

Characterization of Acrylate-based ChemFET Sensor for Nitrate Sensing and Monitoring

Nor Farhana Nazarudin, Mohd Adam Mohd Noor, Nora'zah Abdul Rashid, Dr. Gunawan Witjaksono
MIMOS Berhad, Technology Park Malaysia,
57000, Kuala Lumpur, Malaysia.
adam.noor@mimos.my

Dr. Nazrul Anuar Nayan
Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia,
43600, Bangi, Selangor, Malaysia.

Abstract—Solid-state nitrate ion sensor or nitrate-ChemFET (N-ChemFET) based on polymeric membrane materials was fabricated and developed for the determination of nitrate ion in aqueous solution. The membrane materials used consisted of methylmethacrylate (MMA) and tetrahydrofurfuryl-acrylate (THFA) as copolymers, tetraoctylammonium nitrate (TOAN) as an ion-exchanger and other lipophilic additives. N-ChemFET characterizations included a study on sensitivity, pH effect, interference, temperature effect and lifetime demonstrated good performance of N-ChemFET in sensing nitrate as an ion of interest. N-ChemFET sensor showed a lifetime of at least 3 months at room temperature (RT) where no leaching and detachment of the membrane layer occurred. Therefore, this requirement is applicable for the purpose of sensor application in the industry for monitoring the level of nitrate in aquatic environment by periodical measurement method.

Keywords—ChemFET, acrylate, nitrate sensor, plasticizer-free, nitrate monitoring.

I. INTRODUCTION

In Malaysia, human activities associated with agricultural, industrialization, urbanization, deforestation and mining activities are the main anthropogenic sources of environmental and groundwater pollution [1]. One of the major groundwater pollution comes from a high level of nitrate concentration. National Water Quality Standard (NWQS) Malaysia reported that the maximum amount of nitrate concentration in groundwater is 7 mg/L. The study conducted around Semenyih River (Selangor) and Bertam River (Cameron Highland) found that nitrate level were still below the permissible limit (< 7 mg/L) while certain areas in Kelantan River reported that nitrate level exceeding the threshold value (> 7 mg/L) [1,2,3]. River water with high level of nitrate is potentially harmful to the aquatic life and human as well [4]. Based on the literature, most of the researchers had employed the electrochemical method for the reduction or elimination of nitrate in groundwater environment [4,5,6,7,8]. However, before applying the electrochemical denitrification method, nitrate level monitoring using nitrate sensor device can be an

efficient way to ensure nitrate ion is under controlled concentration level.

Nitrate sensor or known as nitrate selective chemically modified field effect transistor (ChemFET) is a type of electrochemical sensor. Ion selective field effect transistor (ISFET) as shown on Figure 1 is an integrated circuit built from ion-selective electrode (ISE) and microelectronic technology [9]. ISFET consists of gate insulator (Si_3N_4) and metal gate oxide (SiO_2) [10,11]. By depositing a layer of ion-selective membrane on the ISFET transducer surface, ChemFET (Figure 2) is formed and developed. The response of ChemFET based on a surface active polymeric membrane is the potential difference arising at the interface of membrane/aqueous solution due to the complexation of the analyte with the ion carrier at the outer phase boundary [10]. Furthermore, ChemFET can selectively detecting ion activities of chemical elements by virtue of a selective membrane [12,13]. For instance, nitrate-selective membrane based on photocurable materials [14], ammonium ion membrane based on self-plasticising material [15] and potassium ion membrane based on acrylic material [11] were successfully fabricated and developed as ion selective ChemFET sensor device as reported in the literature.

Generally, the response of a chemical sensor is commonly influenced by membrane materials and sensor lifetime [13]. As for plasticized PVC, these widely used membrane material for ISFET suffer from the adhesion issue as well as serious limitations with respect to lifetime in various applications. The lifetime can be shortened due to leaching of the plasticizer and the electroactive components from the membrane to the contacting solution [16,17] as a result of membrane detachment from the transducer surface. The weak interaction between PVC-based membrane and ISFET surface is a disadvantage for the long-term durability of the sensor due to the lack of mechanical stability [18]. In order to prevent the leaching of ion active components from the membranes, the plasticizer-free or self-plasticizing membrane materials have been introduced [19]. This work was performed by Heng *et al.* (2001) [20] who studied on different copolymers based on acrylate-methacrylate materials. Another plasticizer-free

polymer membrane based on methyl methacrylate and decyl methacrylate (MMA-DMA) copolymer was proposed by Qin *et al.* (2003) [21]. Therefore, in this work, a nitrate ion sensor based on methacrylate-acrylate (MMA-THFA) membrane with TOAN as an ion-exchanger and other lipophilic additives has been developed and studied. The response and selectivity of nitrate ChemFET sensor in a varying ionic concentration are observed and evaluated. Temperature effect and the lifetime of the sensor have been studied as well.

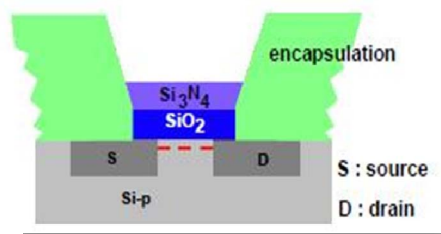


Figure 1: Cross-section view of ISFET.

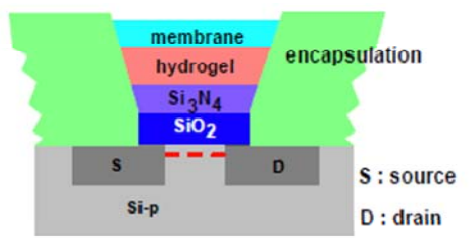


Figure 2: Cross-section view of ChemFET.

II. EXPERIMENTAL

A. Reagents and Membranes

Technical grade of 1,6-hexanedioldiacrylate (HDDA) (90% wt), methyl methacrylate (MMA) (99% wt), tetrahydrofurfuryl acrylate (THFA) and 2,2-dimethoxy-2-phenylacetophenone (DMPP) (99% wt) were purchased from Sigma-Aldrich. Chemicals of polyvinylpyrrolidone K-90 (PVP-K90), 2-hydroxyethyl methacrylate (HEMA), tetraoctylammonium nitrate (TOAN) and ethylene glycol dimethacrylate (EDGMA) were supplied by Fluka. Potassium nitrate (KNO_3), potassium sulfate (K_2SO_4), di-potassium hydrogen phosphate (K_2HPO_4) and tris(hydroxymethyl)-aminomethane hydrochloride (Tris-HCl) were obtained from Merck. Potassium chloride (KCl) with a molecular weight 74.54 g mol^{-1} was purchased from Acros Organics. All standard solutions were prepared with deionized water (DW). All chemicals used were of analytical grade and without further purification.

B. Nitrate ChemFET Fabrication

Cocktail Preparation:

Poly(2-hydroxyethyl methacrylate) or polyHEMA cocktail was prepared by mixing DMPP, PVP-K90, HEMA, EDGMA and 0.1 M potassium chloride (KCl) solution. Nitrate-membrane (N-membrane) cocktail contained a mixture of MMA, THFA, HDDA, DMPP and TOAN. The ratio of MMA to THFA used was 2 to 8 (MMA:THFA = 2:8). HEMA and N-membrane cocktails were shake slowly in a separate bottle samples until homogen. Then, the bottle samples were covered with aluminium foil and stored at room temperature for overnight prior to use for dispensing process.

Dispensing Process:

Dispensing process of polyHEMA and N-membrane cocktail was based on solvent casting technique [10,22]. $1 \mu\text{L}$ of liquid HEMA mixture was dispensed on the gate surface of ISFET. ISFET with dispensed HEMA mixture was photocured by exposure to UV light under nitrogen atmosphere for 180 s. Then, $2 \mu\text{L}$ of N-membrane cocktail was dispensed on top of the polyHEMA-based ISFET followed by photocuring or polymerization process under nitrogen atmosphere for 210 s. This N-ChemFET was conditioned with 0.01 M potassium nitrate (KNO_3) solution for 10 min. 3 units of N-ChemFETs were prepared for each measurement.

C. Nitrate-ChemFET Measurements

The response of N-ChemFET was tested in a series of KNO_3 solutions with concentration 0.1 M to 0.0001 M for sensitivity test. The effect of pH towards N-ChemFET response was tested in buffer solutions at pH 4, pH 5, pH 6, pH 7 and pH 10. For selectivity test, the response of N-ChemFET was measured with 0.1 M KNO_3 solution and the other competing ion solutions including 0.1 M sulphate (SO_4^{2-}), 0.1 M phosphate (HPO_4^{2-}) and 0.1 M chloride (Cl^-) by using separate solution method (SSM) [11,15]. The potentiometric selectivity coefficient ($\text{Log } K_{A,B}^{\text{pot}}$) of N-ChemFET towards the competing ions was calculated according to Nicolski-Eisenman equation (1).

$$\text{Log } K_{A,B}^{\text{pot}} = \frac{(E_B - E_A)_{Z_A F}}{RT \ln 10} + (1 - Z_A/Z_B) \text{Log } a_A \quad \text{Eq. (1)}$$

For temperature effect, N-ChemFET was tested in KNO_3 solutions of 0.1 M, 0.01 M, 0.001 M and 0.0001 M at temperature 15°C , 25°C and 40°C , respectively. The output signal of N-ChemFET was recorded at constant drain-current mode ($I_d = 100 \mu\text{A}$) using Agilent B1500A. For lifetime study, the stability of N-ChemFETs in accordance to the response of NO_3^- in aqueous solutions was evaluated throughout 3 months of storage at room temperature. The response measurement was measured on weekly basis.

III. RESULTS AND DISCUSSION

Sensitivity of N-ChemFETs towards nitrate ion solutions (0.1 – 0.0001 M)

The sensitivity of N-ChemFETs towards a series of nitrate solutions from 0.1 – 0.0001 M is shown on Figure 3. N-ChemFETs exhibited linear response range to NO_3^- ion from

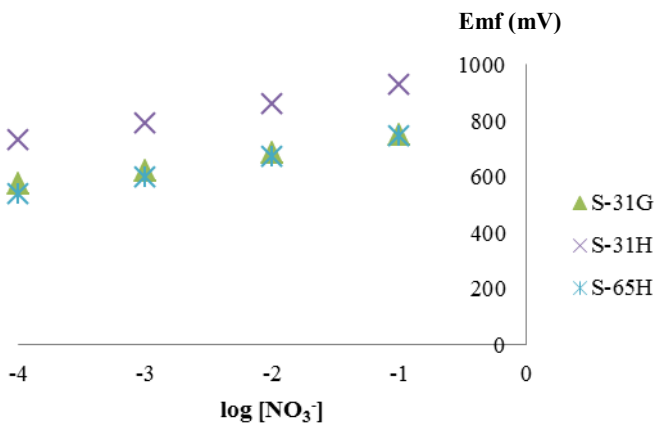


Figure 3: Response of N-ChemFETs in a series of standard KNO₃ solutions.

0.1 – 0.0001 M. The resulting sensitivity value showed within the acceptable range of 45 – 70 mV decade⁻¹ (Table 1) with linearity of $R^2=0.99$ which demonstrated that the polymeric membrane was compatible with the surface of ISFET gate oxide [11]. The acrylate groups of methyl methacrylate (MMA) and tetrahydrofurfuryl acrylate (THFA) enable the covalent binding of the membrane to the intermediate hydrogel layer or transducer surface and increase the mechanical strength of the membrane by photopolymerised cross-linking characteristic [23]. Hence, well deposited polymeric membrane layer was formed on the ISFET surface. Furthermore, the response of N-ChemFET is based on the potential difference occurred at the interface of membrane/solution due to the formation of NO_3^- -transporter complex at the border of the external phase boundary [10,11].

Table 1: Analytical performance of N-ChemFETs in NO_3^- ion solution.

N-ChemFET	Sensitivity (mv decade ⁻¹)	Linearity (R^2)	Intercept (C)
S-31G	59.20	0.99	804.50
S-31H	65.40	0.99	990.50
S-65H	68.70	0.99	811.00

pH effect of N-ChemFETs towards a series of pH solutions (pH 4, 5, 6, 7 and 10)

The pH effect of N-ChemFETs towards a series of pH solutions from pH 4, 5, 6, 7 and 10 is presented on Figure 4. This test was conducted from pH 4 to pH 10 due to the acceptable pH range that suits with the studies in aquaculture sector [24]. N-ChemFETs showed non-significant response towards protonated ion (H^+) when prepared at various pH solutions. This nitrate-deposited membrane on ISFET gate was selective to the detection of NO_3^- ion in aqueous solution, thus did not involve in the response mechanism towards H^+

ion [10,11,25]. The movement of H^+ ion at solution/membrane interphase was blocked due to the absence of H^+ -transporter complex at the interphase boundary of solution/membrane in order to captured and transported H^+ ion to pass through the

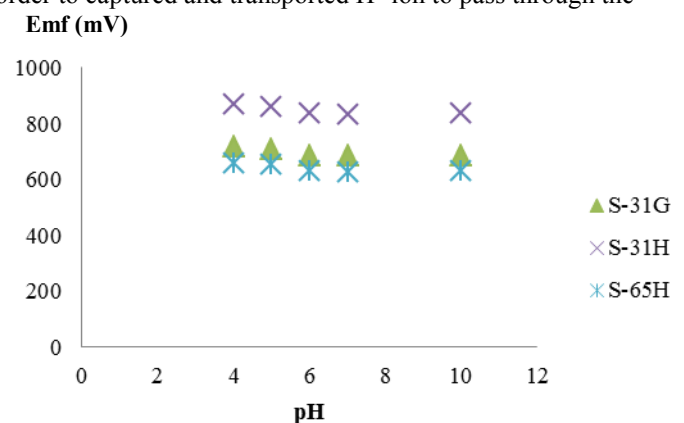


Figure 4: Response of N-ChemFETs in a series of pH solutions.

polymeric membrane layer. However, there was still internal movement of H^+ ion at the interphase of polymeric membrane/ISFET gate oxide occurred as a result of N-ChemFET transducer phenomenon [9,10].

Response of N-ChemFETs towards interfering ions

N-ChemFET was selective towards NO_3^- ion as compared to other ions especially anions due to the presence of tetraoctylammonium nitrate (TOAN) as a selective ion-exchanger for NO_3^- ion. TOAN works as a specific anion-exchanger for NO_3^- by assisting the movement of NO_3^- across membrane from aqueous solution to the transducer gate surface through ion exchange process. Thus, N-ChemFET demonstrated large response towards NO_3^- ion in sample solution [26]. Based on the results (Table 2), SO_4^{2-} and HPO_4^{2-} showed the least interfering ion to the response of N-ChemFET as compared to Cl^- . This phenomenon could be due to the smaller charge (the more negative the ionic charge) and bigger size of SO_4^{2-} and HPO_4^{2-} which caused lesser affinity of those anions to be ion-exchanged with TOAN. However, the presence of Cl^- in sample solution could interfere the detection of NO_3^- due to the same charge of NO_3^- and Cl^- which corresponds to the same size of those anions [26] to fit into the ion-transporter binding site and resulting in unstable complex [11].

Table 2: N-ChemFETs selectivity towards interfering ions.

N-ChemFET	Interfering Ion (0.1M)	$\log K_{A,B}^{\text{pot}}$
S-31G	Cl^-	-2
	SO_4^{2-}	-3
	HPO_4^{2-}	-3
S-31H	Cl^-	-2
	SO_4^{2-}	-3
	HPO_4^{2-}	-3

S-65H	Cl ⁻	-2
	SO ₄ ²⁻	-3
	HPO ₄ ²⁻	-3

Temperature effect of N-ChemFETs to the sensitivity value of sensor element at different operating temperature conditions

Temperature effect for N-ChemFETs at 15 °C, 25 °C and 40 °C operating temperature is shown on Figure 5. Operating temperature is the temperature at which the N-ChemFET elements showed stable and valid output signal, where the sensitivity value performed within the acceptable range of 45 mV decade⁻¹ (lower spec limit) to 70 mV decade⁻¹ (higher spec limit). Based on the results, N-ChemFETs exhibited increasing in sensitivity value with the increase in operating temperature from 15 °C to 40 °C. This phenomenon could be due to the rapid ions movement from the additional kinetic energy received by the ions at higher temperature, therefore increase the sensitivity of N-ChemFET sensor element towards NO₃⁻ ion in sample solutions. However, these N-ChemFETs were acceptable to be workable within the range of temperatures studied and could be used for detecting and measuring the analyte in sample solutions under the actual conditions where the temperature change continuously [11].

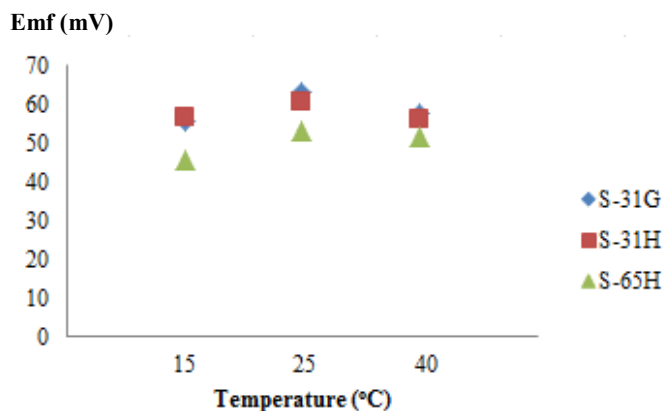


Figure 5: Temperature effect of N-ChemFETs to the sensitivity value of sensor element at 15 °C, 25 °C and 40 °C operating temperature, respectively.

Lifetime study for N-ChemFETs throughout 3 months of storage at room temperature (25 °C)

Figure 6 shows the lifetime study of N-ChemFETs when stored at room temperature (25 °C) for 3 months as standard evaluation to determine the stability of the sensor element in detecting and measuring nitrate ion. Throughout 3 months of storage, all the N-ChemFETs exhibited good response and performance in measuring the sensitivity towards NO₃⁻ ion. This result showed that all the polymeric membrane material compositions used were compatible and suitable to be functioned as nitrate sensing element. Moreover, the employment of plasticizer-free and photocurable methacrylate-acrylate (MMA-THFA) copolymers as membrane materials exhibited good adhesive property due to the covalent binding of the membrane to the transducer

surface of gate oxide [15,23]. These covalent linking in the membrane matrix could prevent the leaching issue from the sensor membrane into sample solution [23]. Hence, no sensitivity performance degradation and detachment of the membrane layer occurred for N-ChemFETs sensor within 3 months period.

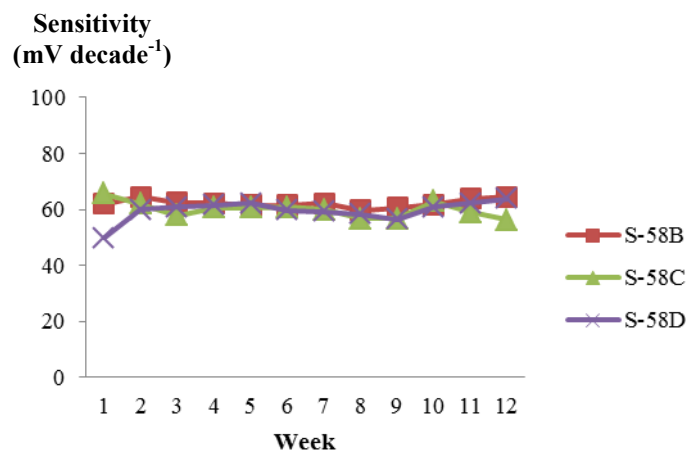


Figure 6: Lifetime of N-ChemFETs throughout 3 months of storage at room temperature (25 °C).

IV. CONCLUSION

Nitrate ion sensor (or N-ChemFET) was successfully developed and fabricated. The polymeric membrane materials composed of methacrylate-acrylate of MMA-THFA, TOAN ion exchanger and other lipophilic additives were compatible to be used and deposited on the ISFET gate surface and showed good electrochemical sensor response in detecting nitrate ion. N-ChemFET demonstrated no significant response towards different concentration of H⁺ ion, but the changes in operating temperature showed good response of N-ChemFET towards varying concentration of nitrate ion. This N-ChemFET sensor exhibited a lifetime of at least 3 months which corresponds to no leaching and no detachment of the membrane occurred within that period. Thus, this newly FET-based nitrate ion sensor showed good membrane adhesion, sensing devices and durability for the development of N-ChemFET sensor element.

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REFERENCES

- [1] F. Al-Badaii, M. Shuhaimi-Othman and M.B. Gasim (2013). "Water quality assessment of the Semenyih River, Selangor, Malaysia." *Journal of Chemistry*. 1- 10.
- [2] M.A.M. Zawawi, M.K. Yusoff, H. Hussain and S. Nasir (2010). "Nitrate-nitrogen concentration variation in

- groundwater flow in a paddy field.” *Journal-The Institution of Engineers Malaysia*. 71: 4.
- [3] W.M.A.W.M. Khalik, M.P. Abdullah, N. Padli and N.A. Amerudin (2013). “Assessment on nutrient status in water and sediment quality of Bertam River, Cameron Highlands.” *International Journal of Chemical Science*. 11: 709-720.
- [4] Z. Abaspoor, A. Goli, A. Talaiekhosani, B. Bayat, P. Ghanbarnejad, M. Bagheri, S. Alaei and G. Ziaee (2014). “Evaluation of nitrate removal from wastewater using electrochemical method.” *Journal of Environmental Treatment Techniques*. 2: 18-21.
- [5] P.K.R. Prasad, M.N. Priya and K. Palanivelu (2005). “Nitrate removal from groundwater using electrolytic reduction method.” *Indian Journal of Chemical Technology*. 12: 164-169.
- [6] L. Szyrkowicz, S. Daniele, M. Radaelli and S. Specchia (2006). “Removal of NO_3^- from water by electrochemical reduction in different reactor configurations.” *Applied Catalysis B: Environmental*. 66: 40-50.
- [7] M. Li, C. Feng, R. Zhao, Z. Zhang, X. Liu, Q. Xue, W. Ma and N. Sugiura (2011). “Efficient removal of nitrate using electrochemical-ion exchange method and pretreatment of straw with by-products for biological fermentation.” *Desalination*. 278: 275-280.
- [8] W.T. Mook, M.H. Chakrabarti, M.K. Aroua, G.M.A. Khan, B.S. Ali, M.S. Islam and M.A.A. Hassan (2012). “Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from agriculture wastewater using electrochemical technology: A review.” *Desalination*. 285: 1-13.
- [9] R. Ulber and T. Scheper (1999). “Enzyme biosensors based on ISFETs.” *Methods in Biotechnology*. 6: 35-50.
- [10] E. Moschou and N.A. Chaniotakis (2001). “Potassium selective CHEMFET based on an ion-partitioning membrane.” *Analytica Chimica Acta*. 445: 183-190.
- [11] Y.P. Ling, M.I. Syono and L.Y. Heng (2009). “A solid-state potassium ion-sensor from acrylic membrane deposited on ISFET device.” *Malaysian Journal of Chemistry*. 11: 64-72.
- [12] P. Bergveld (2003). “Thirty years of ISFETOLOGY. What happen in the past 30 years and what may happen in the next 30 years.” *Sensors and Actuators B*. 88: 1-20.
- [13] W.F.H. Abdullah, M. Othman and M.A.M. Ali (2009). “Chemical field-effect transistor with constant-voltage constant-current drain- source readout circuit.” in IEEE Student Conference on Research and Development (SCORED 2009). 16-18 Nov, 2009, UPM Serdang Malaysia.
- [14] A. Beltran, J. Artigas, C. Jimenez, R. Mas, J. Bartroll and J. Alonso (2001). “Development of durable nitrate-selective membranes for all solid state ISE and ISFET sensors based on photocurable compositions.” *Electroanalysis*. 14: 213-220.
- [15] L.Y. Heng, S. Alva and M. Ahmad (2004). “Ammonium ion sensor based on photocured and self-plasticising acrylic films for the analysis of sewage.” *Sensors and Actuators B*. 98: 160-165.
- [16] D.N. Reinhoudt, J.F.J. Engbersen and Z. Brzozka (1994). “Development of durable K^+ -selective chemically modified field effect transistors with functionalized polysiloxane membranes.” *Analytical Chemistry*. 66: 3618 – 3623.
- [17] Z. Brzozka, M. Dawgul, D. Pijanowska and W. Torbicz (1997). “Durable NH_4^+ -sensitive CHEMFET.” *Sensors and Actuators B*. 44: 527 – 531.
- [18] M.M.G. Antonisse, R.J.W. Lugtenberg, R.J.M. Egberink, J.F.J. Engbersen and D.N. Reinhoudt (1996). “Durable nitrate-selective chemically modified field effect transistors based on new polysiloxane membranes.” *Analytica Chimica Acta*. 332: 123 – 129.
- [19] Abramova, N. and Bratov, A. (2009). “Photocurable polymers for ion selective field effect transistors. 20 years of applications.” *Sensors*. 9: 7097 – 7110.
- [20] Heng, L.Y. and Hall, E.A.H. (2001). “Assessing a photocured self-plasticized acrylic membrane recipe for Na^+ and K^+ ion selective electrodes.” *Analytica Chimica Acta*. 443: 25 – 40.
- [21] Qin, Y., Peper, S., Radu, A., Ceresa, A. and Bakker E. (2003). “Plasticizer-free polymer containing a covalently immobilized Ca^{2+} -selective ionophore for potentiometric and optical sensors.” *Analytical Chemistry*. 75: 3038 – 3045.
- [22] E.J.R. Sudholter, P.D. Van Der Wal, M. Skowronska-Ptasinska, A. Van Der Berg, P. Bergveld and D.N. Reinhoudt (1990). “Modification of ISFETs by covalent anchoring of poly(hydroxyethyl methacrylate) hydrogel. Introduction of a thermodynamically defined semiconductor-sensing membrane interface.” *Analytica Chimica Acta*. 230: 59-65.
- [23] R.J.W. Lugtenberg, R.J.M. Egberink, A. Van Der Berg, J.F.J. Engbersen and D.N. Reinhoudt (1998). “The effects of covalent binding of the electroactive components in durable CHEMFET membranes-impedance spectroscopy and ion sensitivity studies.” *Journal of Electroanalytical Chemistry*. 452: 69-86.
- [24] D.S. Simbeye, J. Zhao and S. Yang (2014). “Design and development of wireless sensor networks for aquaculture monitoring and control based on virtual instruments.” *Computers and Electronics in Agriculture*. 102: 31-42.
- [25] Y. Alifragis, A. Volosirakis, N.A. Chaniotakis, G. Konstantinidis, A. Adikimenakis and A. Georgakilas (2006). “Potassium selective chemically modified field effect transistors based on AlGaN/GaN two-dimensional electron gas heterostructures.” *Biosensors and Bioelectronics*. 22: 2796-2801.
- [26] F. Faridbod, M.R. Ganjali, R. Dinarvand and P. Norouzi (2007). “The fabrication of potentiometric membrane sensors and their applications.” *African Journal of Biotechnology*. 6: 2960-2987.