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Unveiling the Potential of Three-Step Anodization: Enhanced Length and Diameter of Titanium Nanotubes

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ABSTRACT

The titanium nanotubes prepared by anodization process are used in various applications, these nanotubes are typically produced using either a single-step or two-step anodization process. However, these methods focus on improving either the length or diameter of the titanium nanotubes individually. Achieving simultaneous enlargement of both length and diameter during the anodization process has not been previously reported. In this study, a three-step anodization process was introduced, employing a 30% water-containing electrolyte. The simultaneous enhancement of both the length and diameter of titanium nanotubes was successfully fabricated. The three-step anodization process produce average titanium nanotubes with a length of 7.5µm and a diameter of 300nm, as confirmed by surface morphological analysis. The formation of enlarged nanotube by three step anodization reaction was discussed. Comparison with conventional single-step anodization processes reveals a twofold increase in both length and diameter and a one-fold increase compared to two-step anodization process. These findings suggest that the three-step anodization process represents a promising alternative method to existing single or two-step anodization methods, offering enhanced control over the dimensions of titanium nanotubes for various applications.

1.Introduction:

Titanium and its alloys exhibit a compelling combination of lightweight and high strength, making them versatile materials with applications spanning biomedicine, aerospace, solar energy, sensors, hydrogen generation, and energy storage [1, 2]. To enhance the titanium surface properties, the surfaces are modified into nanotube structures to improve the electrolytic and mechanical responses across diverse applications have been explored [3]. Among the various surface modification techniques, the electrochemical anodization process standing out as a versatile method for fabricating nanotube structures over titanium metal [4, 5]. Over past 15 years, synthesizing TiO_2 nanotubes by electrochemical anodization have been extensively studied and discussed [6,7]. From the previous literature, a single-step and two-step anodization processes have been recognized as significant fabrication method to the formation of tube-like

nanotube structures [9]. However, it has been observed that both processes encounter limitations in concurrently achieving increased length and diameter of nanotubes. Specifically, these methods excel at enhancing either the tube diameter or tube length independently but do not effectively increase both parameters simultaneously [SI Table.1]. The fabrication of enlarged length and diameter of the titanium nanotubes offer potential solutions to circumvent practical implications for their intended applications.

The electrochemical anodization process entails simultaneous growth and dissolution reactions. these reactions contribute not only to increased crystallinity but also improved the nanotube length, enhances mechanical and physical behaviour, thereby enhancing overall material performance [8]. Our study involves anodizing titanium metal three times in the same electrolyte, a process known as the three-step anodization process. This method demonstrates a significant advancement in achieving maximum length and diameter of nanotubes simultaneously. The enlarged nanotube length and diameter formation in the three-step anodization process are greatly influenced by the water percentages present in electrolyte. The absence of water content in the electrolyte significantly delays the dissolution process due to strong binding between oxygen and carbon atoms. Consequently, the addition of water proves beneficial in promoting nanotube growth [8]. The present work discusses a mechanistic insight into the dissolution-reformation process not only provides a unique contribution and offering a deeper understanding of the complex reactions involved in TiO_2 nanotube synthesis by three step anodization process. Further, this finding reveals that the three-step anodization approach would surpasses the existing single-step and two-step anodization processes and make significant breakthrough in the anodization process.

2. Experimental

Titanium metal disc with a purity of 99.5% were procured from Sigma Aldrich. The essential chemicals, including ethylene glycol (purchased from Isochem, 98% purity), Ammonium Fluoride (purchased from Avra, 98% purity), ethanol (purchased from Changshu Hongsheng Fine Chemical, 99.9% purity), and acetone (purchased from Isochem), were employed in the experimental procedures. Additionally, diamond paste and aerosol, utilized for metal polishing, and were obtained from Metco.

Titanium metal disc with dimensions of 0.5 cm in thickness and 1cm in diameter used for anodization process. The sandpapers of various grit sizes, ranging from 80 to 1200 were used to polish the metal surface and diamond paste aerosol was applied to achieve a uniform mirror finish surface. The mirror polished titanium discs were rinsed with Ethanol, Acetone, and deionized water to eliminate the residual contaminants.

The Aplab Regulated DC Power Supply L1265 and Keithley 2110 5 1/2 Digital Multimeter were utilized for anodization process.

A two-electrode electrochemical cell configuration was employed, utilizing a

titanium disc as the anode and platinum act as the cathode. The anodizing area of 1cm^2 was maintained constant throughout all the experiments. Ultrasonication was performed throughout the anodization process using ultrasonic cleaner to remove impurities and facilitate the formation of the nanotube structure. The electrolyte containing, 0.3 wt.% ammonium fluoride with varying percentages of ethylene glycol and water specifically 10%, 15%, 20%, 25%, 30%, and 40%, were used to explore their influence on the anodization process. The three continuous anodization processes were performed in same electrolyte solution: The titanium disc was immersed in electrolytes with applied 45V DC potential for 2 hours at room temperature. The formed layer was removed by ultrasonication, it considered as one step anodization process [27].

The one step anodized titanium disc was exposed again with same electrolyte solution by the application of 45V DC potential for 2 hours at room temperature followed by the removal of formed layer by ultrasonication, it considered as two step anodization process [30]. The two-step anodized titanium disc was again underwent same anodization procedure in the same electrolyte with application of 45V DC potential for 2 hours at room temperature, it considered as Three step anodization process. The resulting titanium disc with nanotube formation was washed with ethanol and dried for further analysis. In order to maintain reproducibility, the anodization process was triplicated. The fabricated nanotubes morphology and crystal structures were analyzed by Carl Zeiss scanning electron microscope and the Bruker Eco 8 Advance X-ray diffraction instrument.

3. Results and Discussion

3.1. Electrochemical Anodization:

Figure 1 illustrates the current with respect to time plots was observed across electrolytes by three different anodization processes. The formation of titanium nanotubes by electrochemical anodization process typically involves three stages (I, II and III) are shown in Figure 1. There was a slight but significant shift in the current transient behavior when the anodization reaction was continued in the same solution with same Ti sample [6]. In stage I, all the anodization process showed different current value in the presence of applied potential. The single step anodization process has higher current (0.038A/cm) value compared to two step (0.025A/cm) and three step anodization process (0.008A/cm). This higher current value indicates [23], the release of Ti^{4+} ions from the metal at metal/oxide interface and move towards the oxide/ electrolyte interface. In the equation 1 indicates the continuous dissolution of Ti^{4+} ions from the Ti substrate to the electrolyte during first step of anodization.

$$Ti \rightarrow Ti^{4+} + 4e^{-} \quad (1)$$

At the end of stage I the current values are slowly decreases and the time taken for the formation of the barrier oxide layer increases from single step to three step anodization process. The Eq. 2 denotes the formation of barrier oxide layer the O_2^{-} migrates through the metal oxide interface to

form a TiO_2 layer. This is attributed to the gradual oxidation of the oxygen concentration in the electrolyte over successive anodization cycles.

$$Ti^{4+} + O^{2-} \rightarrow TiO_2 \quad (2)$$

For Stage II, there is a slight difference in the current value between single step, two step and three step anodization process shown in Fig 1. The appearance of small hump in single step and three step anodization process due to the roughness or defects formed in the TiO_2 layer from impurities, dislocation, or grain boundaries [31]. The dissolution of titanium cations (Ti^{4+}) at the metal oxide interface create the irregular pores and continuous vacancy site [21], (Eq 3 & 4) which results the constant current values were observed for all anodization process up to end of stage II.

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad (3)$$

$$Ti^{4+} + 4OH^- \rightarrow Ti(OH)_4 \quad (4)$$

For Stage III, at constant applied voltage the electrode attains a constant current value are shown in Fig 1. Under constant current conditions, the titanium substrate evenly distributes the current across its entire surface.

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O \quad (5)$$

$$Ti(OH)_4 + 6F^- \rightarrow [TiF_6]^{2-} + 4OH^+ \quad (6)$$

The competitive interactions among individual pores, coupled with the etching of the titanium substrate, play a significant role in driving the continued growth of titanium nanotubes. At the end of stage III, the total current value is limited by the diffusion of O_2^-, F^- ion and the formation of $[TiF_6]^{2-}$

$$Ti^{4+} 6F^- \rightarrow [TiF_6]^{2-} \quad (7)$$

The dissolution rate of the TiO_2 layer is controlled by the presence of free H^+ and F^- ions in the electrolyte. Therefore, the electrolytes used for single-step anodization processes, the equilibrium shifts towards the dissolution of the TiO_2 oxide layer (Equation 6). But in the three-step anodization process, due to the usage of same electrolyte the ethylene glycol slowly oxidizes to produces O_2^- ions leads to an increase in concentration of O_2^- ions. At the same time, the F^- ions get neutralized by the formation of $[TiF_6]^{2-}$ complexes upon repeated electrochemical anodization and it reduces the conductivity of the electrolyte.

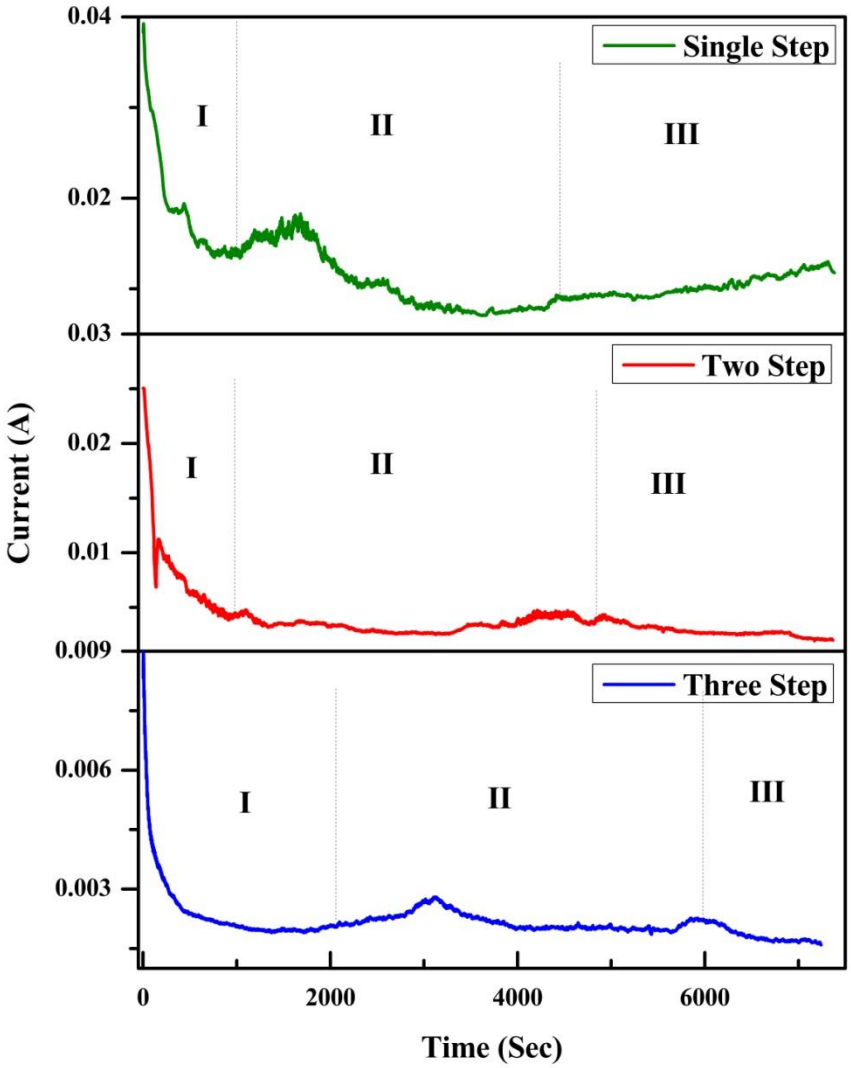


Figure 1: Current vs. Time plot of anodization process

Compared to neutralized F- ions, the increased concentration of O2- ions migrates faster to form a TiO2 layer than the [TiF6]2- complex, leading to the formation of longer and wider nanotubes

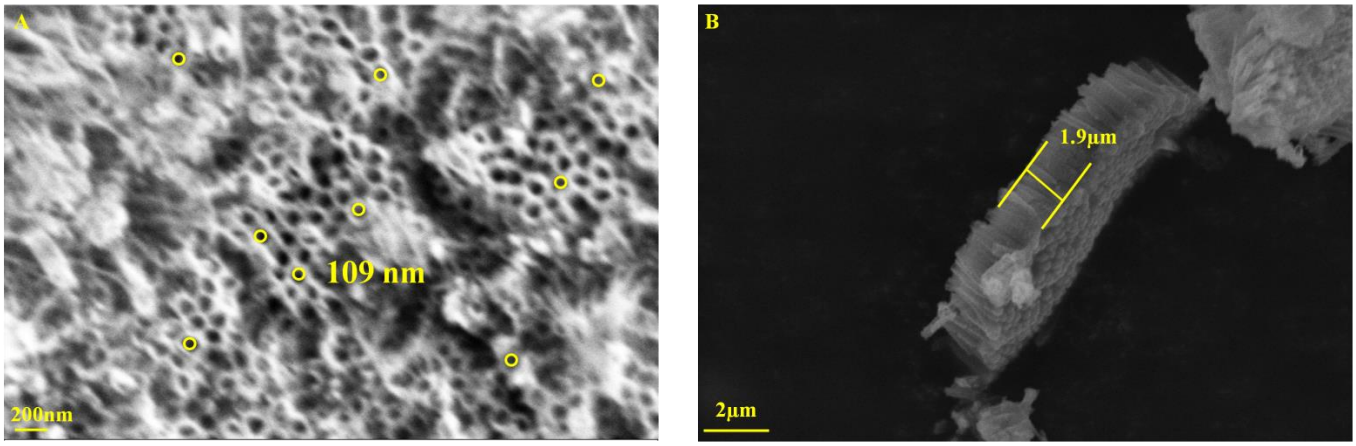
3.2.SEM morphological study:

Figure 2 shows the morphological features of the Ti nanotube formed by single-step, two-step and three step anodization process. Figure 2 (a & b) depict the surface and cross-sectional morphology of titanium nanotubes formed through a single-step anodization process. An average tube diameter of 109 nm and a tube length of 1.9 µm were obtained. The noticeable increases in the gap between individual titanium nanotubes and wall thickness were observed. This phenomenon is attributed to the high oxygen concentration (Eq. 4), which affects the formation of the titanium

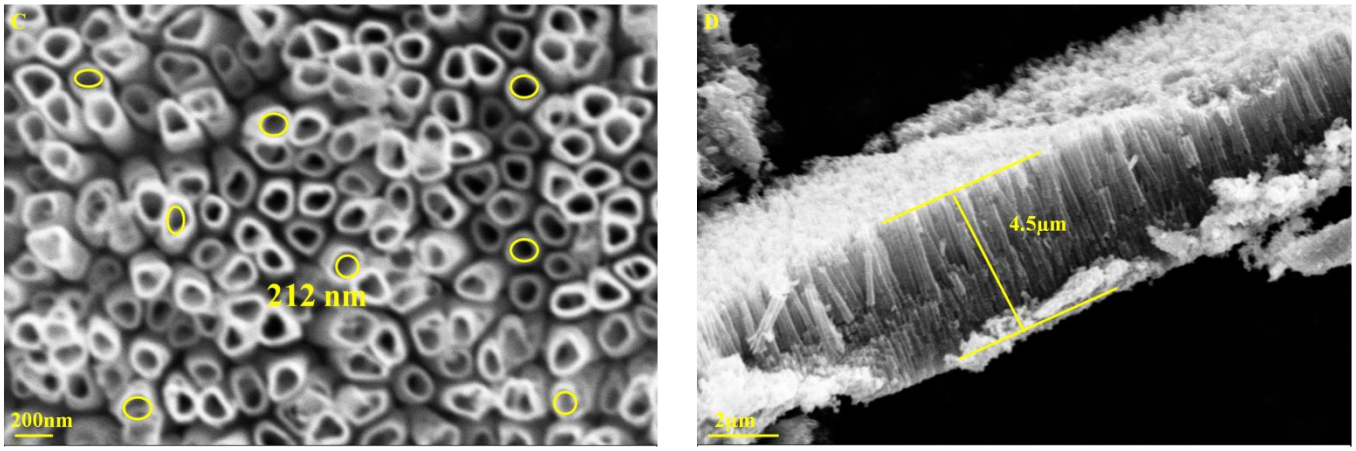
cation complex layer formation [27]. Further, it indicate that the single-step anodization process is inefficient for achieving well-defined and uniform titanium nanotube formation. Figure 2(c & d) shows the tube diameter and length obtained from the two-step anodization process. It is evident that the two-step anodization (Figure 2c) showed a notable enhancement in order and uniformity compared to single-step anodization.

In this process, it is observed that the thickness of the nanotube wall decreases while the inner diameter of the nanotubes increases. This is due to the decrease in oxygen concentration and higher degree of electrolysis undergoes in electrolyte solution compared to the single-step anodization process. Furthermore, the elongation of the tubes is facilitated by the penetration of negatively charged ions through the cation vacancy in the metal/oxide interface (Eq. 5 & 6). Through the two-step anodization process, titanium nanotubes with an average diameter of 212nm and a tube length of 4.5µm are achieved. The three-step anodization process showed in Figure 2 (d and e) results in the formation of titanium nanotubes with an average diameter of a 300nm and a length of 7.5µm. The observed results highlight significant differences in the morphology of nanotube formation among the single-step, two-step, and three-step anodization processes. These findings clearly indicate the essential role of extended electrolysis of the electrolyte solution in facilitating the formation of ordered nanotubes. The electrolyte solution utilized in previous anodization processes enhances the formation of nanotubular morphology, surpassing what is observed in single-step and two-step anodization processes. When the electrolyte with high water content is utilized, the diffusion of H^+ and F^- ions increases in the electrolyte solution with low viscosity (Eq.6 & 7). Furthermore, it is attributed that the formation of titanium nanotubes involves a competitive process of field-assisted electrochemical oxidation at the bottom of the nanotubes and chemical dissolution take placed at the top. As the rate of field-assisted electrochemical oxidation exceeds the rate of chemical dissolution, the length of TiO_2 nanotubes can be increased [25]. Over all the current transient analysis and morphological observations confirmed that the three-step anodization process yields superior length and diameter for titanium nanotubes.

Single Step Anodization



Two Step Anodization



Three Step anodization

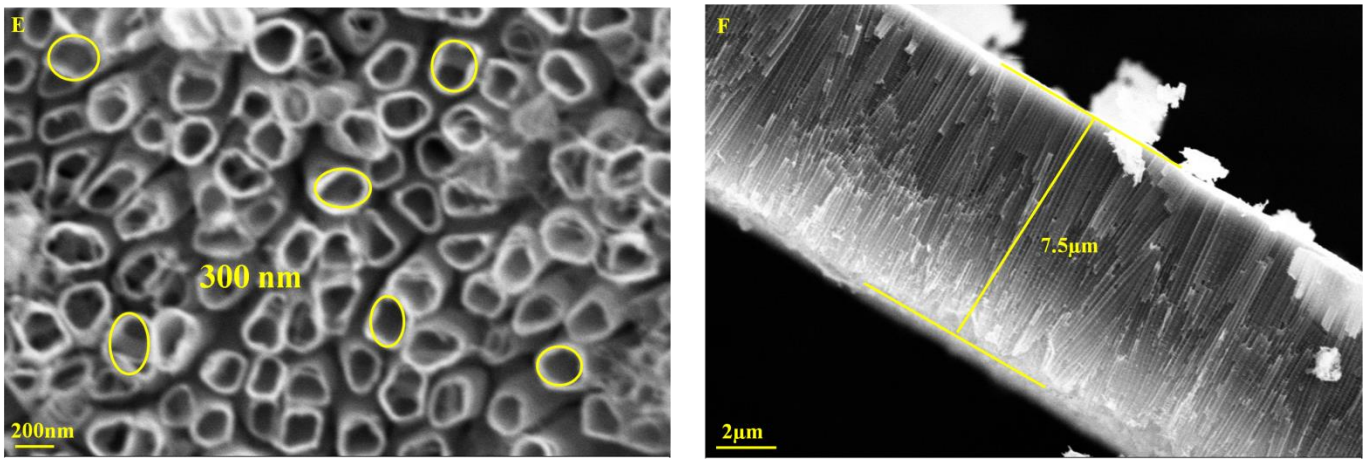


Figure 2: SEM images for Titanium nanotubes for various anodization process

3.3. Phase Analysis:

The XRD pattern of titanium nanotubes annealed at 450°C, along with the significant intensity peaks of TiO_2, is depicted in Figure 3. The anatase phase structure of various anodized samples was analyzed using JCPDS No. 89-4921 [16,8]. The increase in peak intensity indicates enhanced crystallinity with improved length of TiO_2 nanotube formation [17,28]. Finally, titanium nanotubes obtained from three-step anodization exhibit more crystalline peaks intensity compared to those from single-step and two-step anodization.

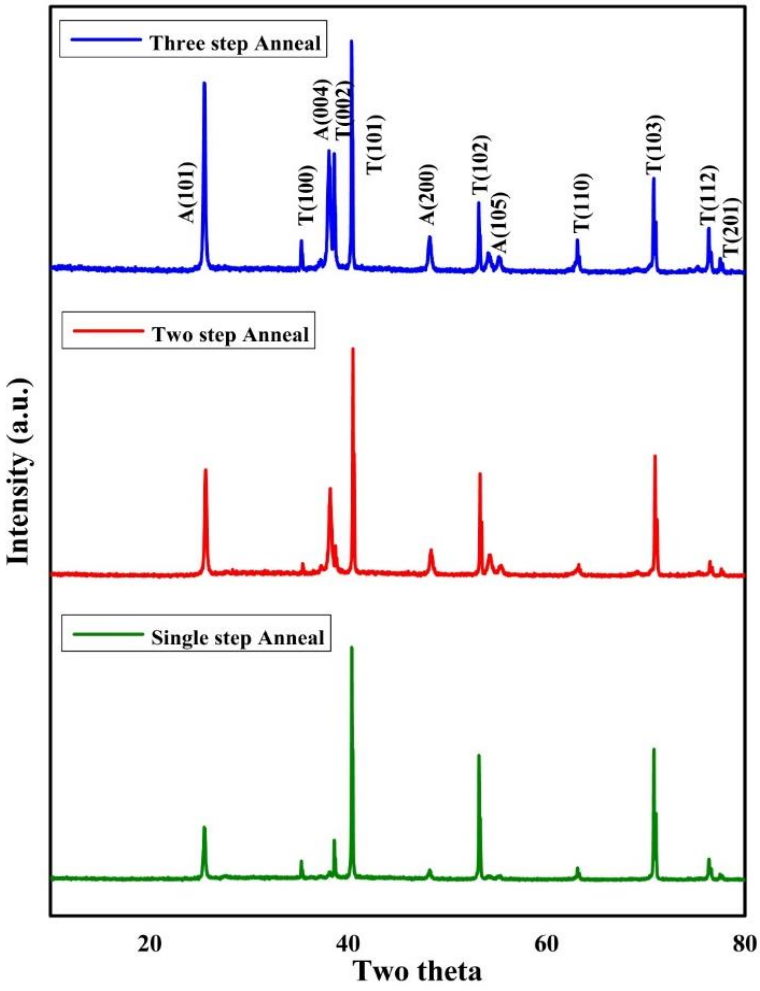


Figure 3: X-ray Diffraction Pattern of anodized TiO_2 nanotubes produced via Single step anodization process, Two step anodization process and Three step anodization process.

4. Conclusions

The fabrication of enlarged length and diameter of the titanium nanotubes was achieved by three step anodization process by using same electrolyte solution. The results revealed that the increased concentration of O_2^- ions place the crucial role to increase the length and diameter of the titanium nanotubes. The anodization process resulted in formation of sharp anatase peaks with enhanced crystallinity was confirmed by X-ray diffraction analysis. The SEM surface morphology confirmed that the three-step anodization process yielded the nanotube lengths of 7.5µm and diameters of 300nm. These results indicate that the maximum diameter and length of nanotube fabrication emerged as the most promising method compared to the existing two-step anodization process.

5. Credit authorship contribution statement

PadmaSanthiya MuthuKrishnan: Writing – review, editing, Methodology, Investigation and Formal analysis. Nagarajan Srinivasan: Writing – Original draft, Project administration, Methodology, Investigation, Formal analysis, Conceptualization.

6. Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

7. Availability of data and materials

The datasets generated during and analyzed during the current study are available from the Corresponding author on reasonable request.

8. Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article

9. Ethical Approval

Not applicable

10. Funding

Not applicable

11. Acknowledgement:

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