Preparation and characterization of antibacterial oxide film with deposited silver on Al alloy

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Abstract
Aluminum (Al) alloy products are widely used in people’s lives, while the existence and breeding of microorganisms on their surface cannot meet the health criteria and even may harm human health. In the present study, we successfully prepared the antibacterial oxide film on the 6063 Al alloy specimens by direct-current anodizing followed by Ag element depositing and the hole sealing process. The results suggested that compared with the Al substrate, the wear resistance of the obtained film was increased to 0.79, and the corrosion resistance was significantly improved. The antibacterial rate against Escherichia coli could be achieved as 94.38 ± 3.23%, and the adhesion force between the film and substrate was about 11 N. With the increase of the deposition time, the surface color of samples was gradually darkened, and meanwhile, the surface became uniform again without particles eventually. Energy dispersive spectroscopy (EDS) results showed the silver element was deposited on the surface and at the bottom of the porous oxide layer, and the amount of silver also increased with prolonging the deposition time. Moreover, x-ray photoelectron spectroscopy (XPS) analysis results on the surface showed the deposited silver element existed in the form of the ion and elemental substance, which indicated that reduction reaction of Ag\textsuperscript{+} appeared on the oxide film surface.

1. Introduction
Aluminum (Al) alloys are widely used in kitchen appliances, medical equipment, food processing facilities, and furniture due to their low density, excellent plasticity, and good corrosion resistance [1–3]. Recent years, with the development of the enlarged health conception, people pay more attention to the impact of the living environment on their health and make a great effort to improve life quality. Bacteria are widespread in the surrounding environment, and the bacterial infection is an important issue causing illness. The growth of bacteria will be detrimental to human health, and even shorten the service time of Al alloy devices by affecting the formation of the oxidation film. Nevertheless, currently used Al alloys cannot hinder the growth of bacteria and other pathogens since the naturally formed oxide layer does not have antibacterial function [4]. Therefore, achieving the antibacterial activity on Al alloys has become a widespread concern for people [5–7].

Alloying and surface treatment are two main methods for achieving the antibacterial function of metals. However, alloying with antibacterial elements may affect the mechanical properties of the original material, and this method is uneconomical. Inversely, surface modification technologies not only can maintain the excellent mechanical properties of aluminum alloys but also improve their corrosion resistance and antibacterial effect [8–11]. Commonly used antibacterial agents are some heavy metal elements and their synthetic substances [12], which has a long-term and effective antibacterial property and do not result in the emergence of drug-resistant...
The raw materials were as-extruded Al alloy plates with a dimension of 50 mm $\times$ 50 mm $\times$ 2 mm. The chemical composition of Al alloy is shown in Table 1. The plate surface was ground up to 1000 grit SiC sandpapers then sandblasted using alumina oxide abrasives, namely 125 $\mu$m particle sizes. The jet was positioned perpendicularly to the surface at a fixed distance of 8 mm with a pressure of 2 bar for 15 s. Prior to anodizing, all specimens were cleaned with the alkali solution containing NaOH (50 g l$^{-1}$), Na$_2$CO$_3$ (20 g l$^{-1}$), Na$_3$PO$_4$ (20 g l$^{-1}$), and sodium gluconate (10 g l$^{-1}$) at the temperature of 30 °C for 5 min, then cleaned by pickling using the nitric acid solution (200 g l$^{-1}$) at the temperature of 35 °C for 5 min. The cleaned samples were washed with absolute ethanol for 10 min and dried in the air.

The anodizing (AAO) was conducted with a direct current in a solution containing sulfuric acid (150 g l$^{-1}$) and aluminum sulfate (1 g l$^{-1}$). The voltage was at 18 V, and all anodizing processes were carried out in a water bath incubator at 10 °C for 5 min. The pretreated sample was the anode, and the graphite plate was the cathode, while the area ratio of the cathode to the anode was 2:1. Two cathodes were used to ensure the uniform distribution and formation of the silver element depositing and the hole sealing process and studied the wear resistance, corrosion resistance, and antibacterial properties of this film. The distribution and formation of the silver element were also investigated. The results presented an insight into the study of an antibacterial oxide film with deposited silver.

In this study, we successfully prepared the antibacterial oxide film by direct-current anodizing followed by Ag element depositing and the hole sealing process and studied the wear resistance, corrosion resistance, and antibacterial properties of this film. The distribution and formation of the silver element were also investigated. The results presented an insight into the study of an antibacterial oxide film with deposited silver and provided a preparation method of antibacterial Al alloys for future application.

### 2. Materials and methods

#### 2.1. Samples preparation

The chemical composition of Al alloy is shown in Table 1. The plate surface was ground up to 1000 grit SiC sandpapers then sandblasted using alumina oxide (Al$_2$O$_3$) abrasives, namely 125 $\mu$m particle sizes. The jet was positioned perpendicularly to the surface at a fixed distance of 8 mm with a pressure of 2 bar for 15 s. Prior to anodizing, all specimens were cleaned with the alkali solution containing NaOH (50 g l$^{-1}$), Na$_2$CO$_3$ (20 g l$^{-1}$), Na$_3$PO$_4$ (20 g l$^{-1}$), and sodium gluconate (10 g l$^{-1}$) at the temperature of 30 °C for 5 min, then cleaned by pickling using the nitric acid solution (200 g l$^{-1}$) at the temperature of 35 °C for 5 min. The cleaned samples were washed with absolute ethanol for 10 min and dried in the air.

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After that, the silver depositing was performed using sinusoidal alternating current on the anodized film at a voltage of 10 V for 30 s, 1 min, 2 min, 3 min, and 5 min, respectively. The deposition solution consisted of AgNO$_3$ (1.5 g l$^{-1}$), H$_2$SO$_4$ (10 g l$^{-1}$), and MgSO$_4$ (5 g l$^{-1}$). Likewise, samples were washed with distilled water and dried in the air. Finally, to improve the corrosion resistance of the anodized Al alloy, the hole sealing process was carried out in a solution containing 4 g l$^{-1}$ NiSO$_4$ at 85 °C for 30 min. Samples were also clean up with distilled water.

### Table 1. Chemical composition of the 6063 Al alloy.

| Composition (wt. %) | Mg       | Si       | Fe       | Zn       | Ti       | Mn       | Cu       | Cr       | Al       |
|---------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 6063 Al             | 0.594    | 0.332    | 0.122    | 0.013    | 0.020    | 0.006    | 0.006    | 0.001    | Bal.     |
water and dried in the air. The final sample was labeled as Al-AAO-D. Figure 1 shows the schematic diagram of whole preparation process.

2.2. Structure and chemical characterization of the oxide film
X-ray diffraction (XRD, SmartLab, Japan) patterns were collected to analyze phase compositions of the anodized film employing a Cu Kα radiation source with a voltage of 40 kV and a current of 30 mA. To exclude the influence of Al substrate, the oxide film of the anodized sample was peeled off by the reverse voltage method, and XRD analysis was carried out on the anodized sample and the oxide film, respectively. The morphology of samples was characterized using a Sirion200 field emission scanning electron microscope (SEM, FEI, Japan) with an acceleration voltage of 20 kV, and a spot size of 4. The chemical composition of the surface and cross profile was detected by energy dispersive spectroscopy (EDS, Oxford, UK), and the surface chemical composition of the sample after depositing was further analyzed by x-ray photoelectron spectroscopy (XPS, Phi 5000 Versa Probe, USA). Curve fittings were determined using a Gaussian Lorentzian function and a Shirley-type background and performed using the Xpspeak 4.1 software.

2.3. Wear resistance and adhesion test
The wear resistance test was conducted using a friction wear testing machine (WTM-2E, China), with a load of 100 g and a speed of 300 r min⁻¹. The diameter of the counter grinding ball was 3 mm and the wear time last for 20 min. Additionally, the adhesion test was carried out by a scratch tester (WS-2005, China), with a load range of 0–20 N, a speed of 30 N min⁻¹, and a scratch length of 3 mm.

2.4. Corrosion resistance test
The corrosion properties of samples were evaluated by both the mass loss and the electrochemical method. The sample for mass loss was firstly immersed in 50 wt.% nitric acid for 10 min, then in a phosphoric chromic acid solution containing Cr₂O₃ (20 g l⁻¹) and H₃PO₄ (35 g l⁻¹) for 15 min. Samples were washed with distilled water and dried in the drying oven at a temperature of 60 °C. After drying, the mass of samples was determined, and mass loss was calculated using the following equations (1) and (2):

\[ \Delta m_{1,2} = \frac{(m_1 - m_2)}{S} \]  
\[ \Delta m_{1,3} = \frac{(m_1 - m_3)}{S} \]

Where \( m_1 \) is the original mass of the sample (g), \( m_2 \) is the sample mass after immersed in 50% (wt.%) nitric acid (g), and \( m_3 \) is the sample mass after soaked in nitric acid followed by the phosphorus-chromic acid solution (g). \( S \) is the sample area exposed to the solution (dm²). The corresponding mass loss was defined as \( \Delta m_{1,2} \) and \( \Delta m_{1,3} \), respectively.

Potentiodynamic polarization measurements (PDP) of samples was conducted in an electrochemical workstation (PARSTAT 3F, AMETEK, USA) with a typical three-electrode cell, in which a saturated calomel electrode (SCE) as a reference electrode, a platinum slice as a counter electrode, and the sample as a working electrode. The exposed surface of sample was 10 mm × 10 mm. All electrochemical experiments were carried out using a quartz cell containing 3.5 wt.% NaCl solution at (37.5 ± 0.5) °C. The scan rate was 2 mV s⁻¹.

2.5. Antibacterial assay
To qualitatively evaluate the antibacterial effect, a plate of 6063 Al alloy and a sample with the antibacterial oxide film were placed in different culture dishes, in which 20 ml sterile milk was added. The culture dishes were incubated with a constant temperature of 36 °C for 24 h. After 24 h, the milk state was observed.
Figure 2. The curve of current density with the anodizing time under the voltage of 18 V and temperature of 10 °C (a), and the corresponding morphologies of surface (b) and cross-section after anodizing (c). EDS mapping data of the anodized film (d) and the elemental composition of the selected area (e). XRD patterns of the anodized sample with and without Al substrate (f).

Figure 3. Macro-morphologies of samples changed with the deposition time (a), and the detailed images of the surface at each time points (b).
Furthermore, the antibacterial rate was determined according to the antibacterial test methods specified in a standard of China GB/T 31402–2015 protocol. The strain of bacteria used in this experiment was *E. coil* (*Escherichia coli*, CICC10899) which was purchased from the China Center of Industrial Culture Collection. In short, the experimental specimens with a dimension of 50 mm × 50 mm × 2 mm were sterilized by ultraviolet radiation. The strains were prepared to 1 × 10^6 colony forming units (CFUs) ml⁻¹ in Luria-Bertani (LB) medium. 400 μl bacterial droplet was placed on the middle of the sample surface. A polyethylene film was set as the control group. Samples with the bacteria were cultured in an incubator with a constant temperature of 36 °C and humidity of 95% for 24 h. Standard of China GB/T4789.2 protocol and the antibacterial ratio was calculated as follows:

\[ X = \frac{A - B}{A} \times 100\% \tag{3} \]

Where A is the average number of bacteria on the control sample (CFU/sample), B is the average number of bacteria on the testing sample (CFU/sample).

### 3. Results and discussion

#### 3.1. Preparation of AAO film on 6063 Al alloy

Figure 2(a) shows the curve of current density (i\textsubscript{AAO}) with the anodizing time when preparing the anodized film. The current density fluctuated at the beginning but tended to be stable as the oxidation progressed. According to the growth mechanism of anodic oxidation film on aluminum alloys [23], the sharp drop of the i\textsubscript{AAO} was related to the formation of the oxide film, and the slow rise of i\textsubscript{AAO} was attributed to the presence of the porous membrane layer. Finally, the porous film grew steadily. The corresponding surface morphology and cross-section of the anodized film were shown in figures 2(b), (c). Moreover, figures 2(d), (e) depicts the element distribution and the elemental composition of the selected area of the anodized film, which exhibited the film was mainly composed of Al, O, and S elements. To further analyze the phase structure, XRD patterns were
collected from the anodized sample with and without Al substrate. Besides peaks of Al indexed (PDF no.2–1109), the peak curve bread appeared in both curves at the 2θ range of 20° to 30°, indicating the formation of amorphous aluminum oxide.

3.2. Deposition of silver on the anodized film
Depositing silver on the anodized film was the key to achieve the antibacterial function. As shown in figure 3(a), the surface color changed versus the depositing time. When conducting the deposition process, the film quickly appeared light yellow at the moment of power on, meanwhile, there were lots of gas bubbles generated near two electrodes. With the deposition reaction going on, fewer bubbles were created, while the anodized film color gradually changed from light yellow to orange, then to dark brown. Herein, under a certain voltage, the prolonging deposition time led to the surface color darkened. Figure 3(b) shows the SEM morphology of the films deposited at 10 V for a different time. After the 30 s of deposition, the micro-morphology of the film did not change. For the film deposited for 1 min, many particles appeared on the surface of the film, which might be...
due to the dissolution of the anodized surface in the acid deposition solution. As the time increases to 3 min, the particles on the film began to decrease but were still existed, suggesting the dissolving reaction slowed down. After deposited for 5 min, the surface recovered uniform without particles. Moreover, particles were further identified as shown in red boxes by EDS analysis (table 2). The content of silver element on the surface reached the highest after 5 min deposition.

To validate the variation of the chemical composition in the inner of anodizing film, chemical element mapping and linear scanning was conducted for analyzing film cross-sections. Figure 4 depicts the distribution of relevant elements in the film cross-section after depositing at 10 V for 30 s and 5 min. As the deposition time of 30 s, there was no obvious silver deposition layer (figure 4(a)), while further analyzing the silver change by line scanning indicated a fluctuation at the film bottom (figure 4(b)). As the time increases to 5 min, the more obvious presence of the silver layer was distinguished as shown in figure 4(c), indicating the element Ag distributed in the film. It should be noted that the silver element could pass through the porous structure of the oxide layer and be deposited preferentially at the bottom of the oxide film (figure 4(d)). Furthermore, the selected area of film neighboring the Al substrate was detected by EDS to analyze the composition ratio of silver, and the curve of silver content versus time was shown in figure 5, suggesting the deposition amount of silver in the film increased with prolonging the deposition time.

XPS measurements were conducted to determine the existence form of Ag element deposited on the film. Figure 6(a) specifies the entire range of binding energy measurements of the sample, showing that the film surface was mainly composed of C, O, S, Al, and Ag elements. Tabulated XPS data were used to investigate the peak position related to Al and Ag and their compounds on the XPS spectra (table 3). Concerning Al 2p spectra (figure 6(b)), the peak could be fully covered by peaks at 73.38 eV and 73.62 eV, which represented the presence of Al₂O₃ and Al₂(SO₄)₃, respectively [24–26]. For the Ag 3d₃/₂ and Ag 3d₅/₂ spectra, peaks were composed of Ag₂SO₄ at 373.8 eV and 367.8 eV and the elemental silver at 374.3 eV and 368.4 eV, respectively [27–29]. This indicated the Ag⁺ in solution was reduced to elemental Ag during the electrodeposition process [30, 31]. Besides, figure 6(d) shows the spectra of S 2p with a binding energy at the range of 166–172 eV. Since the sample were oxidized and deposited based on sulfuric acid solutions, peaks at 168.91 eV and 170.12 eV can be assigned to

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**Table 3. Parameters used for fitting XPS spectra.**

| Spectrum | Corresponding substance | Peak position (eV) | References |
|----------|-------------------------|-------------------|------------|
| Al 2p    | Al₂O₃                   | 73.38             | [24, 25]   |
|          | Al₂(SO₄)₃               | 73.62             | [26]       |
| Ag 3d₃/₂ | Ag                      | 374.3             | [27, 28]   |
|          | Ag₂SO₄                  | 373.8             | [29]       |
| Ag 3d₅/₂ | Ag                      | 368.4             | [27, 28]   |
|          | Ag₂SO₄                  | 367.8             | [29]       |
| S 2p     | S 2p₃/₂                 | 168.91            | [12]       |
|          | S 2p₁/₂                 | 170.12            | [12]       |
| O 1s     | S-O                     | 531.5             | [29]       |
|          | Al₂O₃                   | 532.63            | [24, 25]   |
S2p3/2 and S2p1/2, corresponding to the S\\(^{6+}\) oxidation state of Al\\(_2\)(SO\(_4\))\\(_3\) and Ag\(_2\)SO\(_4\) [32]. The fitting result of O 1s also demonstrated the bond of S–O, indicating the presence of SO\(_{4}^{2-}\) [29].

At present, although the mechanism of silver deposition by alternating current has not reached a consensus, the deposition reaction in the anodized aluminum film is similar to other electrodeposition processes. At the

![Figure 8. Typical PDP curves of samples immersed in 3.5 wt.% NaCl solution.](image)

![Figure 9. Images of the state of milk with the untreated Al substrate (a) and the Al-AAO-D sample (b) after 24 h culture, and the E. coli colonies re-cultured on agar after incubating around the blank control group (c) and the Al-AAO-D sample for 24 h (d).](image)

| Table 4. The mass loss of the sample AAO and Al-AAO-D after immersed in nitric acid and in nitric acid followed by the phosphorus-chromic acid solution. |
|---|---|---|
| | Al-AAO-D (mg dm\(^{-2}\)) | Al-AAO (mg dm\(^{-2}\)) |
| \(\Delta m_{1,2}\) | 6.37 | 6.86 |
| \(\Delta m_{1,5}\) | 79.90 | 235.29 |
followed by Ag element depositing and the hole sealing process. The porous anodized alumina provided a channel for exchanging ions. In this study, the antibacterial effect. Furthermore, the antibacterial rate of the Al-AAO-D sample was determined using the counting method, as shown in figure 8(a). With the test going on, the surface was gradually smoothed owing to the increase of real contact area, resulting in the slowing down of the wear rate. The friction coefficient also tended to steady at this time. The average friction coefficient of Al substrate and Al-AAO-D is 0.79 and 0.45, respectively, suggesting the deposited film had a better anti-friction effect than that of Al substrate. Moreover, the adhesion test result with the corresponding micrograph of the film is shown in figure 7(b). Based on the change of signal intensity, the adhesion force of the film was about 11 N, at which the film was completely scratched.

3.4. Corrosion property
To understand the corrosion resistance of the prepared samples, the mass loss was carried out on the sample Al-AAO and Al-AAO-D. Table 4 lists the mass loss after soaked in nitric acid and in nitric acid followed by the phosphorus-chromic acid solution, respectively. The $\Delta m_{1,2}$ and $\Delta m_{1,3}$ of the Al-AAO-D sample were both less than those of the anodized samples. Since the smaller $\Delta m_{1,2}$ and $\Delta m_{1,3}$ represented the better corrosion resistance, the sample underwent the silver deposition and the hole sealing process exhibited a better corrosion resistance. Moreover, figure 8 shows the PDP curves of the Al substrate, Al-AAO, and Al-AAO-D samples, and the relative electrochemical corrosion parameters are listed in table 5. The corrosion current density ($i_{corr}$) was a kinetic parameter to evaluate the corrosion rate, while the corrosion potential ($E_{corr}$) was a thermodynamic parameter to estimate corrosion tendency. $E_{corr}$ increased to $-0.49$ V versus SCE and $i_{corr}$ decreased to $4.74 \times 10^{-7}$ A cm$^{-2}$ when the Al substrate was after anodizing. Furthermore, when the Al-AAO sample deposited by silver then dealt with the hole sealing process, the Al-AAO-D sample exhibited an $E_{corr}$ of $-0.38$ V versus SCE and an $i_{corr}$ of $1.05 \times 10^{-10}$ A cm$^{-2}$. Consistently, the obtained antibacterial oxide film exhibited a low tendency toward corrosion and good corrosion resistance in 3.5 wt.% NaCl solution.

3.5. Antibacterial property
To qualitatively evaluate the antibacterial effect, the prepared film was immersed into the sterile milk, and the state of milk was observed after 24h culture. As can be seen in figures 9(a), (b), there was no significant change in the milk with the Al-AAO-D sample, while the color of the milk with the Al substrate turned yellow. The spoiled milk had poor fluidity and a slight odor. This qualitative result indicated the Al-AAO-D sample had a certain antibacterial effect. Furthermore, the antibacterial rate of the Al-AAO-D sample was determined using the E. coli. The bacteria suspensions cultured on the sample surface for 24 h were re-cultivated on agar according to the bacteria counting method, as shown in figures 9(c), (d). It could be seen that the percentage reduction of E. coli colonies on the Al-AAO-D sample was 94.38 ± 3.23% compared with that on the blank control group, demonstrating the prepared film presented a good antibacterial effect on E. coli.

4. Conclusions
In this study, the antibacterial film was successfully prepared on the Al substrate by direct-current anodizing followed by Ag element depositing and the hole sealing process. The porous anodized film was observed through

| Samples   | $i_{corr}$ ($10^{-4}$A·cm$^{-2}$) | $E_{corr}$ (V) |
|-----------|---------------------------------|----------------|
| Al-AAO-D  | $1.05 \times 10^{-4}$           | $-0.38$       |
| Al-AAO    | $4.74 \times 10^{-1}$           | $-0.49$       |
| Al        | $2.59$                          | $-0.72$       |
the cross-sectional and further identified as amorphous by XRD analysis. The silver element was deposited on the surface and at the bottom of the porous oxide layer, and the amount of silver increased with prolonging the deposition time. The deposited silver element existed in the form of the ion and elemental substance. Moreover, the adhesion force between the prepared antibacterial film and Al substrate was about 11 N, and both the wear resistance and corrosion resistance were significantly better than those of the Al substrate. The antibacterial rate towards *E. coli* could be achieved as 94.38 ± 3.23%, which could meet the requirement of products against bacteria in life.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Wang G W, Song D, Zhou Z K, Klu E E, Liu Y, Liang N N, Jiang J H, Sun J P and Ma A B 2020 *Coatings* **10** 216
[2] Rahkmonov J, Liu K, Rometsch P, Parson N and Chen X G 2020 *Materials* **2020** 13 5295
[3] Tian W M, Li Z L, Kang H F, Cheng F S, Chen F F and Pang G X 2020 *Materials* **13** 3236
[4] Dickson M N, Liang E I, Rodriguez L A, Volleraneus N and Yee A F 2015 *Biomater* **2015** 10 021010
[5] Chi G J, Yao S W, Fan J, Zhang W G and Wang H Z 2002 *Surf. Coat. Technol.* **157** 162–5
[6] Frantziskonis G N, Simon L B, Woo J and Matikas T E 2000 *Eur. J. Mech. A-solid* **19** 309–18
[7] Zhang Y, Cao J, Wang X L, Liu H, Shao Y, Chu C L, Xue F and Bai J 2021 *Biomater* **7** 217–26
[8] Saravanam I, Perumal A E, Issar R F, Vettivel S C and Devaraju A 2016 *Mater. Des.* **92** 23–35
[9] Ghasemnia S, Shanaghaia A and Chub P K 2017 *Surf. Coat. Technol.* **326** 156–64
[10] Wan Q, Ding H, Yousaf M I, Chen Y M, Liu H D, Hu L W and Yang B 2016 *Thin Solid Films* **616** 601–7
[11] Zhang Y, Chen K Y, Liu H, Shao Y, Chu C L, Xue F and Bai J 2020 *J. Mater. Sci.* **55** 17170–82
[12] Somlyai-Sipos I, Baumlil P, Sychev A, Kaptay G, Szibrigi-Doroghazi E, Kristaly F, Mikő T and Janovszky D 2020 *Appl. Surf. Sci.* **533** 147494
[13] Ghosh T, Chattopadhya A, Mandal A C, Pramanik Sand Kuir K K 2020 *Chin. J. Phys.* **68** 835–48
[14] Nakajima D, Kitkuchi T, Yoshioika T, Matushima H and Natsui S A 2019 *Materials* **12** 3497
[15] Shi H B, Yu M, Liu J H, Rong G, Du R T, Wang J and Li S M 2020 *Corros. Sci.* **169** 108642
[16] Diggle J W, Downie T C and Goulding C 1969 *Chem. Rev.* **69** 365–405
[17] Shibraen M H M A, Ibrahim O M, Asad R A M, Yang S G and El-Assar M R 2021 *Colloids Surf. A* **610** 125921
[18] Zou Y, Zhang Y X, Yu Q and Chen H 2021 *J. Mater. Sci. Technol.* **70** 24–38
[19] Calabrese G, Petralia S, Franco D, Nocito G, Fabbi C, Forte L, Guglielmino S, Squarzoni S, Traina F and Conoci S 2021 *Mater. Sci. Eng. C* **118** 113994
[20] Tomoioka T and Yoshida A 2001 US Patent 6168869
[21] Raad S S, Anwar H A A and Hamed K H 2017 *J Adhes Sci Technol* **32** 874–88
[22] Ikeda T, Kinj T and Matsuo Y 2001 EP01125530A
[23] Parkhutik V and Shershulsky V 1992 *J Phys D Appl Phys* **25** 1258
[24] Tago T, Kataoka N, Tanaka H, Kinoshita K and Kishida K 2017 *Procedia Engineering* **216** 175–81
[25] Moroz B L, Pyrjaev P A, Zaikovskii V I and Bukhtiyaro V I 2009 *Catal. Today* **144** 292–305
[26] Li Y and Church B C 2018 *Appl Surf Sci* **440** 861–72
[27] Figueiredo N M, Carvalho N J M and Cavaleiroa A 2011 *Appl Surf Sci* **13** 5793–8
[28] Tian W M, Li Z L, Kang H F, Cheng F S, Chen F F and Pang G X 2020 *Mater. Lett.* **242** 114236
[29] Cao W R, Chen L F and Qi Z W 2015 *J Mol Catal A-Chem* **401** 81–9
[30] Kulal D and Kodialbab V S 2021 *J Environ Chem Eng* **9** 105389
[31] Corro G, Vidal E, Cebada S, Pal U, Bafuelos F, Vargas D and Guillenminot E 2017 *Appl Catal B-Environ* **216** 1–10
[32] Duong L V, Wood B J and Kloprogge T 2005 *Mater Lett* **59** 1932–6
[33] Lu C, Shi X L, Zhang J, Zhou H Y, Xue Y Y and Ibrahim A M M 2020 *Surf. Coat. Technol.* **387** 125540