each other. Besides that, the growth of TiO_2 particles for 0.6 M sample clearly happens both horizontally and vertically, unlike the previous sample. The shape is comparable to reported work that used TiO_2 nanopowder in the sol-gel processing [29].

The sample being prepared using solution of 0.8 M concentration is presented in Fig. 2d. The structure of the sample is completely different from the lower concentration samples where the particles might have completely merged with each other as a result of the high concentration used, forming a dense TiO_2 film. The film has smooth-surface film with cracks existing at many places. The high precursor concentration might had caused additional stress on the films during annealing steps, creating the macroscopic cracks [30]. The same can be said for the subsequent sample of 1.0 M but with one major difference. The cracks that existed is far bigger and these cracks separate dense TiO_2 blocks from one another.

The crystalline quality of the TiO_2 samples were determined using X-ray diffraction (XRD) technique and the results are shown in Fig. 3. For 0.2 M sample, no peaks appeared, indicating it is not crystalline and thus amorphous [31]. This amorphous nature of the first sample means its atoms has no long-range order of preferred atomic arrangement. As the concentration being raised to 0.4 M, several distinctive peaks emerged. There is one major peak at 2-theta (2θ) of 25° and five minor peaks at 38°, 48°, 54°, 55° and 63°. These peaks correspond to Miller indices of (101), (112), (200), (105), (211) and (204) respectively.

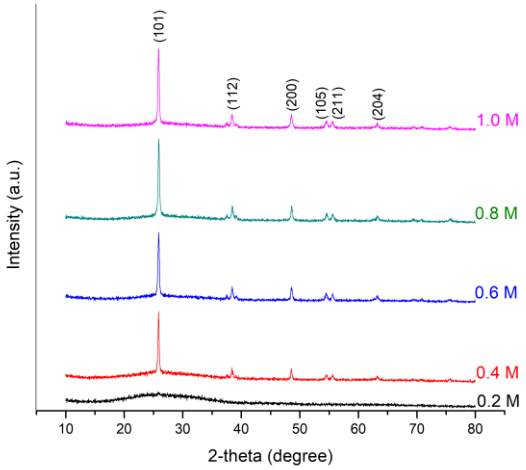


Fig. 3. XRD peaks for TiO_2 thin films with varied sol-gel concentration

Based on available literature [32] and standard card JCPDS 00-021-1272, these peaks confirms that the produced 0.4 M sample contains anatase phase. The common reported crystal arrangement for TiO_2 are tetragonal (anatase and rutile) [33]. However, the reason for anatase to become dominant in this sample might be due to the low annealing temperature applied in this study which is 400 °C. Rutile on the other hand can only be obtained using high temperature treatment (800 °C-1000 °C) [34-35]. Besides, synthesis of TiO_2 generally formed anatase as the initial crystalline phase and this is caused by two factors. First is the tendency of short-ranged order TiO_6 to arranged into long-range ordered anatase structure and second is due to the thermodynamic characteristics of both anatase and rutile may had favored crystallization of anatase [36]. When concentration of sol-gel being further increased to 0.6 M, the same pattern of peaks is also observed for the sample. The same can be said for the subsequent samples of 0.8 M and 1.0 M but the major peak of these two samples shows a slight increment in the intensity value.

The TiO_2 thin films were then characterized for their pH sensitivity and linearity to determine its sensing performance. Since TiO_2 is a metal oxide, it has hydroxyl (OH) [37] groups that can interact with acidic and basic solutions, displaying amphoteric behavior [38]. This means that TiO_2 is capable of interacting with both hydrogen and hydroxide ions in solutions [39]. When TiO_2 films were used as pH sensing membrane, the output voltage of EGFET pH sensor would differs depending on acidity and basicity of solutions being measured. The graph of output voltage, V_{out} vs pH recorded for all samples are plotted in Fig. 4.

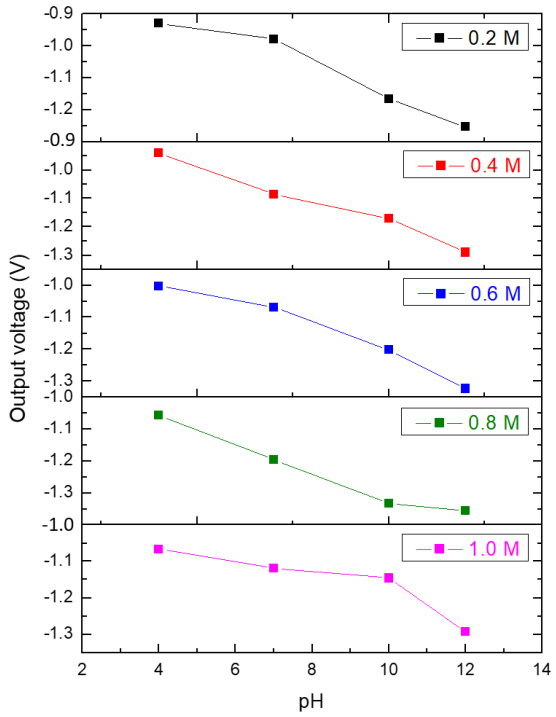


Fig. 4. TiO_2 sensing membrane output voltage, V_{out} vs pH results

All the lines in graph in Fig. 4 is almost linear, suggesting good correlation between the two variables. Different V_{out} was produced by sensing membrane when being measured in different pH buffer solution. The reason behind it is that the amount of pH potential determining ions (H^+ and OH^-) vary according to the solution's pH value and this affect surface potential, Ψ_0 produced at the surface of sensing membrane. According to site binding theory based on Gouy-Chapman-Stern Model [40], the relationship and dependency of Ψ_0 with solution's pH value can be expressed using equation (1) [41]:

$$2.303\left(pH_{pzc} - pH\right) = \frac{q\Psi_0}{kT} + sinh^{-1}\left(\frac{q\Psi_0}{kT}.\frac{1}{\beta}\right) \qquad (1)$$

Where pH_{pzc}, q, k, T and β are pH at point of zero charge, electron charge, Boltzmann's constant, absolute temperature and sensitivity parameter respectively. The output voltage, V_{out} was seen to become more negative as pH value becomes higher. One possible explanation is that as pH value rises, amount of OH^- increases, producing negative surface potential, Ψ_0 at TiO_2-solution interface. As a result, I_{DS} in MOSFET is reduced [42] and thus this lead to decreased in V_{out} values. In contrast, the higher V_{out} achieved by more acidic solution might due to presence of many H^+ (hence positive Ψ_0) on the surface of TiO_2 sensing membrane.

The pH sensitivity and linearity value for each TiO_2 sample was extracted from the slope of the graphs in Fig. 4, and shown in Fig. 5. The sensitivity of the first sample (0.2 M) is 42.6 mV/pH with linearity of 0.9497. The second sample (0.4 M) possessed slightly lower sensitivity of 41.7 mV/pH and its linearity is 0.9853. This declining pH sensitivity trend continues with all the subsequent TiO_2 samples. TiO_2 thin films with 0.6 M, 0.8 M and 1.0 M have sensing performance of 40.1 mV/pH (0.9615), 39.0 mV/pH (0.9692) and 25.1 mV/pH (0.8213) respectively.

The declining sensitivity pattern can be seen in Fig. 5. The TiO_2 film's sol-gel concentration and its pH sensitivity having inversely proportional relationship can probably be attributed to the increment of the film's thickness as reported by other researchers. The investigation from work done by Stephen Lourduraj et al., [43] reported that as molarity of sol-gel increases, the resultant film thickness also increased. While Pin Chuan Yao et al., [27] reported that thicker film has lower sensitivity. However, the films thicknesses in our work are shown in Fig. 6 below. The error bar showing the highest and lowest values are also incorporated with the marker showing the average thickness value. The measurements were done using the surface profiler by taking a few points on the same sample. It can be seen that in average, the thickness increases with the molarity, however, at higher molarity, it can be observed that the uniformity of the thin film is not as good as those of the lower molarity. This may be related to the viscosity of the solution; higher viscosity solution has a higher tendency to produce a thin film with non-uniform thickness compared to those with lower viscosity. Thus, relating the sensor results in Fig. 5 to the thicknesses in Fig. 6, we may not be able to correlate the film thickness and uniformity to the sensor performance. The performance pattern seen in Fig. 6 may be attributed to various factors such as surface morphology and crystalline quality, which need to be studied further.

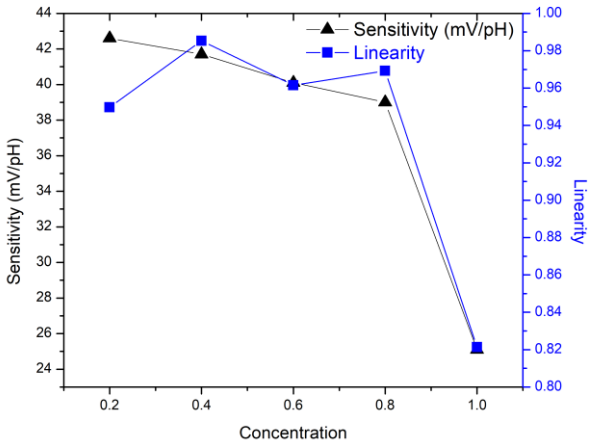


Fig. 5. Effect of varying TiO_2 sol-gel concentration on pH sensitivity

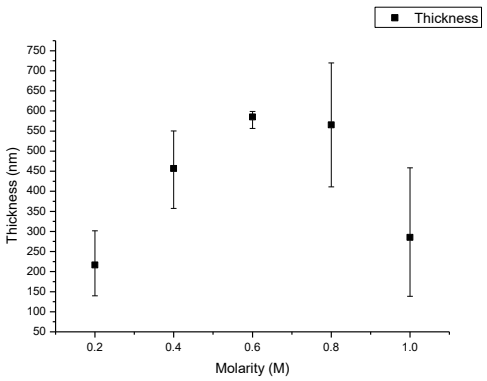


Fig. 6. TiO_2 thin film thickness dependence on the molarity

While there are many reports on the single material sensing layer and sensing membrane made up of doped materials, only limited number of reports found for pH sensing layer using more than one material in the form of composite bilayer structure. Hence in an attempt on increasing the sensitivity, TiO_2-based composite bilayer structure were fabricated. This is because the highest pH sensitivity obtained above is still far from the Nernstian theoretical value of 59 mV/pH. In this bilayer configuration, a layer of ZnO is added on top of (TiO_2/ZnO) or at the bottom of TiO_2 layer (ZnO/TiO_2).

The results from examination of surface of TiO_2/ZnO and ZnO/TiO_2 samples are shown in Fig. 7. For TiO_2/ZnO sample, the structure is similar to structural formation in Fig. 2 (b) while ZnO/TiO_2 is made up of numerous nanocrystallites [44] that is almost densely packed together. The structural differences between both films resulted in different roughness on the surface. From From the AFM images in Fig. 8, the surface roughness for TiO_2/ZnO and ZnO/TiO_2 are 2.228 nm and 1.266 nm respectively.

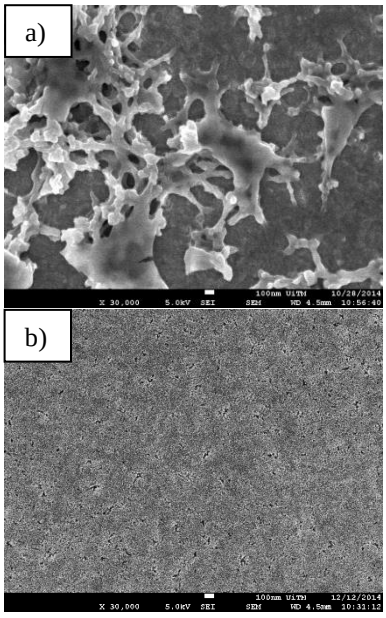


Fig. 7. Surface structure on (a) TiO_2/ZnO and (b) ZnO/TiO_2 composite bilayer samples

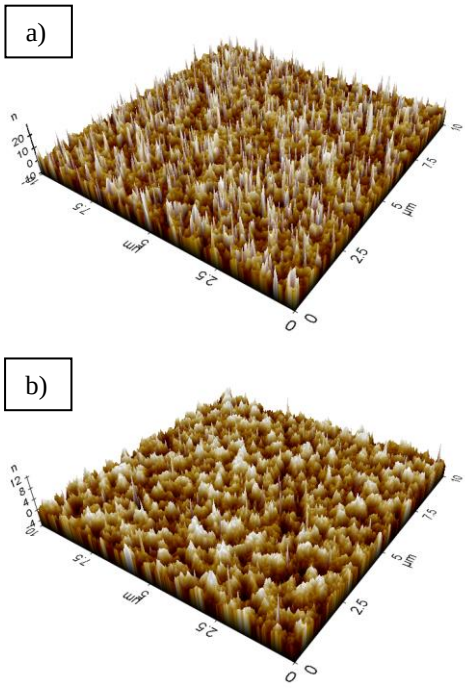


Fig. 8. AFM images for (a) TiO_2/ZnO and (b) ZnO/TiO_2 sample

To determine the sensitivity of both composite bilayer samples, V_{out} vs pH graph is plotted as in Fig. 9. In term of sensitivity, there is an increment for ZnO/TiO_2 composite bilayer sample (46.9 mV/pH) compared to single layer TiO_2 sample (42.6 mV/pH). On the other hand, the sensitivity was significantly enhanced when TiO_2/ZnO composite bilayer configuration was used. The pH sensitivity for this sample is 57.1 mV/pH and thus approaching the Nernst theoretical value of 59 mV/pH. The sensitivity improvement caused by the usage of composite bilayer configuration is yet to be determined. However, it is clear that the synergetic effects arising from the combination of the two materials used can be beneficial in producing high performance pH sensing membrane.

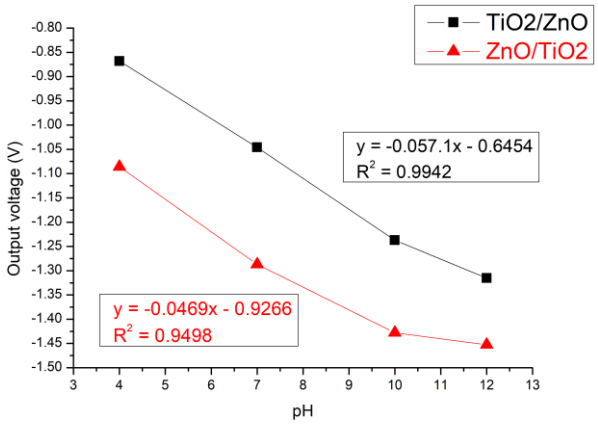


Fig. 9. pH sensitivity and linearity for the composite bilayer samples

IV. Conclusion

The results presented in this study showed that fabricated sol-gel spin coated TiO_2 thin films are capable of acting as pH sensing membrane, with the highest sensitivity achieved was 42.6 mV/pH. The properties of the films were found to be dependent on concentration of precursor used. By increasing molarity of TiO_2 sol-gel solution, the pH sensing performance of TiO_2 sensing membrane were observed to experience deterioration, as shown by declining sensitivity values. The surface structure of TiO_2 films also changes when molarity being changed with 0.6 M sample exhibit nanostructure growth. In term of crystalline quality, although amorphous characteristics displayed by 0.2 M sample, all other TiO_2 samples with higher concentration demonstrated high degree of crystallinity. It was also found that the sensitivity of the sample can be improved when TiO_2 film was combined with ZnO film (and thus forming composite bilayer structure). The TiO_2/ZnO has pH sensitivity of 57.1 mV/pH while ZnO/TiO_2 sample has pH sensitivity of 46.9 mV/pH.

References

[1] D. Janczak, A. Peplowski, G. Wroblewski, L. Gorski, E. Zwierkowska, and M. Jakubowska, "Investigations of Printed Flexible pH Sensing Materials Based on Graphene Platelets and Submicron RuO_2 Powders," *J. Sensors*, vol. 2017, Article ID 2190429, 6 pages, 2017.

[2] N. P. de Moraes, T. Carvalho, M. L. C. P. da Silva, T. M. B. Campos, G. P. Thim, and L. A. Rodrigues, "A novel synthesis route of titanium dioxide with $(NH_4)_{0.3}TiO_{1.1}F_{2.1}$ as by-product," *Ceram. Int.*, vol. 43, no. 16, pp. 13677–13682, 2017.

[3] A. Hartwig, O. Klein, and H. Karl, "Sputtered titanium dioxide thin films for galvanic corrosion protection of AISI 304 stainless steel coupled with carbon fiber reinforced plastics," *Thin Solid Films*, vol. 621, pp. 211–219, 2017.

[4] H. B. Mantravadi, "Effectivity of titanium oxide based nano particles on E. Coli from clinical samples," *J. Clin. Diagnostic Res.*, vol. 11, no. 7, pp. DC37–DC40, 2017.

[5] V. Castrejón-Sánchez, R. López, M. Ramón-González, Á. Enríquez-Pérez, M. Camacho-López, and G. Villa-Sánchez, "Annealing Control on the Anatase/Rutile Ratio of Nanostructured Titanium Dioxide Obtained by Sol-Gel," *Crystals*, vol. 9, no. 1, p. 22, 2018.

[6] A. M. Alotaibi, S. Sathasivam, B. A. D. Williamson, A. Kafizas, C. S-. Vazquez, A. Taylor, D. O. Scanlon, and I. P. Parkin, "Chemical Vapor Deposition of Photocatalytically Active Pure Brookite TiO_2 Thin Films," *Chem. Mater.*, vol. 30, no. 4, pp. 1353–1361, 2018.

[7] T. Balaganapathi, B. Kaniamuthan, S. Vinoth, T. Arun, and P. Thilakan, "Controlled synthesis of brookite and combined brookite with rutile phases of titanium di-oxide and its characterization studies," *Ceramics International*, vol. 43, no. 2, pp. 2438–2440, 2017.

[8] E. C. Dell'Orto, S. Caldirola, A. Sassella, V. Morandi, and C. Riccardi, "Growth and properties of nanostructured titanium dioxide deposited by supersonic plasma jet deposition," *Appl. Surf. Sci.*, vol. 425, pp. 407–415, 2017.

[9] A. J. Haider, Z. N. Jameel, and I. H. M. Al-Hussaini, "Review on: Titanium dioxide applications," *Energy Procedia*, vol. 157, pp. 17–29, 2019.

[10] P. J. Lu, S. W. Fang, W. L. Cheng, S. C. Huang, M. C. Huang, and H. F. Cheng, "Characterization of titanium dioxide and zinc oxide nanoparticles in sunscreen powder by comparing different measurement methods," *J. Food Drug Anal.*, vol. 26, no. 3, pp. 1192–1200, 2018.

[11] S. Middlemas, Z. Z. Fang, and P. Fan, "A new method for production of titanium dioxide pigment," *Hydrometallurgy*, vol. 131–132, pp. 107–113, 2013.

[12] Z. Zhu, H. Cai, and D. W. Sun, "Titanium dioxide (TiO_2) photocatalysis technology for nonthermal inactivation of microorganisms in foods', *Trends Food Sci. Technol.*, vol. 75, pp. 23–35, 2018.

[13] J. R. Nataraj, P. Y. Bagali, M. Krishna, and M. N. Vijayakumar, "Development of silver doped titanium oxide thin films for gas sensor applications," *Mater. Today Proc.*, vol. 5, no. 4, pp. 10670–10680, 2018.

[14] D. Majumder and S. Roy, "Room Temperature Synthesis of TiO_2 Nanospheres: Ammonia Sensing Characteristics," *Mater. Today Proc.*, vol. 5, no. 3, pp. 9811–9816, 2018.

[15] I. S. Brandt, C. C. P. Cid, C. G. G. Azevedo, A. L. J. Pereira, L. C. Benetti, A. S. Ferlauto, J. H. D. da Silva, and A. A. Pasa, "Influence of substrate on the structure of predominantly anatase TiO_2 films grown by reactive sputtering," *RSC Adv.*, vol. 8, no. 13, pp. 7062–7071, 2018.

[16] E. H. Kim, M. H. Lim, M. S. Lah, and S. M. Koo, "Synthesis and characterization of heteroleptic titanium MOCVD precursors for TiO_2 thin films," *Dalt. Trans.*, vol. 47, no. 7, pp. 2415–2421, 2018.

[17] T. Dhandayuthapani, R. Sivakumar, R. Ilangovan, C. Gopalakrishnan, C. Sanjeeviraja, A. Sivanantharaja, and R. H. Krishna, "Efficient electrochromic performance of anatase TiO_2 thin films prepared by nebulized spray deposition method," *J. Solid State Electrochem.*, vol. 22, no. 6, pp. 1825–1838, 2018.

[18] L. D. Trino, E. S. Bronze-Uhle, A. George, M. T. Mathew, and P. N. Lisboa-Filho, "Surface Physicochemical and Structural Analysis of Functionalized Titanium Dioxide Films," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 546, pp. 168–178, 2018.

[19] T. Hashimoto, H. Kitabayashi, K. Ito, H. Nasu, A. Ishihara, and Y. Nishio, "Effect of heat-treatment on the pH sensitivity of stainless-steel electrodes as pH sensors," *Heliyon*, vol. 5, no. 3, p. e01239, 2019.

[20] U. Hashim, S. W. Chong, and W.-W. Liu, "Fabrication of Silicon Nitride Ion Sensitive Field-Effect Transistor for pH Measurement and DNA Immobilization/Hybridization," *J. Nanomater.*, vol. 2013, Article ID 542737, 9 pages, 2013.

[21] G. M. da Silva, S. G. Lemos, L. a Pocrifka, P. D. Marreto, a V Rosario, and E. C. Pereira, "Development of low-cost metal oxide pH electrodes based on the polymeric precursor method," *Anal. Chim. Acta*, vol. 616, no. 1, pp. 36–41, 2008.

[22] J. van der spiegel, I. Lauks, P. Chan, and D. Babic, 'The extended gate chemically sensitive field effect transistor as multi-species microprobe," *Sensors and Actuators*, vol. 4, pp. 291–298, 1983.

[23] P. Bergveld, "Development, Operation, and Application of the Ion-Sensitive Field-Effect Transistor as a Tool for Electrophysiology," *IEEE TRANSACTIONS ON BIOMEDICAL ENGINEERING*, no. 5, pp. 342–351, 1972.

[24] H. S. Rasheed, N. M. Ahmed, M. Z. Matjafri, N. H. Al-Hardan, M. A. Almessiere, F. A. Sabah, and N. Z. Al-Hazeem, "Multilayer ZnO/Pd/ZnO Structure as Sensing Membrane for Extended-Gate Field-Effect Transistor (EGFET) with High pH Sensitivity," *J. Electron. Mater.*, vol. 46, no. 10, pp. 5901–5908, 2017.

[25] M. Zhang, R. Wang, Z. Shen, and Y. Ji, "Extended Gate Field Effect Transistor Using GaN/Si Hybrids Nanostructures for pH Sensor," *Nano*, vol. 12, no. 9, p. 1750114, 5 pages, 2017.

[26] J. C. Chou, C. H. Liu, and C. C. Chen, "Electrochromic Property of Sol-Gel Derived TiO_2 Thin Film for pH Sensor," *5th Kuala Lumpur International Conference on Biomedical Engineering 2011. IFMBE Proceedings*, pp. 69–72, 2011.

[27] P. C. Yao, M. C. Lee, and J. L. Chiang, "Annealing Effect of Sol-Gel TiO_2 Thin Film on pH-EGFET Sensor," *2014 Int. Symp. Comput. Consum. Control*, pp. 577–580, Jun. 2014.

[28] W. F. H. Abdullah, M. Othman and M. A. M. Ali, "Chemical field-effect transistor with constant-voltage constant-current drain-source readout circuit," *2009 IEEE Student Conference on Research and Development (SCOReD)*, pp. 219-221, 2009.

[29] I. H. H. Affendi, M. S. P. Sarah, S. A. H. Alrokayan, H. A. Khan, and M. Rusop, "Effect of precursor concentration and film thickness deposited by layer on nanostructured TiO_2 thin films," *AIP Conf. Proc.*, vol. 1963, pp. 2–7, 2018.

[30] D. Fattakhova-Rohlfing, A. Zaleska, and T. Bein, "Three-Dimensional Titanium Dioxide Nanomaterials," *Chem. Rev.*, vol. 114, no. 19, pp. 9487–9558, 2014.

[31] Z. H. Stachurski, "On structure and Properties of amorphous materials," *Materials*, vol. 4, pp. 1564-1598, 2011.

[32] P. Srinivasu, S. P. Singh, A. Islam, and L. Han, "Novel approach for the synthesis of nanocrystalline anatase titania and their photovoltaic application," *Adv. Optoelectron.*, vol. 2011, Article ID 539382, 5 pages, 2011.

[33] M. M. El-Nahass, M. H. Ali, and A. El-Denglawey, "Structural and optical properties of nano-spin coated sol–gel porous TiO_2 films," *Trans. Nonferrous Met. Soc. China*, vol. 22, no. 12, pp. 3003–3011, 2012.

[34] Y. U. Ahn, E. J. Kim, H. T. Kim, and S. H. Hahn, "Variation of structural and optical properties of sol-gel TiO_2 thin films with catalyst concentration and calcination temperature," *Mater. Lett.*, vol. 57, no. 30, pp. 4660–4666, 2003.

[35] A. Nakaruk, D. Ragazzon, and C. C. Sorrell, "Anatase-rutile transformation through high-temperature annealing of titania films produced by ultrasonic spray pyrolysis," *Thin Solid Films*, vol. 518, no. 14, pp. 3735–3742, 2010.
[36] D. A. H. Hanaor and C. C. Sorrell, "Review of the anatase to rutile phase transformation," *J. Mater. Sci*., vol. 46, no. 4, pp. 855–874, 2011.
[37] W. Li, D. Du, T. Yan, D. Kong, J. You, and D. Li, "Relationship between surface hydroxyl groups and liquid-phase photocatalytic activity of titanium dioxide," *J. Colloid Interface Sci*., vol. 444, pp. 42–48, 2015.
[38] N. Yacoub, A. R. Ramadan, and J. Ragai, "Ion-Exchange and Adsorption Properties of Titania Gels Prepared from Titanous Chloride and Hydrogen Peroxide," *Adsorpt. Sci. Technol*., vol. 23, no. 3, pp. 215–224, 2005.
[39] H. Kita, N. Henmi, K. Shimazu, H. Hattori, and K. Tanabe, "Measurement of acid-base properties on metal oxide surfaces in aqueous solution," *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, vol. 77, no. 10, pp. 2451–2463, 1981.
[40] C. Hazarika and S. Sharma, "Survey on Ion Sensitive Field Effect Transistor from the View Point of pH Sensitivity and Drift," *Indian J. Sci. Technol*., vol. 10, no. 37, pp. 1–18, 2017.
[41] C.-T. Lee, Y.-S. Chiu, L.-R. Lou, S.-C. Ho, and C.-T. Chuang, "Integrated pH Sensors and Performance Improvement Mechanism of ZnO-Based," *IEEE SENSORS JOURNAL*, vol. 14, no. 2, pp. 490–496, 2014.
[42] J.-Y. Li, S.-P. Chang, S.-J. Chang, and T.-Y. Tsai, "Sensitivity of EGFET pH Sensors with TiO_2 Nanowires," *ECS Solid State Lett*., vol. 3, no. 10, pp. P123–P126, 2014.
[43] S. Lourduraj and R. V. Williams, "Effect of molarity on sol–gel routed nano TiO_2 thin films," *J. Adv. Dielectr*., vol. 7, no. 6, p. 1750042, 7 pages, 2017.
[44] R. Paul, R. N. Gayen, S. Biswas, S. V. Bhat, and R. Bhunia, "Enhanced UV detection by transparent graphene oxide/ZnO composite thin films," *RSC Adv*., vol. 6, no. 66, pp. 61661-61672, 2016.

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