

Anodized Aluminium Oxide Coating for Sensitive Sensing of Folic acid in Vegetables and Control of Dyeing

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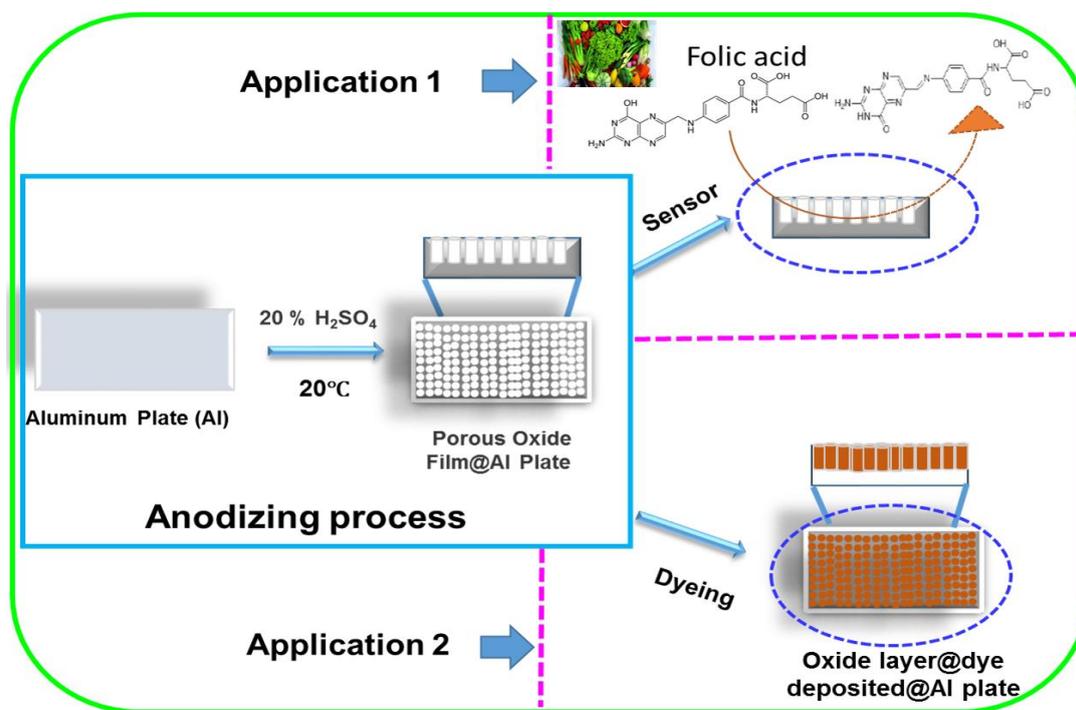
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Aluminum electrochemical anodizing dyed products have been widely used in various sectors of industries including cell phone, laptop computers, bikes and aero-space technologies. During the process of aluminum electrochemical anodizing dyeing industry, and waste water which contains dyestuffs tend to be emitted and most of them comes from the color bleeding during the process of sealing; therefore, the topic of how to reduce the color bleeding efficiency during the sealing process and decrease dyed waste water generated becomes a huge environmental issue. In the research, the factors which cause the color bleeding during the sealing process are thoroughly discussed and ratified in a careful manner. Statistical analysis is conducted to analyze how color bleeding is influenced by different dyeing temperatures and various film thickness formed in different time frame of aluminum electrochemical anodizing dyeing. Moreover, aluminum electrochemical anodizing electrode carried out into electrochemical process; the porous oxide film modified electrode is employed to detection of folic acid (FA) in vegetables. The sensor linear range is 0.1 to 897 μM , LOD=54 nM, and sensitivity is 5.18 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$.

Keywords: Electrochemical, Alumina, anodization, dyeing, sealing process, folic acid, vegetables sample, porous materials.

1. INTRODUCTION

Over the past several decades, electrochemical anodizing of aluminum is a significant process in the industry due to the long and diverse applications [1]. For instance, electrochemical anodized aluminum alloys have been widely used in outdoor architectural components, appliances, furniture, sports equipment, and boat, airplane, and automobile components [2]. The electrochemical anodized aluminum alloys showed superior surface properties and corrosive resistance than aluminum’s natural oxide coating, has been most viable for a wide range of applications including architectural and aerospace industries [3]. Anodizing of aluminum is usually carried out by the electrochemical process where metal piece to be anodized in different electrolyte solutions [4]. The unique structure of anodized aluminum is more favorable for the coating of organic dyes and inorganic pigments, or deposition of metals on the pores [5]. Till date, different electrochemical anodizing experiments have been previously reported and demonstrated, in which sulfuric acid has been mostly used as an electrolyte and organic dyes have been used as a coloring agent on the anodized aluminum piece [6]. Furthermore, organic dyes and additives can be electrostatically interacting with the pores of electrochemical anodized Al and result in the transparent color layer [7]. It is also noted that the additives play a vital role in the coloring of the aluminum, while the temperature and concentration of additives can be more important for dyeing the aluminum [8]. In this present work, we have investigated the factors which cause the color bleeding during the sealing process and discussed in a careful manner. Statistical analysis is also conducted for the effect of color bleeding is influenced by different dyeing temperatures and various film thickness formed in different time frame of aluminum anodizing dyeing.



Scheme 1. Electrochemical anodization process and it applications of electrochemical detection of folic acid in vegetables and dyeing methods.

Moreover, owing to the advantages of aluminum alloys carried out into electrochemical process; the porous oxide film modified electrode is employed to detection of folic acid (FA). FA are mostly presents in the leafy vegetables (such as broccoli, and spinach), and fruits (such as lemons and banana) [9]. FA is used to preventing health defects. But excessive intake of FA leads to human risk; cancer, heart diseases, and vitamin deficiency [10]. This makes attention to the researchers to detect FA and quantify [11]. To best of our knowledge, we found that porous oxide film modified electrode can be also used for the detection of FA [12]. Due to the density, thickness of porous layer, and also size of the porous have behavior to show good electron transfer in the electrochemical reaction [13]. Aluminum based materials have high thermal capacity and electrical conductivity properties [14]. Consequently, the porous oxide film modified is also well suitable for the electrochemical sensor of FA.

2. EXPERIMENTAL SECTION

2.1 Materials and Apparatus

The substrate for testing Aluminum plate (type: 1050, and size: 40*50*0.5 mm) was used as a substrate for testing. NaOH, Na₂CO₃, folic acid and H₂SO₄ (98%) chemicals were purchased from Sigma Aldrich, and used as received. All other reagents and chemicals were purchased from Sigma Aldrich. Z701 and EVERANOD YELLOW L-03 were used as a sealing agent, and dyestuff for the experiments. Direct current power supply (30 V, 20 A), cooling water circulation device (0~30 °C), model: P-20 Sheng Hsin instruments, thermal water bath tank (30~99 °C), DENG YONG G-20 electronic weight scale (0.1 mg), Precisa XS 625M, color measuring instrument: Konica 2500, and UV-Visible Spectrometer : JASCO V-650 were used for the characterizations. Scanning electron microscopy (SEM) was performed using JSM-6500F. Electrochemical studies were used in CHI 900.

2.2 Anodization, Dyeing, and Sealing procedures

Immerse aluminum plate (scheme 1) into solution of 40 % NaOH (W/W %) 10 g L⁻¹ + Na₂CO₃ 20 g L⁻¹ at 55 °C for 3 minutes to eliminate fat (treatment with base). Next, immerse in 20 % HNO₃ (W/W%) solution for 30 min (neutralization of acid). Then, electrochemical anodization was done by following steps (scheme 1), Place the electrochemical anodized aluminum plate into 20 % H₂SO₄ (W/W%) at 20 °C and pass it with current of density 1.3 A dm⁻² for 30 min [15] (anodization). Then, immerse aluminum plate in 3 g L⁻¹ dye solution at 25 °C and 55 °C for 3 min. Finally, immerse the dyed aluminum plate in solution made with sealing agent Z701 of concentration: 5 g L⁻¹ (use 5 g of Z701 sealing agent to make up to 1 L of solution) at 70 °C for 15 min (sealing).

2.3 Method of color strength measurements

Outdoor-sunlight is the environment for color measurement which one can easily obtain it. However, recently, there are several artificial light sources developed. Type A light source is also

called tungsten light sources (absolute temperature is approximately 2854 K). Type C light source is the light reflected by white cloud at 45 degree elevated angle in the north direction; however, it has been gradually replaced by light source D65 (absolute temperature is 6740 K). Light source D65 is similar to average of natural sun light (absolute temperature is 6500 K), which has been used the most on color matching. Light source F is the light emitted by florescence light bulb. Once the theory of color and how light sources different from one to another are understood, it is reasonable to select D65 light as the light source for this research since it is the most commonly used light source in the sector of industry today; also, method of specular component exclude is applied along in the case to make sure that the data measured are reliable .

2.4 Method of color strength and electro-conductivity techniques

Color strength is the ratio between absorption rate of standard and absorption rate of sample. The equation is as following:

$$K/S (\text{Batch})/K/S (\text{Std.}) * 100 = \text{Batch Strength. Where } K/S = [(1-R)^2 / 2R]$$

R is the reflectance, K is absorbance and S is the scattering. The dyestuff can be divided into three different categories: cationic, anionic and disperse. Different types of dyestuff will create different electro conductivity dissolving in water as solution. Therefore, one can tell whether there is a relationship between dyeing efficiency and electro conductivity by examining the measurement of electro-conductivities in the research through electro-conductivity meter.

3. RESULTS AND DISCUSSION

3.1 Morphological studies

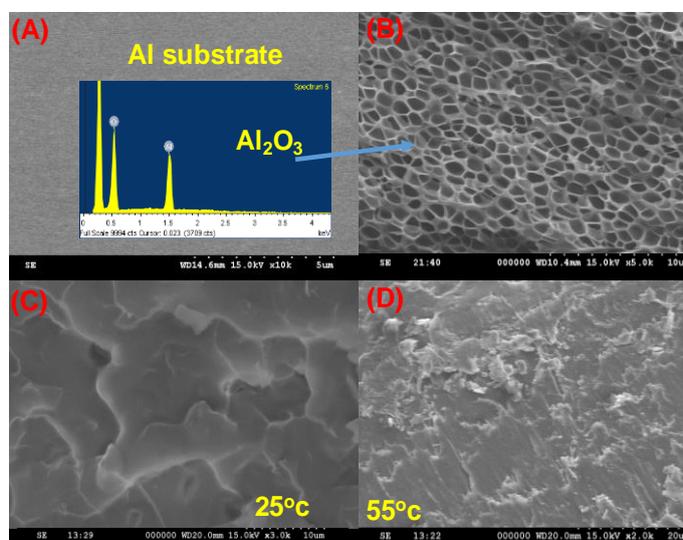


Figure 1. SEM images of Al substrate (A). Al₂O₃@Al (B) (after the anodization process) with (EDX) elemental analysis (inset). Dyeing process at 25 °C (C) and 55 °C (D).

Figure 1A shows, that morphology of Al substrate in SEM, anodized $\text{Al}_2\text{O}_3/\text{Al}$ (B), and dyeing of $\text{Al}_2\text{O}_3/\text{Al}$ at different temperature morphologies were studied under SEM in Figure 1C-D. Figure 1A displays the smooth surface area of the Al substrate and inset is elemental analysis (EDX) of anodized $\text{Al}_2\text{O}_3/\text{Al}$. It is shows Al and O. Figure 1B displays the images of $\text{Al}_2\text{O}_3/\text{Al}$ after the anodization process was done and obvious porous was observed in the anodized $\text{Al}_2\text{O}_3/\text{Al}$. Figure 1C-D displays the images of anodized $\text{Al}_2\text{O}_3/\text{Al}$ in organic dyeing at various temperature (25°C and 55°C).

3.2. Electrochemical detection of FA using cyclic voltammetry method

Cyclic voltammetric method is one of the preliminary studies in electrochemical sensor. The CV curves of Al_2O_3 modified electrode and bare electrode was observed in presence of PB solution (pH 7.0) at scan rate of 50 mVs^{-1} with $50 \mu\text{M}$ concentration of FA and displayed in Figure 2A. The CV curves of Al_2O_3 modified electrode obtained high intensity with higher potential compared to Al electrode CV curves intensity and potential, respectively. The comparison plot between current verse electrode was also displayed (Figure 2B) [10]. Following as result, the Al_2O_3 modified electrode was carried to perform in various concentration of FA ($50 \mu\text{M}$ - $250 \mu\text{M}$) in presence of PB solution (pH 7.0) at scan rate of 50 mVs^{-1} . Consequently, increasing in concentration of FA shows enhancement in the intensity of peak (Figure 2C). Figure 2D displays the plot between current verses concentration of FA [9].

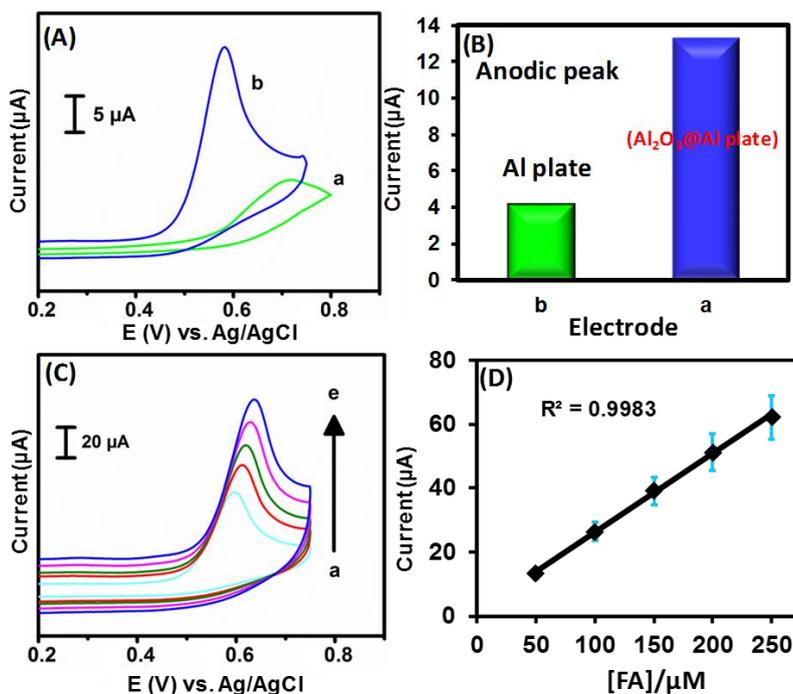


Figure 2. (A) the CV curves of Al_2O_3 modified electrode (b) and bare electrode (a) in the presence of PB solution (pH 7.0) at scan rate of 50 mVs^{-1} with concentration of FA ($50 \mu\text{M}$). (B) corresponding comparison plot. (C) Al_2O_3 modified electrode in different concentration of FA (50 - $250 \mu\text{M}$) in PB solution. (D) Corresponding plot between current vs concentration of FA.

3.3 Amperometric detection of FA and selectivity of sensor at modified electrode

Amperometric method is more sensitive studies for low concentration of FA. The Al_2O_3 modified electrode was used to examine towards FA by amperometric method with applied potential (E_{app}) is +0.52 V. The rotation speed of electrode is 1200 RPM. Figure 3A shows the amperometric response of Al_2O_3 modified electrode for various concentrations (0.1 to 894 μM) of FA into the PB solution (pH 7.0). For each addition of FA shows well defined responses was obvious observed that increase in concentration of FA shows enhancement amperometric response current. The steady current was obtained within 10 s. Figure 3B displays the linear relationship $R^2 = 0.995$ between concentration of FA and current. The detection limit was calculated to be and the sensitivity was facilitated to be $5.18 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ and LOD was calculated 54 nM. Hence, the Al_2O_3 modified electrode has the potential materials for FA detection. Furthermore, Figure 3C displays the selectivity of Al_2O_3 modified electrode towards detection of FA in presence of common oxidation interfering molecules. The applied potential was held at +0.52 V and the rotation speed was 1200 RPM. The Al_2O_3 modified electrode possess well defined amperometric response for the addition of FA. However, there is nil peak response was appeared for the addition of interfering; glucose, epinephrine, catechol, folic acid, H_2O_2 , uric acid, dopamine, ascorbic acid, and norepinephrine. Notably, good peak response was clearly appeared for the addition of FA to same PB solution containing aforementioned interfering. This result shows that the performance of Al_2O_3 modified electrode for excellent selectivity of FA. The electrochemical sensor parameters are comparing with previous report in Table 1. Our modified electrode as good sensitivity and wide linear range compare with other reports [16].

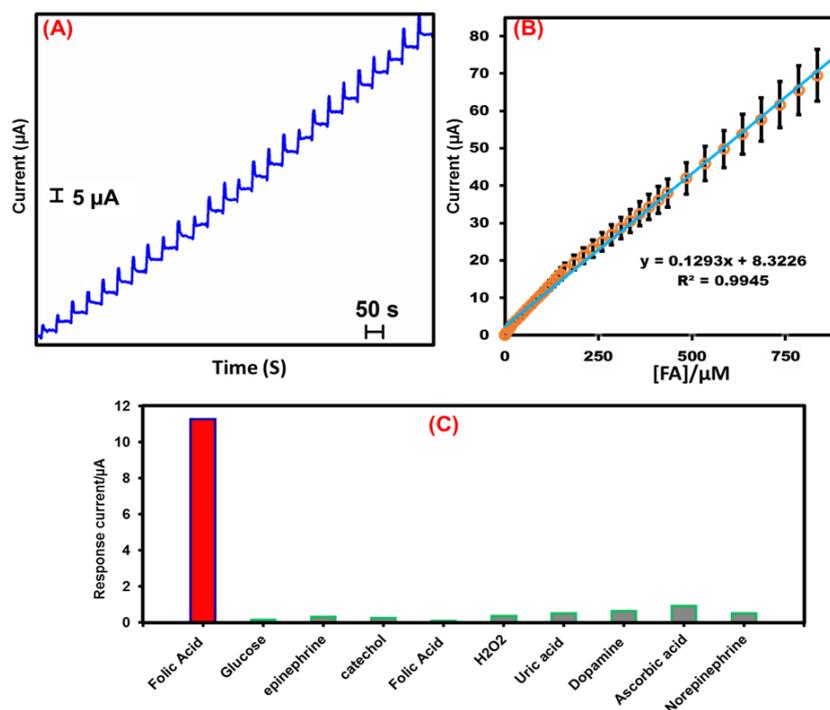


Figure 3. (A) Amperometric response of Al_2O_3 modified electrode in the presence of PB solution (pH 7.0) with different concentration of FA, $E_{app} = +0.52$ V and (B) corresponding plot between current vs concentration of FA. (C) Selectivity studies of FA at Al_2O_3 modified electrode.

Table 1. Comparison of analytical parameters for the determination of FA at Al₂O₃ modified electrode with other reports

Modified Electrode	Sensor range/ μM	Detection limit/ μM	Ref.
ZrO ₂ /carbon paste electrode	20–250	9.8	[17]
methylene blue/reduced graphene oxide	200–3200	25	[18]
Fe ₃ O ₄	0.065–98	2	[19]
Carbon nanotubes (CNTs)	1–400	0.58	[20]
Ferrocene dicarboxylic acid/MWCNT	4.6–152	1100	[16]
Porous silicon	1–1000	800	[21]
Reduced graphene oxide /MoS ₂	0.01–100	10	[22]
CNTs/carbon paste electrode	1.1–300	6.2	[23]
Al ₂ O ₃ modified electrode	0.1–894	0.054	This work

3.4. Real sample analysis

The real sample analysis of Al₂O₃ modified electrode has been demonstrated in vegetables samples (broccoli and cauliflower samples). Directly FA powder was dissolved in vegetables extract solution (extract prepare form broccoli and cauliflower). Next, amperometric experiments were carried out using Al₂O₃ modified electrode in the FA spiked real samples. The known concentration of FA was spiked into electrolyte solution. The added, found and recovery are presented in Table 2. The results suggest that the modified electrode can also be used for the determination of FA present in other food samples. Thus, the Al₂O₃ modified electrode has great potential in health safety testing.

Table 2. Determination of folic acid in real samples using Al₂O₃ modified electrode

Samples	Added (μM)	Found (μM)	Recovery (%)	RSD*(%)
Cauliflower	10	11.25	112.5	2.26
	20	21.64	107.0	3.17
Broccoli	10	10.95	109.5	2.36
	20	21.34	106.7	2.14

* RSD (Relative Standard Deviation) of three individual experiments

3.5 Influence of different film thickness and different temperature for dyeing with metal salts to color bleeding

Immerse the electrochemical anode treated aluminum plate in dye solution of 3 g L⁻¹ and operate the dyeing process at 25 °C and 55 °C for different film thickness (Table 2). Both time of dyeing process should set to be the same 3 min. Dry the aluminum plate after the sealing and drying procedures. Color dyed on the aluminum plate is then measured by computer and the color strengths measured are recorded for further study. Sealing solutions are analyzed by UV-visible spectrometer to obtain the absorption value. Data of different film thickness, and different temperature (dyeing) are collected to help finding out how color bleeding influences the dyeing process and the results are summarized in Table 2.

Table 3. Influences of metal salts to color bleeding in different film thickness and dyeing temperatures.

Factor 1*	Dyeing time	3 min
Factor 2*	Film thickness	7 μm, 11 μm, 16 μm
Factor 3*	Metal salts added %	1 %, 3 %, 5 %
Factor 4*	Dyeing temperature	25 °C, 55 °C

*The percentage of metal salts added is the ratio to the weight of the dyestuff used. Then, software, JUMP, is used to find out the relations in between and to ratify the factors which can be further analyzed and researched.

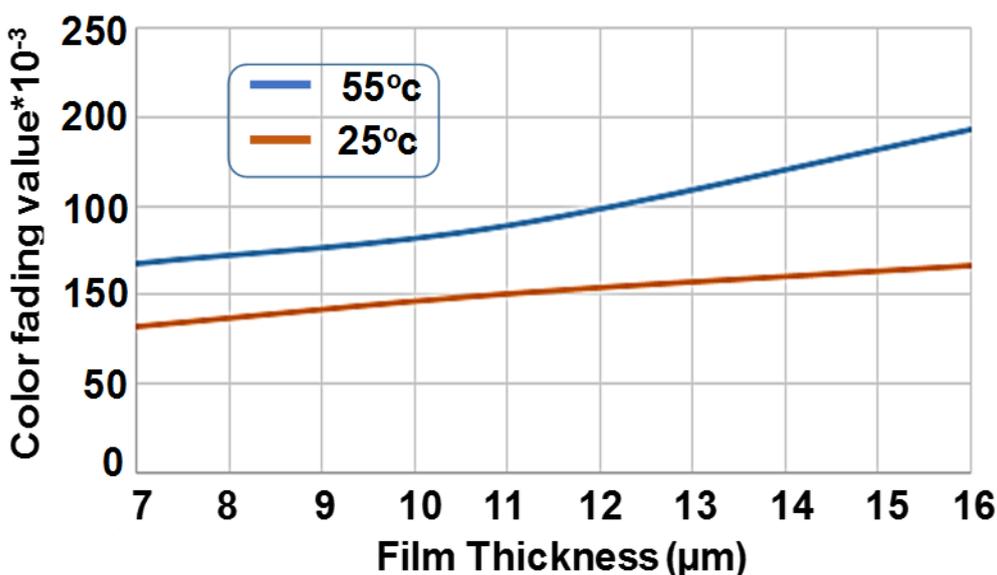


Figure 4. The trend of color bleeding under different film thickness and different dyeing temperature

The addition of metal salts to aluminum anodizing dyeing process can be a fairly good attempt to help reduce the color bleeding problem. The influences of metal salts to color bleeding in different film thickness are shown in Figure 4, and Table 3. Color bleeding problem is decrease when metal

salts increased in Figure 4. In this results, UV-visible spectrometer is applied to examine the situation of color bleeding in sealing solution which allows one to see how bad the color bleeding is occurs. Statistical software is then used to find the relations which give one more advantages to find the most important factors. On the other hand, the method not only helps one find out the trend and relations. But also helps one to verify whether the additional of metal salts can reduce the color bleeding during dyeing process Figure 5A, B. All the above mentioned data can be useful and helpful references to on-sight operators on the selection of auxiliary agents.

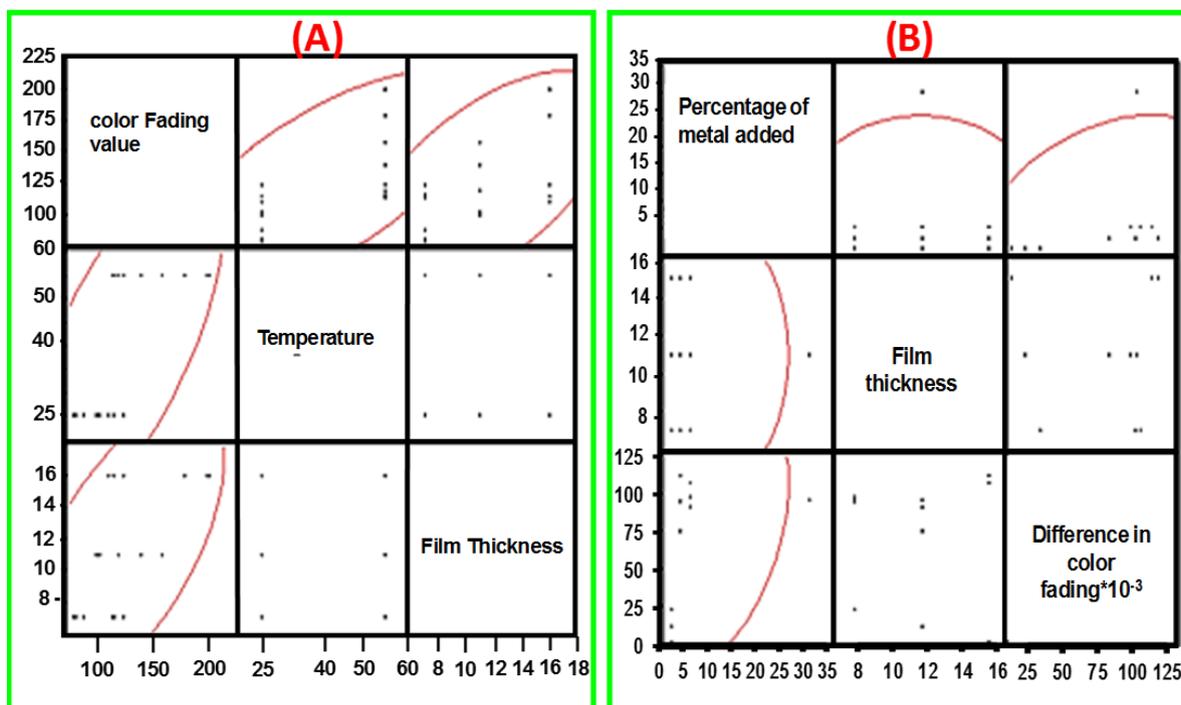


Figure 5. (A) Graphical analysis on the relations between dyeing under different film thickness, different dyeing temperatures and color bleeding. (B) Graphical analysis on the relations between addition of metal salts, film thickness and color bleeding

From Table 4, the co-efficient of relation between dyeing temperature and color bleeding is 0.69 which represents a medium level of positive relation, compare to the film thickness versus color bleeding is 0.62 which shows a medium level of positive relation as well. By knowing the above facts, one can say that the higher the dyeing temperature or the thicker the film by the dyeing process, the worse the color bleeding becomes. There are two different operating conditions in on-sight aluminum anodizing dyeing in production scale. one at room temperature and Another one at high temperature. From the research, it shows that color bleeding is not as bad in room temperatures comparing to operation at high temperature. In aluminum anodizing dyeing, temperature and film thickness by the dyeing process are considered two extremely important factors which can greatly alternate dyeing time, color strength and even on color shading (which operators would not want to deal with). Hence,

it is difficult and risky to make such kind of adjustments. However, metal salts seem to be a good candidate on solving the color bleeding problem after sealing process at high temperature.

Table 4. Analysis on the relation between dyeing under different film thickness, different dyeing temperatures and color bleeding.

	Color bleeding value	Temperature	Film thickness
Color bleeding value	1	0.6942	0.6261
Temperature	0.6492	1	0
Film Thickness	0.6261	0	1

* 0 ~ 0.3: low level of relation, 0.3~0.7: medium level of relation, 0.7~1.0: high level of relation.

3.6. The effect of addition of metal salts on aluminum electrochemical anodizing dyeing at high Temperature

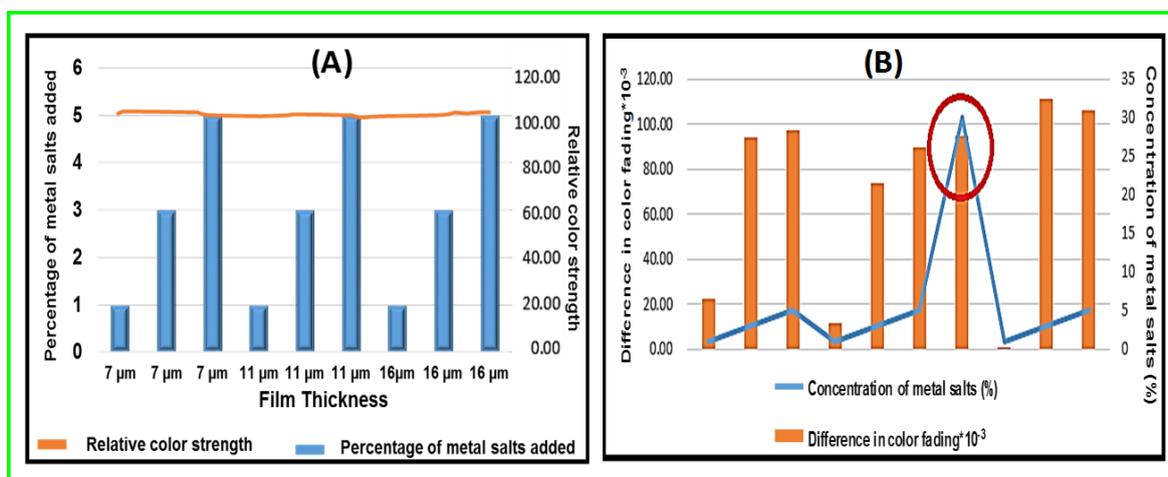


Figure 4. (A) Graphical analysis on the influence of amounts of metal salts added and film thickness to color strength at 55°C. (B) Different degrees of color bleeding due to different amount of metal salts added under different film thickness.

In regard of additional metal salts during aluminum electrochemical anodizing dyeing, one can see from Figure 4A and Table 5. It is a medium level of positive relation between the additional of metal salts and color bleeding which means that addition of metal salts can suppress the color bleeding effectively. In the research, the color strength is analyzed after addition of metal salts into dyeing process at 55 °C to determine the effects of addition of metal salts on color strength through improvement of color bleeding condition. From the Figure 4A-B one can see that addition of metal salt of 1~5 % has no influences on color strength.

Table 5. Analysis on the relation between addition of metal salts, film thickness and color bleeding.

	% of metal salts added	Film thickness	Color bleeding value
% of metal salts added	1	0	0.3513
Film thickness	0	1	0.0524
Color bleeding value	0.3513	0.0524	1

* 0 ~0.3 : low level of relation, 0.3~0.7 : medium level of relation, 0.7~1.0 : high level of relation

*The percentage of metal salts added is the ratio to the weight of the dyestuff used.

4. CONCLUSION

In this report successfully modified an Al₂O₃/Al via anodization and it was characterized by SEM, EDX, UV-Vis, CV techniques. Non-enzymatic biosensor was fabricated for the sensitive detection of FA in food samples with nano-molar detection limit (54 nM). In the research, one learns that dyeing temperature and film thickness in aluminum electrochemical anodizing dyeing process both have tremendous influences on the degree of color bleeding. However, solving the color bleeding problem by changing the dyeing temperature costs much more since its chemical parameters such as color shading, color strength and stability need to be tested and reset all over again. Finally, addition of metal salt is proposed as a solution to color bleeding problem. From the experimental result, one can conclude that the addition of metal salts can effectively solve the color bleeding problem. Addition of 5% metal salts is enough to create the best effect and stability without change of any operational conditions. The research can help fulfill the goals of both promoting the green environmental preservation and improving the dyeing efficiency at the same time.

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