Journal Homepage: - www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
Article DOI: 10.21474/IJAR01/4181
DOI URL: http://dx.doi.org/10.21474/IJAR01/4181
ISSN NO. 2320-5407

RESEARCH ARTICLE

STUDY OF THE KINETIC RELEASE OF METHYLENE BLUE USINGTIO$_2$ NANOTUBES COATED WITH ARABIC GUM.

Ahmed makki sadda and Zainab T Y Al-Abdullah*
University of Basrah, College of Education for Pure Sciences, Chemistry Department, Basrah-Iraq.

Manuscript Info

Manuscript History

Received: 14 March 2017
Final Accepted: 16 April 2017
Published: May 2017

Key words:-
Anodisation, TiO_2 nanotubes, Drug release Arabic gum.

Abstract

TiO_2 nanotube array was fabricated by anodisation of a pure titanium plate. The anodisation process was carried out in ethylene glycol electrolyte; the applied voltage was 65 volt. The average length and diameter of the nanotube were (1.27 µm) and (68.5 nm) respectively. After annealing of TiO_2 nanotube at (400 °C) for (2 h), the amorphous nanotube walls converted into anatase. X-ray spectra prove the conversion of TiO_2 from amorphous to crystal phase. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were employed for characterization of TiO_2 nanotubes. The release of methylene blue from the tubes was controlled by coated with Arabic gum on TiO_2 nanotubes.

Introduction:-

Recently, most exceptional field for generating new applications is Nanotechnology. However, only few nanoproducts are now in use for medical purposes [1]. Nanotubes are the most common promising approaches of nanotechnology. TiO_2 nanotubes show great biocompatibility, thus making them satisfactory materials for the application in drug release mechanism. However, their usage as drug carriers is limited because of uncontrolled release. The geometry of TiO_2 nanotube as a membrane makes it appropriate for placement for both injected capsules and biomedical implant [2]. Xiao and his workers [3] showed outstanding biocompatibility of both TiO_2 nanotube arrays that prepared by anodisation and annealed in a carbon atmosphere. Application of drug delivery system was accomplished by various methods [4]. A number of drugs were tested for release mechanism such as ampicillin [5] and ibuprofen [6]. Popat and his worker established that TiO_2 nanotube arrays were used for local delivery of antibiotics at the site of implantation [7]. This proved the prevention of bacterial adhesion. However, the specific control of the nanotube length and diameter premits different amounts of drugs to be released at diverse rates at the implantation site. However, in their work, only straight, circular TiO_2 nanotubes were investigated. Recently Song and co researcher created amphiphilic TiO_2 nanotubes with a hydrophobic monolayer modification after the first step in the anodisation process. These tubes could be invested for bimolecular carriers, in which the outer hydrophobic barrier provides an efficient cap against drug release to the environment. By using the photo catalytic property of TiO_2, a specificly controlled removal of the cap with a excellent control of release of the hydrophilic drug payload and this was attained under UV illumination [8]. Wang and his worker used mesoporous titanium zirconium oxide for drug delivery applications [9]. Biomaterials polymers were also used [10], [11]. Bioactive porous networks of titanium dioxide templated with collagen for drug delivery was also employed [12], [13], [14], [15], [16].

Corresponding Author:- Zainab T Y Al-Abdullah.
Address:- University of Basrah, College of Education for Pure Sciences, Chemistry Department, Basrah-Iraq.

Using Arabic gum as an outer layer covering the nanotubes mouth is one of the aims of the work illustrated in this paper thus studying the kinetic of MB release from TiO_2 nanotubes that were synthesized by anodisation this successful approach is the first of its kind that is using Arabic gum as the outermost layer of TiO_2 nanotubes. Arabic gum is one of the exceedingly accepted ingredients in the food and pharmaceutical industry.

Experimental:-

Titanium foils (99.6% purity) were degreased priory to anodisation by sonicating them in acetone, rinsed with deionised water (DI). The electrochemical anodisation set-up was composed of a high-voltage power supply, leaving the electrodes at distance (6) cm and Ti surface at (1) cm^2 open to the electrolyte. The anodisation was carried out in a two-electrodes electrochemical system at a constant voltage of (60) V and the time of anodisation was (120) min. The Ti plates were used as anode and cathode, immersed in electrolyte contain ammonium fluoride, ethylene glycol and water, (2 vol% H_2O and 0.5 wt% NH_4F and 97.5 wt% EG) at room temperature. After 120 min, nanotubes with lengths of 12 µm and 100 nm in diameter were obtained. SEM and TEM were employed for the morphological characterization of the TiO_2 nanotubular layers. The annealing of TiO_2 nanotubes arrays was moniterod in air at (400°C for 2h) by XRD spectra. For release application the dipping of TiO_2 nanotubes arrays in (50) ppm MB was carried out for (2) weeks. Then after drying and rise the plate the coated by Arabic gum was achieved by spin coating at constant rate.Biological activity was examined using E-Coli.

Result and Discussion:-

Anodisation:-

New development in the concept of self-ordering growth by anodic oxidation have made this approach. The most commonly methods for enhancing ordered nanotubes arrays of various metals like Ti, Al, etc [17]. Anodisation of the metal Ti that creates TiO_2 nanotubes represents the conventional example of electrochemical self-ordering like in the anodisation of Al to form ordered porous alumina (Al_2O_3) and that silicon forming porous Si structures.

In the anodisation process water in the solution reacts with the titanium metal surface leading to the formation of oxide layer under an applied electric field as seen in equation1, 2.

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$ ..... (1)

$Ti + O_2 \rightarrow TiO_2$ ..... (2)

TiO_2 oxide layer is then etched into as it is dissolved with assistance of fluoride ions as seen in equation 3.

$TiO_2 + 4H^+ + 6F^- \rightarrow [TiF6]^{2-} + 2H_2O$ ..... (3)

Chemical dissolution of the oxide layer is caused by the presence of fluoride ions. A great advantage of anodisation is their ability to tune the size and shape of nanotubular arrays on varied kinds of materials, viz., metals and metal alloy substrates, to achieve precise dimensions, satisfying the requirements of specific applications by means of controlled anodic oxidation. It can be categorized as one of the most basic, cheep and most straight-forward approaches to develop ordered porous nanostructures under suitable conditions.

Current and anodisation time:-

When an oxide layer is formed on the titanium plate, the current rapidly decreases exponentially for the reason that the oxide layers inhibit electronic charge from reaching the substrate underneath.

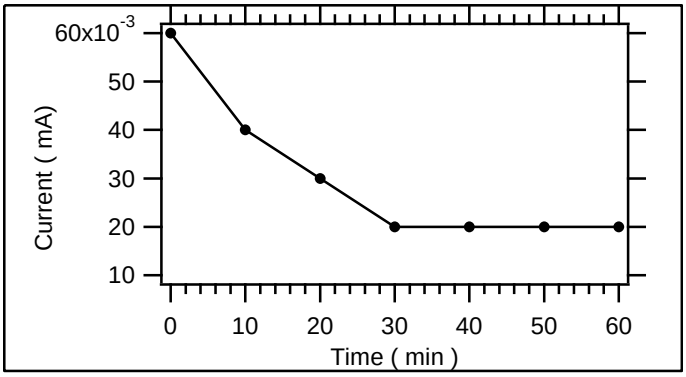

Figure 1:- shows the relationship between the scheme anodizing and severity of the current flowing time at constant voltage (65V).

(Fig.1) shows at the beginning of the reaction we note that the current in the highest peak and when to continue the reaction decreases the current value is significantly until it reaches zero then rise slightly and then remains the status of the stability and explains that the highest possible current starters that titanium superconductor and continuously reaction least because of the current competition between the fluoride ion (F^-) and ion oxide to form a complex [TiF_6] and between a binary composition and titanium oxide [TiO_2] by ion oxide (O^-) [18]. [19]. The involvement of multiple competitive reactions in the initial anodisation process makes it impossible to build a quantitative model for the time-dependent behaviour. During the first 10 min, an oxide layer is gradually developed and the anodic voltage drops within this oxide layer. This leaves a much lower anodic bias for H_2O electrolysis at the oxide/electrolyte interface. Meanwhile, the oxide layer allows migration of oxide anions so the ionic conductivity increases. The overall current becomes stable at this stage. In this region, the nature of conductivity changes from electronic to ionic.

Characterisation using SEM and TEM:-

The size and shape of the TiO_2 nanotubes were examined clearly under scanning electron microscope (SEM). The SEM images in (Figure 2) shows that the tubes are self ordered and cylindrical in shape. The average tube lengths was (1.27μm) and the average diameters of the tubes was (68.5nm).Moreover, the mabrane of TiO2naotubes was examined by TEM as can be seen in (Figure.3).

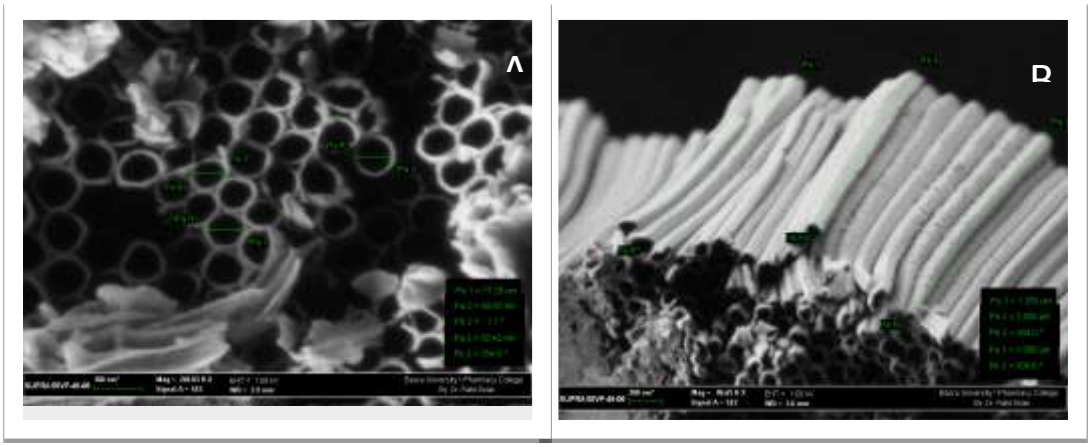

Figure 2:- SEM images show (a) top view (b) cross section image of TiO_2 nanotubes.

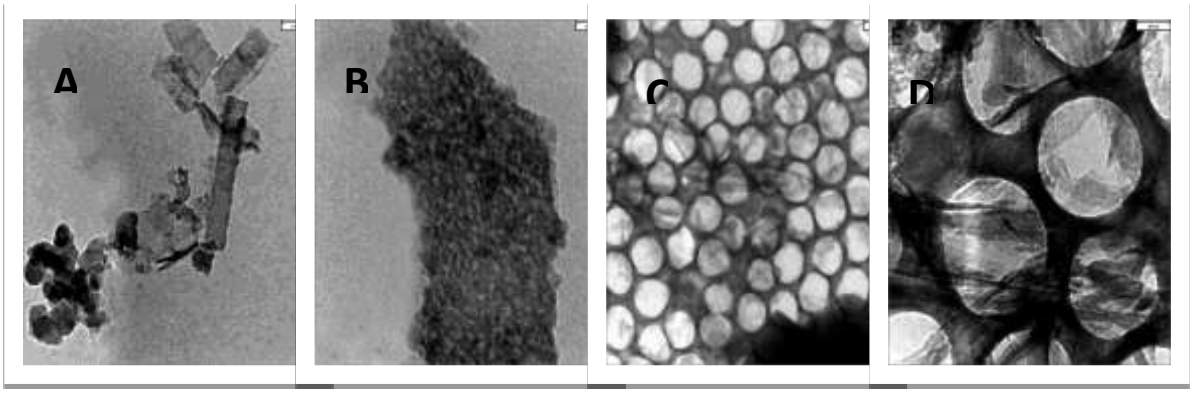

Figure 3:- TEM images show (A) cross section image of TiO_2 nanotubes (B) top view (C,D) bottom view of TiO_2 nanotubes.

XRD spectra:-

The diffraction data show two phases: anatase(A), and Ti metal(B). In general, samples annealed at low temperature show only the presence of anatase with the 101peak at $2\theta = 24.95^{\circ}$. anatase peaks were calibrated by standard patterns [24]. The diffraction peaks from the Ti substrate can also be observed.Figure 4 show these detailes.

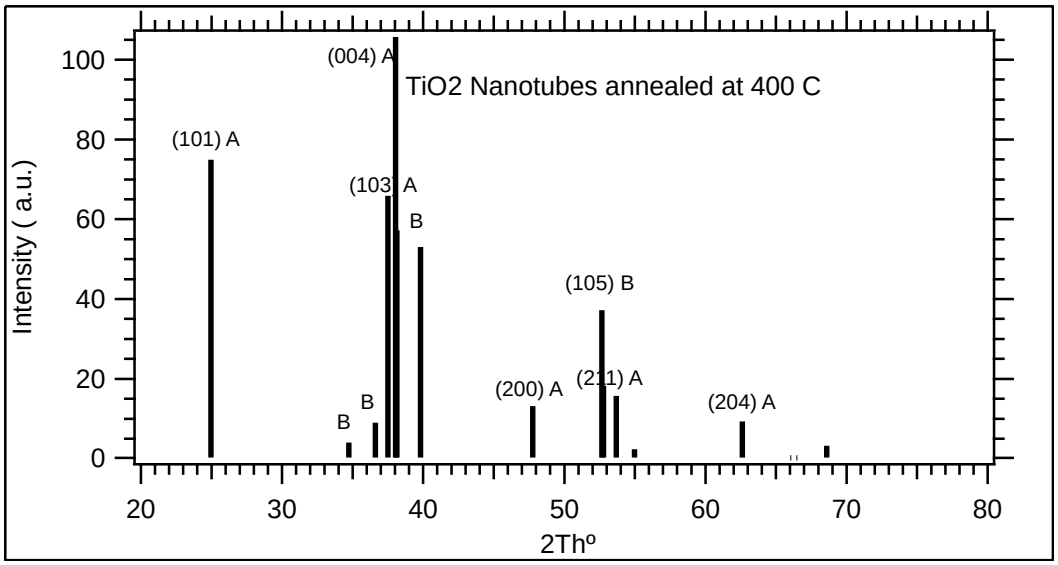

Figure 4:- X-ray diffraction pattern of TiO_2 nanotubes annealed to 400 °C.

Contact angle Measurements:-

The contact angle measurement was carried out on TiO_2 nanotubes using drops from MB the results showed high hydrophilic of TiO_2 nanotubes surface.

Table 1:- show the contact measurements for Ti and TiO_2 nanotubes.

Compounds	Tubes dimensions	Contact angle (degree)
Titanium plate		80
TiO_2 nanotubes anodised at (60min),(65v)	L = 1.2 µm	55
TiO_2 nanotubes anodised at (90 min),(65v)	L = 2.8 µm	43
TiO_2 nanotubes anodised at (120 min), (65v)	L = 3.0 µm	36
TiO_2 nanotubes anodised at (60 min), (55v)	D = 60.67 nm	62
TiO_2 nanotubes anodised at (60 min), (65v)	D = 68.50 nm	55
TiO_2 nanotubes anodised at (60 min), (75v)	D = 91.39 nm	37

Biological activity:-

The antibacterial of the TiO_2 nanotubes was carried out against S. *aureus*. Using of titanium plate without nanotubes does not show any biological activity. However, using TiO_2 nanotubes was inhibiting the growth of *S. aureus* underneath TiO_2 nanotubes as seen in figure 5(A). The super hydrophilic of the surface after synthesise of TiO_2 nanotube on titanium enable from prevent of bacteria growth hence it can't adhesion on the surface because of its super hydrophilic.

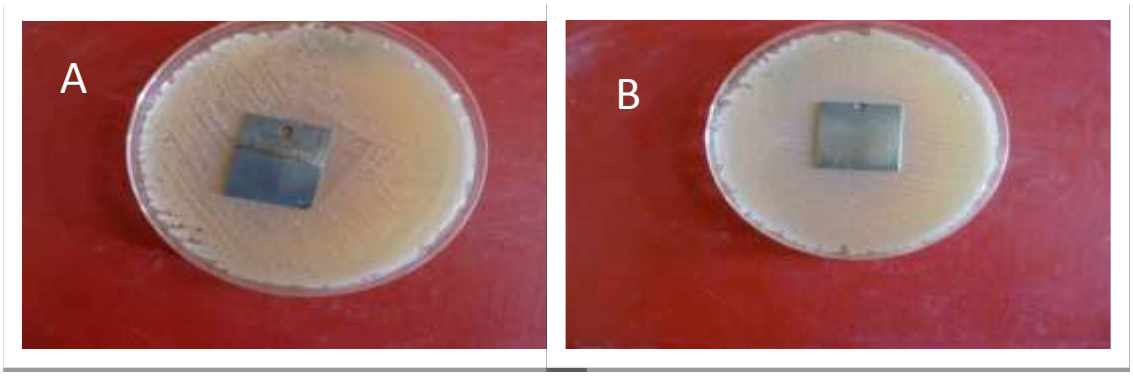

Figure 5:- Antibacterial activities of TiO_2 nanotubes against S. *aureus* using agar-well diffusion method.

The Release kinetics of MB:-

Synthesis TiO_2 nanotubes was applied on drug release activity. Standard drug release measurements are typically made in media such as saline, water or other buffered aqueous solutions [20]. In our experiments methylene blue release kinetics, was measured in (20) ml deionised water at (25) ºC. The concentrations of released MB were measured by UV-Vis spectrometry at (663) nm where the MB has maximum absorbance. Under controlled conditions, MB elution was measured at various times up to (1) week, after which the MB concentration reached an area of constancy and release completed. Fig.6 shows the chart for MB release process. From this figure the release was controlled by using Arabic Gum from our research this is the first time for using Arabic gum on TiO_2 nanotubes for control the release. Arabic Gum is biocompatible, economical and green material for using in drug release purposes.

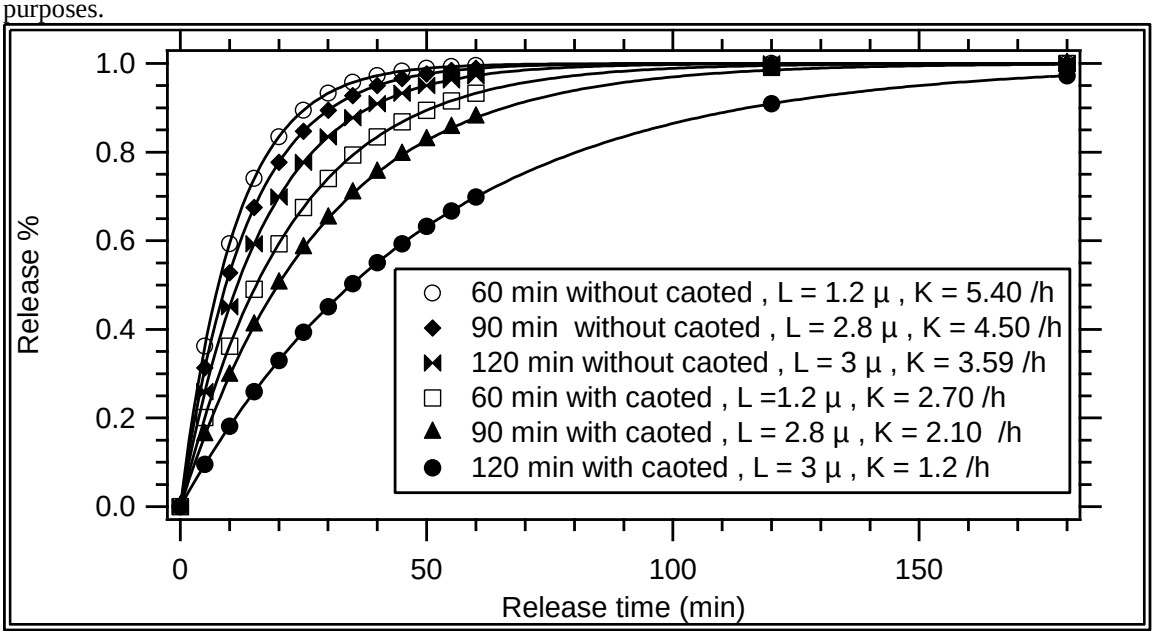

Figure 6:- Release of methylene blue dye from coated and non-coated TiO_2 nanotubes.

Conclusion:-

TiO_2 nanotubes were synthesis by anodisation which is economy, fast, reproducible method. TiO_2 nanotubes arrays then were applied on drug release activity. The release was controlled more by coated with Arabic gum on TiO_2 nanotubes which is first time used for such purpose. This coated will lead to use other green chemistry materials for coating on another nano material for drug release.

References:-

1. *Nano silver based targeted drug delivery for treatment of cancer Royyuru Sree Soumya1 and Pamidipati Gayatri Hela2. Scholars Research Library,* NTU, H., India and B. SiRi Life Sciences, India, 2013. **5**((4)): p. 189-197.
2. Nabeen K. Shrestha, e.a., *Magnetically Guided Titania Nanotubes for Site-Selective Photocatalysis and Drug Release.* ,. AngewandteChemie-International Edition, 2009. **48**(5): p. 969-972.
3. XiLin Xiao, e.a., *Biocompatibility and in vitro antineoplastic drug-loaded trial of titania nanotubes prepared by anodic oxidation of a pure titanium.* Science in China Series B-Chemistry, 2009. **52**(12): p. 2161-2165.
4. PeishengXu, e.a., *Intracellular Drug Delivery by Poly(lactic-co-glycolic acid) Nanoparticles.* Molecular Pharmaceutics, 2008. **6**(1): p. 190-201.
5. Catauro M, R.M., Convertito C, Melisi D, Rimoli MG, *Characterization,, bioactivity and ampicillin release kinetics of TiO_2 and TiO_2SiO_2 synthesized by sol-gel processing.* Journal of Materials Science-Materials in Medicine, 2006. **17**: p. 5413-420.
6. Zhang Wang, F.C., Ping Li,, and Xiufeng Xiao,, *P25 nanoparticles decorated on titania nanotubes arrays as effective drug delivery system for ibuprofen. .:* . Applied Surface Science,, 2015. **324**: p. 621-626.
7. Ketul C Popat, e.a., *Titania nanotubes: A novel platform for drug-eluting coatings for medical implants.:* . Small,, 2007. **3(11)**: p. 1878-1881.
8. Yan-Yan Song, F.S.-S., Sebastian Bauer and PatrikSchmuki, *Amphiphilic TiO_2 Nanotube Arrays: An Actively Controllable Drug Delivery System.* ,Journal of the American Chemical Society, 2009. **131(12)**: p. 4230-4232.
9. Xiaojian Wang, D.C., Lu Cao, Yuncang Li, Ben J. Boyd, and Rachel A. Caruso, , *Mesoporous Titanium Zirconium Oxide Nanospheres with Potential for Drug Delivery Applications.* . ACS Applied Materials & Interfaces, 2013. **5(21)**: p. 10926-10932.
10. Kumaresh S Soppimath, T.M.A., Anandrao R Kulkarni, Walter E Rudzinski,, , *Biodegradable polymeric nanoparticles as drug delivery devices. Journal of Controlled Release,.* 2001. **70(2)**: p. 1-20.
11. Langer, R.a.N.A.P., *Advances in biomaterials, drug delivery and bionanotechnology.* . Aiche Journal, 2003. **49(12)**: p .2990-3006.
12. Mc Master, W.A., X. Wang, and R.A. Caruso, , *Collagen-Templated Bioactive Titanium Dioxide Porous Networks for Drug Delivery.* ACS Applied Materials & Interfaces, 2012. **4(9)**: p. p. 9,4717-4725.
13. S. Al-Assaf, M.S., C. McKenna, H. Aoki, G.O. Phillips, Structural Chemistry, 2009. **20::** p. p. 325-336.
14. Sun, T.S., K, . Chem. Rev., Chem. Rev., 1994. **94**: p. p. 857.
15. M.R. Mucalo, C.R.B., M. Manley-Harris, . Materials Science, (2002. **37**: p. p. 12.
16. H. Aoki, S.A.-A., G.O. Phillipssaf, T. Katay,.Food Hydrocolloids, 2007. **21**: p. 329-337.
17. Macak JM, T.H., Ghicov A, Yasuda K, Hahn R, Bauer S, Schmuki P., *TiO_2 nanotubes: Self-organized electrochemical formation, properties and applications.* Curr. Opin. Solid State Mater.Sci., 2007. **11:18** .
18. Su, Z.X.a.W.Z.Z., *Formation Mechanism of Porous Anodic Aluminium and Titanium Oxides.* Advanced Materials, 2008. **20(19)**: p. 3663.
19. Su, Z.X.a.W.Z.Z., *Formation, microstructures and crystallization of anodic titanium oxide tubular arrays. p.* Journal of Materials Chemistry, 2009. **19(16)**: p. p. 2301-2309.
20. Langer, R.a.N.A.P., *Advances in biomaterials, drug delivery, and bionanotechnology.* Aiche Journal,, 2003 **49(12).** p. 2990-3006.