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Preliminary Study of pH Sensor for Engine Oil Deterioration Detection Using Anodized Ta_2O_5 Nanotubular

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Abstract: pH sensor is one of the sensing principles that can be employed in detection of engine oil deterioration. To avoid unnecessary changing of engine oil while maintaining the oil quality consumed by car's engine, engine oil deterioration sensor is required to continuously monitor the oil condition. In this work, we fabricated pH sensor sensing layer made up of tantalum thin film. Ta_2O_5 nanotubular was constructed as the medium of interaction to measure the quality of engine oil. Anodization synthesis method was used to fabricate the sensing layer by varying the anodization time. Two samples anodized at 30 min and 60 min were tested in pH buffer solution at pH ranging from 2, 4, 7, 10 and 12. Further characterization using field emission scanning electron microscope (FESEM) was conducted to investigate the surface morphology properties, while X-ray diffraction (XRD) was conducted to obtain crystal properties of Ta_2O_5 nanotubular. A homogeneous Ta_2O_5 nanostructures with cubic crystal structure and pore diameter ranging between 15 to 20 nm was obtained. 30 min sample tested in pH buffer solution has better adsorption of H^+ ions with linear pH sensitivity of 31.616 mV/pH and good stability. Therefore, anodization method can be an alternative to fabricate pH sensor for oil deterioration detection system. Additionally, other study on chemical sensor for the detection of engine oil deterioration level was also discussed in this paper.

Keywords: Anodization, nanostructures, Ta_2O_5, pH sensor,

1. Introduction

In an automotive system, engine lubricant oil is one of the important components to facilitate the system performance. Engine oil acts as a lubricant to reduce friction, heat generation, and wear and tear on moving elements of the engine [1]. The continuous system operation will increase the consumption of lubricant oil by the car's engine and will degrade the oil quality with the increasing operation time. To maintain the performance of the automotive system. Oil must be changed in time to avoid possible engine failures. While considering the environmental and economic factors, an unnecessary oil change should be avoided. Other common issues related to the fabrication of engine oil deterioration

detection sensors are expensive cost, the complexity of fabrication method, and time-consuming other than the accuracy of the detection and sensor time response which contribute to the reliability of the sensor.

Several attempts have been made to develop engine oil deterioration sensors for rapid detection of oil properties. Previous researchers have agreed that the parameter that can be used to detect engine oil quality is in terms of total acid number [2][3][4], oil viscosity [5][6][7][8][9], oil acidity [10], oxidation index [4]. The output of oil deterioration detection can be measured by its capacitance, transmittance, and conductivity.

Previously, oil deterioration sensor systems were fabricated as capacitance sensors made up of a pair of soft copper adhesive foil quarter-cylindrical electrodes which measure the oil viscosity [8]. A metal-core piezoelectric fiber/aluminum composite was utilized to design a vibration viscosity measurement sensor capable of measuring the viscosity of engine oil, which was then used to monitor the deterioration of the oil [6]. Various concentrations of glycerin solution are used to characterize the viscosity which assembled the oil properties. To determine the oxidation level in engine oil across a range of working hours, the transmittance measurement from the IR-absorption sensor system was evaluated [11]. According to this method, the researchers discovered that engine oil with a darker colour and more working hours had a lower transmittance than engine oil with a lighter colour and fewer operating hours.

Many researchers agree that acidity is a good indicator of engine oil deterioration where the engine oil conductivity is determined by its acidity level. For the thick film H^+ ion selectivity electrochemical sensor, output voltage was generated as the result of its acidity level variation [2]. The pH sensor works by sensing the H^+ ion concentration in a solution, and a change in H^+ concentration affects the output voltage potential [12]. Metal oxides have a wide range of capabilities for detecting H^+ molecule concentrations. pH sensors have been developed by employing a variety of metal oxides because they are considered to be dependable indicators of H^+ content.

A variety of ion-sensitive metal oxides such as Iridium Dioxide (IrO_2), Ruthenium Oxide (RuO_2), Tin Oxide (SnO_2), Platinum Oxide (PtO_2), Zirconium Dioxide (ZrO_2), Tantalum Pentoxide (Ta_2O_5) are used in the production of electrochemical pH sensors [13]. Ta_2O_5 has received a lot of attention as a pH-sensitive material for the production of thin-film pH sensors due to its stability to operate in all pH ranges. Due to its unique physical features and possible applications, nanotubular metal oxide has recently piqued researchers' curiosity. By providing an immediate and quick route for electron transit, metal oxide nanotubes offer a great advantage, boosting the electron life of semiconductors. Consequently, the production of Ta_2O_5 nanotube structures is likely to be beneficial in a wide range of industries.

Several papers are available on various methods of synthesis to produce nano-structured Ta_2O_5, including anodization, sol-gel dip-coatings, hydrothermal, pulsed laser deposition, and electrodeposition. Anodization has been studied as one of the reliable methods to synthesis metal oxide nanostructures. Electrochemical reactions occur on the metal electrode's surface when an electrical flow or voltage is applied to the metal. The oxide coating will then take on a variety of shapes, including nanotubes. There are many advantages to anodizing nanotubes since the process can be precisely controlled to achieve the appropriate size and shape [14]. It is also cost-effective and easy to manipulate parameters to regulate the thickness and shape of Ta_2O_5 films by controlling the acid and chemical additive contents [15].

The properties of metal oxide nanostructures are highly dependent on their synthesis method. When a metal oxide has been synthesized, nanostructures can be constructed and it offers a high surface area to volume ratio while altering the physical and chemical properties to enhance the surface interaction. Meanwhile, synthesizing nanostructures through anodization offers great benefits because it does not require numerous steps and is easy to scale up. As the anodization parameter can be easily controlled, this method is capable to create different types of nanostructures such as nanowires [16], nanotubes [17], and nanodimpled [18].

With related to specific operating conditions, only sensors installed directly in the engine can detect the current oil condition so that the right time for an oil change can be obtained. For this purpose, suitable sensor concepts for the design of sensing elements to calculate crucial lubricant parameters have been evaluated. The anodic oxide film's growth and morphology greatly depend on the applied anodization voltage, electrolyte composition, electrolyte temperature, and length of anodization to form highly porous and ordered oxide morphology into Ta_2O_5 [19]. In this report, a potential sensing layer is introduced for oil deterioration detection based on a nanoporous Ta_2O_5 film synthesized via an anodization process.

Acknowledging the superior function of nanostructure to be developed through anodization and the outstanding properties of Ta_2O_5 in the detection of H^+, we propose a preliminary study for engine oil deterioration detection which involves the fabrication of pH sensors electrode using the anodization synthesis method. This study will develop the pH sensing layer and fabricate a reliable, simpler, and cost-efficient pH sensor with promising physical and chemical properties through anodization for engine oil deterioration from metal oxide by constructing a novel shape of Ta_2O_5 nanostructures. In addition, this research investigated the effect of different anodization duration on the properties of nanoporous Ta_2O_5.

2. Materials and Methods

2.1 Fabrication of Sensing Layer via Anodization Synthesis Method

PH sensors were fabricated, characterized, and tested with a buffer solution at different pH values. Since this is a preliminary investigation into the detection of engine oil deterioration, different pH buffer solutions are used to represent the model of used engine oil. A tantalum-based pH sensor was used as a medium to measure the interaction of pH solutions with the nanostructures constructed. To maximize the contact between the metal oxide and H^+ ions, anodization was employed to prepare nanostructures on tantalum thin film.

Tantalum anode and platinum cathode were anodized in electrolytes using the mixture of 50 ml ethylene glycol, 0.675 g of ammonium fluoride (NH_4F), 0.25 ml of sulphuric acid (H_2SO_4), and 2 ml of distilled water. The composition of this anodization electrolyte has been optimized by a previous study that is capable to create Ta_2O_5 nanotubes on the surface of tantalum thin film [17]. Each sample was anodized at ambient temperatures with durations of 30 and 60 minutes. During each experiment, the samples were anodized at a constant voltage of 20 V. Annealing process took place following the anodization. Both samples were annealed in a furnace chamber at 500°C for 2 hours.

2.2 Fabrication of pH Sensor

The sensor was fabricated by using Ta_2O_5 as the sensing layer. Approximately 30 nm of silver (Ag) was deposited via thermal evaporation on the Ta_2O_5 surface as metal contact. For its capacity to improve both electrical and mechanical qualities [20] and with great sensor stability [21], Ag was chosen as an electrode in this device fabrication. These are the elements to be considered in the fabrication of tantalum-based pH sensors which has been believed to improve sensor detection. The Electron Beam Thermal Evaporator (EBTE) was used to deposit Ag on the Ta_2O_5 layer at a pressure of 4 x 10^{-4} Pa [22]. This method can improve the metal-metal contact for electron transport.

2.3 pH Buffer Solution Testing

The Graphic User Interface (GUI) was designed using Arduino UNO hardware and MATLAB software to access the output of the fabricated sensor. After the circuit installation was performed, the Ta_2O_5 sensor was attached to the circuit and tested in 2, 4, 7, 10, and 12 buffer pH. 30 min and 60 min sensors, were dipped in the pH buffer solution, and the voltage potential for each pH buffer solution was presented in the GUI. The configuration of pH buffer testing is represented in Fig. 1.
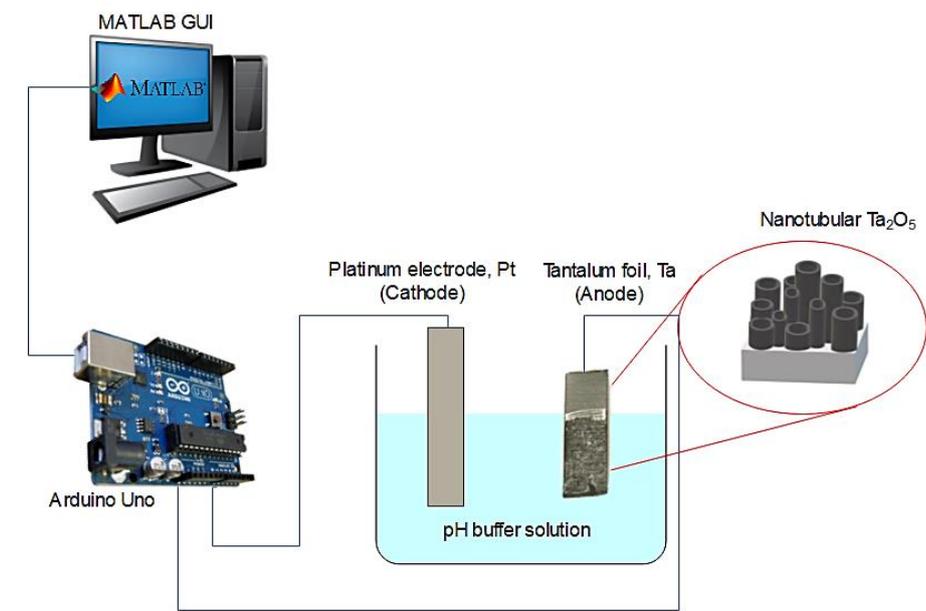

Fig. 1 - Schematic diagram of the pH sensor testing configuration for Ta_2O_5 nanotubular tested in pH 2, 4, 7, 10 and 12 pH solution

2.4 Characterization

After the Ta_2O_5 sensing layer was prepared through anodization and annealing, characterization was conducted to obtain the physical and chemical properties of Ta_2O_5 nanotubular. The properties of the Ta_2O_5 were investigated by field emission scanning electron microscope (FESEM) for surface morphology and structural analysis, and their crystalline properties by X-ray diffraction (XRD).

3. Result and Discussion

3.1 Formation of Ta_2O_5 and Highly Crystalline Nanotubular

Anodization is one of the simplest, inexpensive, and best methods to shape a sample of nanoporous Ta_2O_5. The preparation was also easy to understand, as the majority of the tools and equipment used were readily available, making it one of the most effective methods of synthesizing nanoporous samples. Normal anodization setup included the application of a power source to two electrodes that were submerged in an electrolyte. An electrical current or voltage was applied which resulted in an electrochemical reaction occurring on the metal electrode surface and thus forming an oxide film. Once anodization started, compact oxide layer started to form on top of the tantalum layer [24]. Further anodization will produce porous structure and prolong the anodization time will lead to rupture of porous wall, and leaving nanotubular structure at nanoscale diameter [25]. As anodization time can be manipulated, we can control the morphology and size of nanostructures constructed. Thus, this method is efficient to optimize the nanostructures.

The anodized sample was primarily amorphous, and it needed a post-annealing process to turn it into a highly crystalline nanoporous morphology [26]. Highly crystalline Ta_2O_5 nanotubular was established by annealing after anodization. Heat treatment can be used to alter the physical and chemical properties of nanostructured materials while boosting their functionality, hardness, and ductility. When samples of Ta_2O_5 are heated to the recrystallization temperature for two hours at 500°C in a furnace chamber, this process is known as annealing. Changing a Ta_2O_5 nanotube structure from crystalline to nanotubular necessitated this step. Fig. 2 depicts a comparison of the samples before and after annealing. Samples become whiteish-gray in colour and smooth in texture after being annealed. This physical appearance can be an initial indicator to report that the crystallinity of Ta_2O_5 nanotubular has been improved. In the following part, the crystal characteristics are confirmed using XRD characterization.
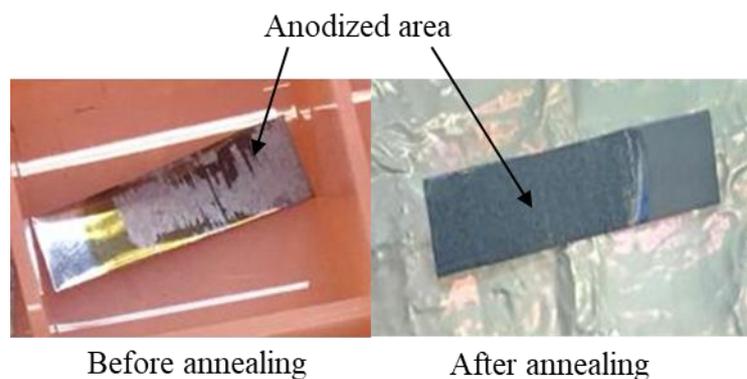

Fig. 2 - Effect of annealing treatment produce whitish-gray structure as the initial indicator for crystalline structure of Ta_2O_5 nanotubular

3.2 Surface Morphology by Field Emission Scanning Electron Microscopy (FESEM) Characterization

The Ta_2O_5 nanotubular surface morphology was visualized with the aid of FESEM characterization. FESEM was used to examine the formation of nanostructure and pore dimension. Fig. 3 shows the surface of nanotubular Ta_2O_5 after it has been subjected to an anodization and annealing process. The nanotubular Ta_2O_5 structures were constructed by anodizing samples for 30 min and 60 min in an optimum electrolyte. Nanotube structures became more visible and thicker pore walls as anodization time went on for longer periods. Fig. 3(a) shows high homogeneity possessed of Ta_2O_5 nanotubular distribution formed at 50 000× magnifications. Similar to previous studies conducted using the same material and electrolyte composition for fabrication of UV sensor [17] and humidity sensor [27], the average diameter of the pores constructed in this study ranged from 15 to 20 nm as visualized in Fig 3(b) at 100 000× magnifications. The high homogeneity of Ta_2O_5 nanotubular achieved through anodization provides high surface area for the medium of interaction for H^+ ions interaction which facilitates the pH sensor mechanism. Hence, this method can establish a reliable surface for interaction with H^+ ions in pH detection.
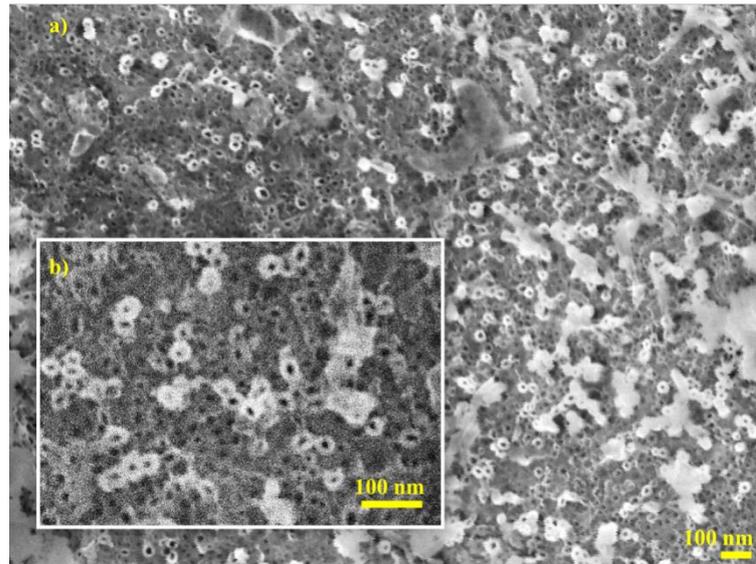
Fig. 3 - FESEM image display the homogenous Ta$_2$O$_5$ nanotubular at (a) 50 000× magnifications with pore diameter between 15 to 20 nm measured at; (b) 100 000× magnifications

3.3 Crystal Properties by X-Ray Diffraction (XRD) Characterization

The crystallinity of Ta$_2$O$_5$ has been investigated by XRD (PANalytical X'Pert PRO). Before annealing, the physical structure of the anodized part appears to be grey in colour and the XRD result shows an amorphous structure due to the presence of an amorphous peak. After annealing at 500 ºC for 2h, the amorphous nanostructure has been transformed into a cubic crystalline structure where we can see the anodized part turns to the white surface and XRD result shows the decreasing in amorphous peak intensity and Ta$_2$O$_5$ peak starts to appear. After the annealing procedure, a Ta$_2$O$_5$ nanotubular structure with a high degree of crystallinity can be formed. The crystallinity qualities of materials can be altered through annealing. To prepare a good interaction medium for the pH sensor, Ta$_2$O$_5$ must be annealed at a temperature where it transitions from an amorphous to a cubic crystal structure.

Due to its lack of crystallinity, the peak of amorphous Ta$_2$O$_5$ has shown a minor peak in Fig. 4. Peaks has been observed at 37.8°, 54.9°, and 69° in the as-anodized sample which correspond to amorphous peak. Ta$_2$O$_5$ cubic phase peaks appeared at 30.3°, 50.9°, and 66.1° in the 2-theta diffraction spectrum after annealing. According to the XRD results, nanotubular Ta$_2$O$_5$ as-anodized only reveals the metallic phase of Ta, indicating that the as-anodized was amorphous. To obtain crystallized material, an annealing step is necessary for this work. Thermal, mechanical, electrical, and optical stability of the Ta$_2$O$_5$ metal oxide structure can be improved through the crystalline structure. There may have been an influence on the formation of distinct electronic orbitals and lattice defects that are typically responsible for catalysis by the presence of crystalline walls [28]. As previously reported, a cubic crystalline structure can be formed after 2 hours of heating at 500°C, as demonstrated in this study [29].
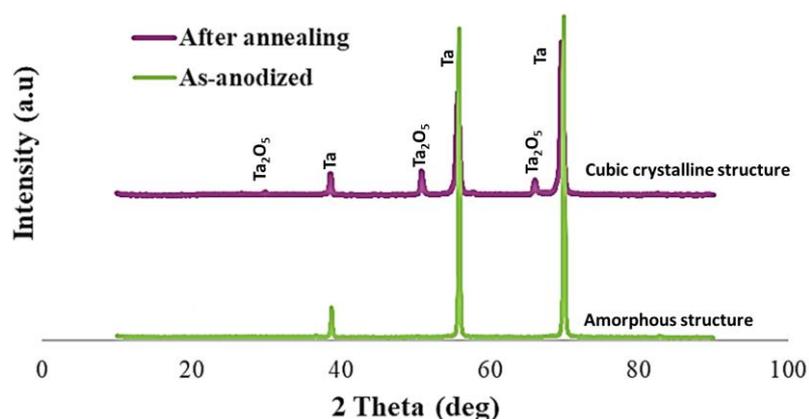

Fig. 4 - XRD diffraction peak indicate the transformation of amorphous structure to cubic crystal structure of Ta$_2$O$_5$ nanotubular after annealing at 500 ºC for 2 h, reprinted from [23] with permission from IEEE Xplore

3.4 Performance of Ta_2O_5 Nanotubular as Ph Sensor

The sensitivity of the Ta_2O_5 pH sensor for 30 min and 60 min samples were obtained as in Fig. 5. It can be observed that 30 min and 60 min anodized samples give the same trend when immersed in different pH solutions ranging from 2, 4, 7, 10, and 12. Based on the output voltage, both sensors operated at different sensitivity in acidic and alkaline environment. Voltage output decrease linearly with increasing of pH as recorded in Table 1. This can be concluded that voltage output varies linearly with the H^+ content in the solution. The alkaline solutions give lower voltage reading than the neutral solution and acidic solutions for both 30 min and 60 min anodized samples as acidic solution contain higher concentration of H^+ ions. In alkaline solution, the sensitivity of 30 min sensor is 51.4 mV/pH and the sensitivity of 60 min is 35 mV/pH. Meanwhile, 30 min and 60 min sensor operated at 11.8 mV/pH and 14.2 mV/pH, respectively, in acidic solution.

Table 1 - Output voltage reading for 30 min and 60 min in different pH solution

pH Value	30 min	60 min
2	4.555	4.532
4	4.543	4.520
7	4.496	4.461
10	4.461	4.438
12	4.239	4.286
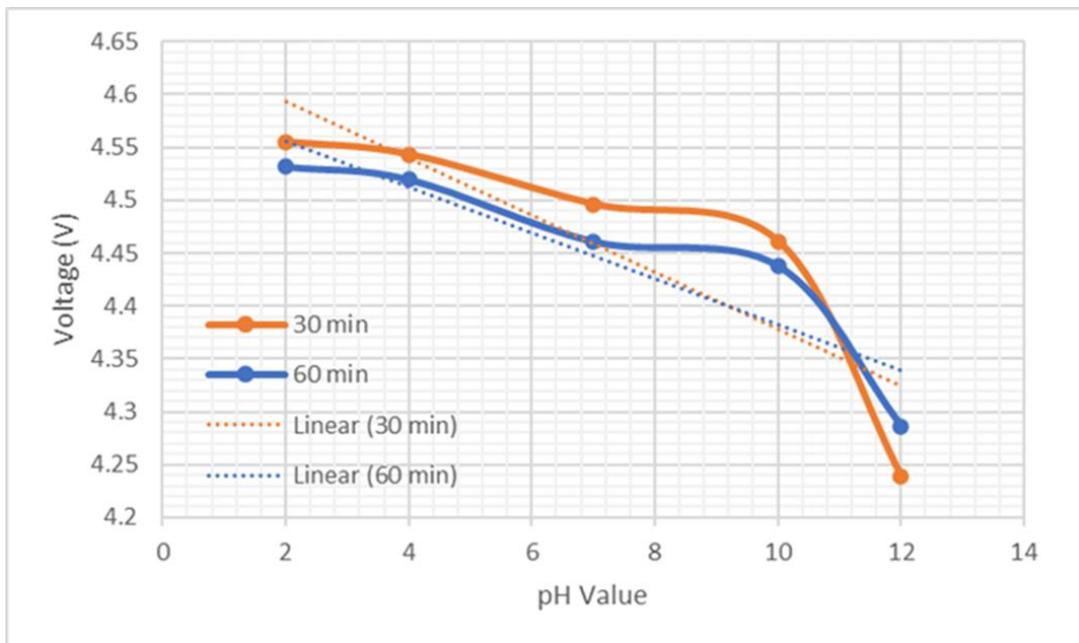
Polynomial and linear function of the curve:

30 min $\quad y = -0.0003x^4 + 0.0065x^3 - 0.0563x^2 + 0.1818x + 4.3462$

60 min $\quad y = -0.0003x^4 + 0.007x^3 - 0.0582x^2 + 0.1826x + 4.3714$

Linear (30 min) $\quad y = -0.0269x + 4.6468$

Linear (60 min) $\quad y = -0.0217x + 4.5993$

Fig. 5 - Sensitivity of 30 min and 60 min sensor in acidic and alkaline solution

Engine oil or lubricant oil is composed of hydrocarbon. Increasing the operating hour or mileage of vehicles will increase water content inside the engine oil [3][4]. This condition will result in decreasing of fuel and anti-wear agent in the oil and as the consequence, H^+ molecules will increase in which decrease the pH value. By testing in acidic and alkaline pH conditions, we can observe the relationship between pH and voltage output. Increasing the pH resulted in a decrease in voltage. Voltages were higher in an acidic environment compared to an alkaline one. pH is a measurement of a solution's acidity level based on the concentration of the H^+ ion. When the pH is low, which is linked with a high acidity level, the concentration of hydrogen ions that interact with the surface area of Ta_2O_5 is larger, resulting in a higher potential for voltage generation [30]. In comparison to the 60 min sample, the 30 min sample produced a larger voltage output, indicating that the Ta_2O_5 nanotubular created as the medium of interaction on the 30 min sensor is more conducive for H^+ ion binding.

In sensing detection, the morphology of the nanostructures is an important key factor to determine the sensor performance. For Ta_2O_5 pH sensors, the oxygen-vacancy on nanostructures plays a crucial role. During the fabrication of Ta_2O_5 nanotubular, anodization time will give significant effects on the thickness of the oxide layer, the diameter of the pore, and the wall of the pore. pH sensitivity had been calculated using the voltage reading of pH solution ranging from pH 2 to pH 12 solution for both samples. These voltage values were used in the equation as below [3],

$$pH\ Sensitivity = \left|\frac{v_{pH2} - V_{pH12}}{pH_2 - pH_{12}}\right| \qquad (1)$$

From the equation, the pH sensitivity for 30 min and 60 min samples were 31.616 mV/pH and 24.591 mV/pH, respectively. 30 min sample achieved better sensitivity than 60 min due to the structure of Ta_2O_5 nanotubular produced on the thin film surface consisting of thinner pore wall which could be the reason to facilitate the binding of H^+ ions on the surface. A thicker pore wall requires a longer time for the H^+ ions to adsorb into the Ta_2O_5 surface which slows the process and make the Ta_2O_5 surface less sensitive to detect the analyte.

The response time is the time it takes for the sensor resistance to reach 90% of its steady-state value for the current to accumulate from baseline to the highest peak. The recovery time is the time it takes for the total resistance change to reach 90% of its steady-state value where the current decreases to the lowest peak [31]. The pH value is alternately changed from acidic to basic solution and vice versa to study the response time of the sensor, and the output potential is measured. The response time of the pH sensor is highly influenced by the morphology of the sensing layer [32]. Nanostructures homogeneity, pore diameter, pore thickness, and the thickness of the oxide layer can directly affect the performance of the pH sensor.

As the comparison for time response with the existing research, 30 min sample of Ta_2O_5 nanotubular in this study has obtained response time of 20 s while recovery time of 90 s. response and recovery time are often associated with the energy required to break the bond between the surface and the molecules. Rapid desorption of water molecules resulted in a shorter recovery time because the energy required to break the link between Ta_2O_5 and water molecules was lower than the energy necessary to bind them together during adsorption, resulting in a longer response time [22]. The response time for RuO_2-Ta_2O_5 is more than 15 s [33] and Tungsten Oxide is 150 s [12] had been obtained from previous research. The response time of the RuO_2-Ta_2O_5 based pH sensor is shorter and more dependent on the solution pH. Besides, the response time of the metal oxide-based pH sensor may likewise be subject to the structural properties and morphology of the film. The nanostructured nature and porosity of the fabricated film may improve the response time of the sensor [34].

To evaluate the stability and repeatability of Ta_2O_5 nanotubular pH sensor performance, the sensor was exposed to a maximum and minimum pH range to obtain three repetitive cycles of the voltage output response The stability of the Ta_2O_5 nanotubular pH sensor is visualized in Fig. 6. The voltage output for each cycle were computed based on the Table 1. By consecutively measuring sample in neutral pH, measured pH and back to neutral pH, the voltage output for 1 complete cycle is obtained. A pH buffer solution of 2, 4, 7, 10 and 12 are involved in this measurement. This method was repeated for 3 repetitive cycle to determine the repeatability and stability of the testing sensor. Both 30 min samples and 60 min samples are said to exhibit stable voltage output in different pH solutions. The output pattern shows a decreasing steady-state voltage with an increasing pH. This condition can be said that voltage output decreases linearly with the content of H^+ ions in the solution. Since the output voltage is constant throughout three repetitive cycles; thus, this sensor is considered to perform excellent stability in long-term exposure. 30 min sensor require a shorter time to achieve one complete cycle and fewer ripples are produced in 30 min sensor output signal indicates its long-term stability.

In this project, the tantalum thin film has been fabricated through the anodization and annealing process to obtain cubic crystalline structure with pore diameter ranging between 15 to 20 nm. Ta_2O_5 metal oxide has many useful potential applications as sensor and oil detection mechanisms. The existing research has proved that metal oxide material can be a good detection or sensor mechanism to check the quality of any type of engine oil, thus the literature on oil deterioration detection was carried out [2]. The researcher mentioned that the thick film (TF) which is the metal oxide can be helpful in the ionization and detection mechanism of H^+ of engine oil. The Ruthenium Oxide based sensor as shown in Fig. 7 is used in this work in the detection of acid content in chemically aged base and fully refined engine oil. acidity was the comparatively long response time of the sensor and the effect of lubricant operating conditions, e.g. water, wear debris, etc. on sensor responses under actual operation conditions. To determine oil acidity, thick-film ion-selective electrodes

(ISE) and bare silver reference electrodes function together as a pH sensor generating an electro potential voltage output. Two different types of TF working electrodes were fabricated which are a Platinum gold conductor with a layer of polymer-based ruthenium oxide (RuO_2) and a Platinum gold conductor with a layer of glass-based ruthenium oxide (RuO_2). In this case, the polymer-based electrode only works and can be tested up to a maximum temperature of approximately 100 °C. Meanwhile, glass-based electrodes can be tested at a higher temperature. Engine oil typically operates in combustion cylinders in extremely high-temperature conditions and the oil should be heated to close to 400 °C to 600 °C [35].
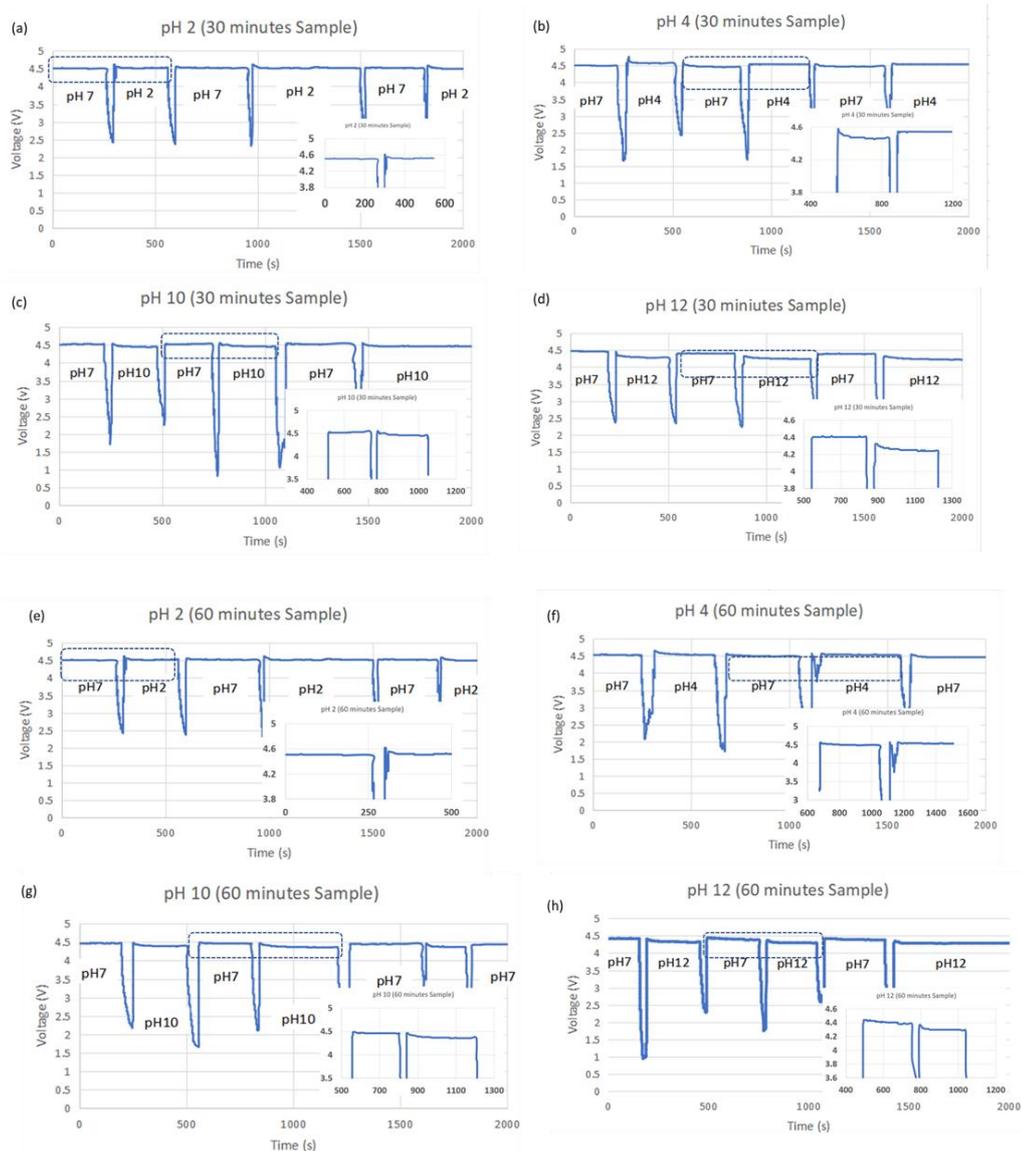

Fig. 6 - Output voltage in 3 repetitive cycles for 30 min in pH (a)7-2-7; (b) 7-4-7; (c) 7-10-7; (d) 7-12-7 and 60 min sample in pH; (e) 7-2-7, f) 7-4-7; (g) 7-10-7; (h) 7-12-7 tested in both acidic and alkaline pH condition to obtain the repeatability and stability for both sensor

Several studies have been reported on the oil deterioration detection mechanism which is the capacitive engine oil sensor to detect the effect of engine oil deterioration of change in viscosity and capacitance [8]. To demonstrate the feasibility of a viscometer for measuring the oil viscosity and capacitance, oil samples were collected from cars at random intervals after the oil change. Then, the sensor is fabricated and the sample of the oil was being tested with an interface circuit that connected to a computer.

Additionally, several researchers have applied metal-core piezoelectric fiber/aluminum composite as a sensor for monitoring engine oil viscosity [6]. This material is a piezoelectric ceramic (Fig. 8), reinforced by a metal matrix; it is intended to be used in extreme conditions such as the interior of an engine. To track differences in the viscosity of glycerin solution as a liquid pattern, an active form measurement system was employed. In this approach, a self-generated vibration is compared to a liquid's viscosity by calculating the intensity of the damp vibration and the resonance frequency

variance. Results showed a high sensitivity of the vibration to the liquid viscosity; further, it was observed that the resonance frequency shift correlated to a wider range of measurable viscosity. Both determined parameters suggest that the piezoelectric metal-core fiber/aluminum composite is a viable sensor for tracking the deterioration of engine oil.
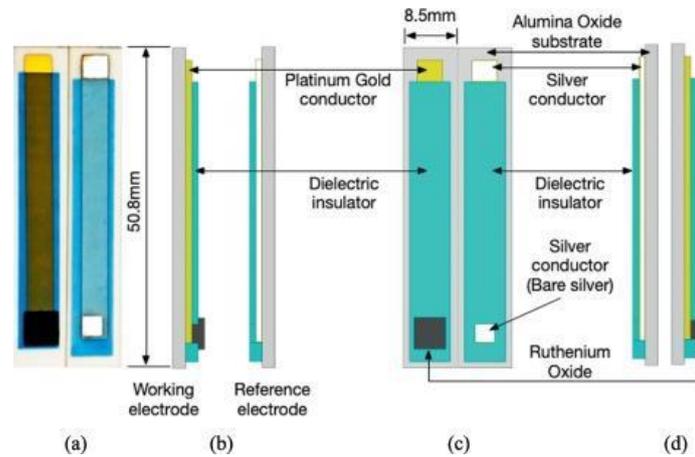

Fig. 7 - Dimensions of the thick-film sensor and working and reference electrode placements (a) TF sensor WE and RE; (b) side to side; (c) side by side; (d) back to back. Reprinted from ref. [2] published by Elsevier as open access

Several researchers have found that the oil deterioration mechanism can be used in the Electrochemical Bead Method which is in this method a polymeric bead matrix comprising group that assists as a conductive terrace for tracking the solvent properties of lubricant oil or engine oil [36]. It functions close to the battery functions in this method. The activated resin beads are embedded in milligram size between two conductive surfaces separated by a non-conductive matrix. In addition, the charged groups of beads composed of both anions and cations can shift to form an electrochemical relation of greater intensity subject to a relative change in oil polarity. As the engine oils are relatively nonpolar and the beads are ionic, a conductive bridge is not designed for the beads. When the lubricant starts to deteriorate, the solvent becomes more polar, as it contributes to ionic connections and a structure starts to shape. The comparative alteration of conductivity between these two conductive surfaces is further evaluated. Thus, to get a value from the testing, a calculation of the oil deterioration is the same as the pH sensitivity calculation method. This is because metal oxide such as Tantalum pentoxide, Ta_2O_5, and Ruthenium Oxide, RuO_2, can measure acidity level in lubricating or engine oil [3]. The oil deterioration sensitivity can be calculated by using the voltage reading value when the expected sample was immersed in engine oil. Equation (2) was the sample calculation of oil deterioration sensitivity.

$$Oil\ deterioration\ sensitivity = \left| \frac{V_{pH\ oil\ deterioration\ 1} - V_{pH oil\ deterioration\ 2}}{pH_{oil\ deterioration\ 1} - pH_{oil\ deterioration\ 2}} \right| \tag{2}$$

From equation 2, the oil deterioration sensitivity calculation uses the same principle calculation as pH sensitivity. This sensor employs a similar mechanism of pH detection as in this study through different synthesis methods to fabricate the sensing layer. To improve the adsorption properties of Ta_2O_5 through anodization, enhancement can be done by manipulating the anodization parameter such as electrolyte composition, anodization voltage, and anodization time to construct novel nanostructures with the desired physical and chemical properties, maximize the surface area for the medium of interaction and improve adhesion of nanotubular on the substrate. Hence, Ta_2O_5 nanotubular fabricated via anodization has proven its reliability to be employed as a sensing layer in pH sensors in the engine oil deterioration detection.
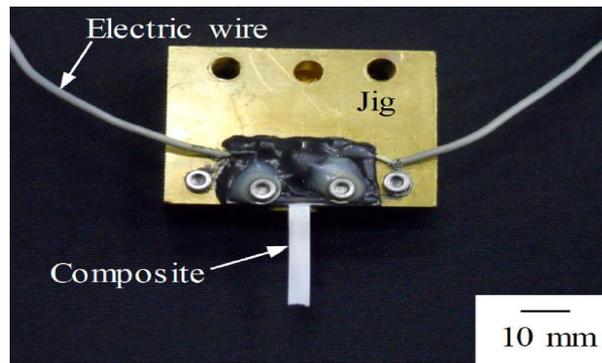
Fig. 8 - Picture of fabricated sensor and jig. Reprinted from ref. [6] published by MDPI as open access

4. Conclusion

This study has successfully fabricated an alternative pH sensor made up of Ta_2O_5 nanotubular to be implemented as a sensing layer in engine oil deterioration detection. Synthesizing nanostructures through anodization method using electrolyte composed of ethylene glycol, H_2SO_4, NH_4F, and distilled water has produced homogeneous Ta_2O_5 nanostructures with pore diameter ranging between 15 to 20 nm. Cubic crystalline structure can be achieved through annealing at 500º C for 2 hours thus improving its crystalline structure and generating a favourable medium of interaction. Shorter anodization duration produces nanostructures with better adsorption of H^+ ions with linear pH sensitivity of 31.616 mV/pH and 24.591 mV/pH for 30 min and 60 min samples respectively. Besides, the anodized Ta_2O_5 based pH sensor possessed good response time as well as constant stability and repeatability in long exposure. Therefore, anodization is a promising method to create nanostructures of metal oxide and enhance the physical and chemical properties to improve H^+ molecules adsorption on the Ta_2O_5 surface.

Acknowledgement

References

[1] A. N. Farhana and M. Z. Bahak, "Engine oil wear resistance," J. Tribol., vol. 53, no. 9, pp. 1689–1699, 2013.

[2] K. Yang, L. Wang, and J. Atkinson, "An investigation of factors influencing the response of screen printed thick film electrochemical sensors in the monitoring of lubrication oil ageing," Sens. Bio-Sensing Res., vol. 23, 2019, doi: 10.1016/j.sbsr.2019.100273.

[3] L. Wang, R. J. K. Wood, and R. I. Taylor, "Engine Oil Acidity Detection Using Solid State Ion Selective Electrodes," Tribiology Int., 2013, doi: 10.1016/j.triboint.2013.02.030.

[4] F. Zhou and K. Yang, "The Influence of Water Content on the Acid Number of Diesel Engine Lubricant in Electrochemical Measurement The Influence of Water Content on the Acid Number of Diesel Engine Lubricant in Electrochemical Measurement," 2021, doi: 10.1088/1757-899X/1043/5/052054.

[5] A. A. Bhosale and P. Mundhe, "Analysis of Lubricating Oil Deterioration in Four-Wheeler," Appl. Mech. Mater., no. November 2013, pp. 1–6, 2015, doi: 10.4028/www.scientific.net/AMM.446-447.558.

[6] T. Yanaseko, H. Sato, I. Kuboki, K. Mossi, and H. Asanuma, "Vibration Viscosity Sensor for Engine Oil Monitoring Using Metal Matrix Piezoelectric Composite," Materials (Basel)., vol. 12, no. 3415, 2019.

[7] H. Shinde, "Analyzing the relationship between the deterioration of engine oil in terms of change in viscosity , conductivity and transmittance," 2017 Int. Conf. Adv. Mech. Ind. Autom. Manag. Syst. Anal., pp. 36–41, 2017.

[8] H. M. Shinde and A. Bewoor, "Capacitive sensor for engine oil deterioration measurement," AIP Conf. Proc. ·, vol. 1943, 2018, doi: 10.1063/1.5029675.

[9] C. Series, "Predicting the next oil change for automotive engine oil," 2019, doi: 10.1088/1742-6596/1349/1/012018.

[10] D. K. Maurya, A. Sardarinejad, and K. Alameh, "Ruthenium oxide ion selective thin-film electrodes for engine oil acidity monitoring," Meas. Sci. Technol., vol. 065102, p. 65102, 2015, doi: 10.1088/0957-0233/26/6/065102.

[11] A. Agoston, C. Ötsch, J. Zhuravleva, and B. Jakoby, "An IR-Absorption Sensor System for the Determination of Engine Oil Deterioration," pp. 463–466, 2004.

[12] M. Jamal, K. M. Razee, S. Han, J. Islam, and I. Ak, "Development of Tungsten Oxide Nanoparticle Modified Carbon Fibre Cloth as Flexible pH Sensor," Sci. Rep., vol. 9, no. 4659, pp. 1–9, 2019, doi: 10.1038/s41598-019-41331-w.

[13] L. Manjakkal, K. Cvejin, J. Kulawik, K. Zaraska, R. P. Socha, and D. Szwagierczak, "X-ray photoelectron spectroscopic and electrochemical impedance spectroscopic analysis of RuO_2-Ta_2O_5 thick film pH sensors," Anal. Chim. Acta J., vol. 931, pp. 47–56, 2016, doi: 10.1016/j.aca.2016.05.012.

[14] P. Batista-Grau, R. M. Fernández-Domene, R. Sánchez-Tovar, and J. García-Antón, "Control on the morphology and photoelectrocatalytic properties of ZnO nanostructures by simple anodization varying electrolyte composition," J. Electroanal. Chem., p. 114933, 2020, doi: 10.1016/j.jelechem.2020.114933.

[15] M. R. Nickel, G. Melligan, T. P. W. Mcmullen, and R. E. Burrell, "The effect of chemical additives in phosphoric acid anodization of aluminum-tantalum thin films," Thin Solid Films, vol. 685, pp. 245–253, 2019, doi: 10.1016/j.tsf.2019.06.033.

[16] P. R. Reddy, K. M. Ajith, and N. K. Udayashankar, "Optical and mechanical studies on free standing amorphous anodic porous alumina formed in oxalic and sulphuric acid," Appl. Phys. A Mater. Sci. Process., vol. 124, no. 11, p. 0, 2018, doi: 10.1007/s00339-018-2163-7.

[17] M. A. Abu Talip et al., "Nanotubular Ta_2O_5 as ultraviolet (UV) photodetector," J. Mater. Sci. Mater. Electron., vol. 30, no. 5, pp. 4953–4966, 2019, doi: 10.1007/s10854-019-00792-5.

[18] R. Kisslinger et al., "Nonlithographic Formation of Ta_2O_5 Nanodimple Arrays Using Electrochemical Anodization and Their Use in Plasmonic Photocatalysis for Enhancement of Local Field and Catalytic Activity," 2021, doi: 10.1021/acsami.0c18580.

[19] L. Fialho, C. F. A. Alves, L. S. Marques, and S. Carvalho, "Development of stacked porous tantalum oxide layers by anodization," Appl. Surf. Sci., vol. 511, no. August 2019, p. 145542, 2020, doi: 10.1016/j.apsusc.2020.145542.

[20] H. Li et al., "Carbon electrode with conductivity improvement using silver nanowires for high-performance supercapacitor," Appl. Phys. A, vol. 0, no. 0, p. 0, 2018, doi: 10.1007/s00339-018-2182-4.

[21] C. Mayousse, C. Celle, A. Fraczkiewicz, and J.-P. Simonato, "Stability of silver nanowire based electrodes under environmental and electrical stresses," Nanoscale, 2014, doi: 10.1039/C4NR06783E.

[22] R. A. Rani, A. Sabirin, M. F. Mohamad, A. S. Ismail, and M. H. Mamat, "High Surface Area to Volume Ratio 3D Nanoporous Nb2O5 for Enhanced Humidity Sensing," J. Electron. Mater., 2019, doi: 10.1007/s11664-019-07126-5.

[23] N. L. S. Ngadiman et al., "Determination of the pH sensitivity level of anodized Ta_2O_5 nanotubular using pH buffer solution: Towards engine oil deterioration sensor," Proc. - 2021 IEEE Reg. Symp. Micro Nanoelectron. RSM 2021, pp. 46–49, 2021, doi: 10.1109/RSM52397.2021.9511581.

[24] M. A. Abu Talip et al., "Mechanism of Nanotubular Ta_2O_5 via Anodization in NH_4F / H_2SO_4 / H_2O Solution," Int. J. Electr. Electron. Syst. Res., vol. 13, pp. 2–9, 2018.

[25] W. Chen et al., "Study on morphology evolution of anodic tantalum oxide films in different using stages of H2SO4/HF electrolyte," Electrochim. Acta, 2017, doi: 10.1016/j.electacta.2017.03.024.

[26] N. Alias, S. A. Rosli, N. Bashirom, M. Rozana, Z. Hussain, and Z. Lockman, "Oxide nanotubes formation by anodic process and their application in photochemical reactions for heavy metal removal," in Nanostructured Anodic Metal Oxides, INC, 2020, pp. 277–304.

[27] N. L. S. Ngadiman et al., "Humidity Response of Ta_2O_5 Sensor at Different Bias Voltages," 2020 IEEE Int. Conf. Semicond. Electron., pp. 33–36, 2020.

[28] W. Yue and W. Zhou, "Crystalline mesoporous metal oxide," Prog. Nat. Sci., vol. 18, no. 11, pp. 1329–1338, 2008, doi: 10.1016/j.pnsc.2008.05.010.

[29] S. Maeng, L. Axe, T. Tyson, and A. Jiang, "An Investigation of Structures of Thermal and Anodic Tantalum Oxide Films," J. Electrochem. Soc. ·, no. August 2015, pp. 3–8, 2005, doi: 10.1149/1.1850362.

[30] J. Yeo, S. Lee, Y. Jo, and H. Jung, "Characterization of Anodic Aluminum Oxide Membrane with Variation of Crystallizing Temperature for pH Sensor," J. Nanosci. Nanotechnol., vol. 15, no. 11, pp. 8642–8646, 2015, doi: 10.1166/jnn.2015.11506.

[31] M. B. Rahmani, M. H. Yaacob, and Y. M. Sabri, "Hydrogen Sensors Based on 2D WO_3 Nanosheets Prepared by Anodization," Sensors Actuators B. Chem., 2017, doi: 10.1016/j.snb.2017.05.029.

[32] L. Manjakkal, D. Szwagierczak, and R. Dahiya, "Metal oxides based electrochemical pH sensors : Current progress and future perspectives," Prog. Mater. Sci., vol. 109, no. December 2019, p. 100635, 2020, doi: 10.1016/j.pmatsci.2019.100635.

[33] L. Manjakkal, K. Zaraska, J. Kulawik, and D. Szwagierczak, "Potentiometric RuO_2-Ta_2O_5 pH Sensors fabricated using thick film and LTCC Technologies," Talanta, 2015, doi: 10.1016/j.talanta.2015.09.069.

[34] S. Y. Hussein, S. A. Kakil, T. A. H. Abbas, and L. H. Slewa, "High-sensitive UV photodetector based on ZrO_2 nanoparticles for humidity applications," J. Mater. Sci. Mater. Electron., vol. 31, no. 18, pp. 15466–15476, 2020, doi: 10.1007/s10854-020-04109-9.

[35] F. Owrang, H. Mattsson, J. Olsson, and J. Pedersen, "Investigation of oxidation of a mineral and a synthetic engine oil," vol. 413, pp. 241–248, 2004, doi: 10.1016/j.tca.2003.09.016.

[36] A. Rammohan, "Engine's lubrication oil degradation reasons and detection methods : A review," J. Chem. Pharm. Sci., vol. 9, no. 4, pp. 3363–3366, 2016.