Effect of Anodization Voltage on TiO_2 Nanotubes for Photodegradation of Formaldehyde

Nurul Tasnim Sahrin, Chong Fai Kait, Lee Siew Ling, and Mohd Dzul Hakim Wirzal

Abstract In this work, titanium dioxide nanotubes (TiO_2 NTs) were prepared via electrochemical anodization of titanium foil in choline chloride-glycerol ionic liquid as the electrolyte. The anodization voltage was varied from 5 to 50 V to investigate its effect on the properties of TiO_2 NTs. The NTs were characterized using FESEM and XRD analyses while the photocatalytic performance of the NTs was investigated for photodegradation of formaldehyde (HCHO) under visible light irradiation. Experimental results showed that the anodization voltage has an important impact on the surface morphology of TiO_2 NTs and the amorphous phase without heat treatment process. Higher anodization voltage led to pore rupture. TiO_2 NTs fabricated at anodization voltage of 30 V showed enhanced photocatalytic performance where 26.99 mg L^{-1} g^{-1} of removal after 120 min of reaction duration in the presence of visible light radiation.

N. T. Sahrin (✉) · C. F. Kait
Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
e-mail: nurul_17007753@utp.edu.my

C. F. Kait
e-mail: chongfaikait@utp.edu.my

C. F. Kait
Centre of Innovative Nanostructures and Nanodevices (COINN), Institute of Autonomous System (IAS), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

L. S. Ling
Center for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, Johor Bahru, Malaysia

Chemistry Department, Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru, Malaysia

L. S. Ling
e-mail: lsling@utm.my

M. D. H. Wirzal
Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
e-mail: Mdzulhakim.wirzal@utp.edu.my

© The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2021

S. A. Abdul Karim et al. (eds.), *Proceedings of the 6th International Conference on Fundamental and Applied Sciences*, Springer Proceedings in Complexity,
https://doi.org/10.1007/978-981-16-4513-6_18

Keywords TiO_2 nanotubes · Ionic liquid · Anodization · Formaldehyde

1 Introduction

TiO_2 is the most important and versatile metal oxide semiconductor photocatalyst and finds an unequivocal prospect in environmental pollutant removal. However, its recovery from waste streams is the crucial drawback owing to its practical application for environmental pollutants removal. The fabrication of TiO_2 nanotubes (NTs) on a substrate is an effective approach to overcome this limitation. In addition, TiO_2 NTs offers several other benefits such as uniform morphologies, high surface-to-volume ratio, well-oriented growth as well as cost effective construction making them a promising functional material for environmental applications [1].

Recently, various techniques especially hydrothermal and electrochemical anodization have been employed to fabricate TiO_2 NTs [2]. Amongst the methods investigated so far, anodization has garnered great interest because of its ease and simplicity, greater control and reproducibility. Moreover, this technique produces strongly adherent nano porous TiO_2 layer on the substrate, which is more desirable for environmental pollutants removal. The TiO_2 NTs fabricated with anodization have been tested and proved useful in several applications including dye sensitized solar cells, photocatalysis, biomedical applications and gas sensing [3].

Several important synthesis parameters such as anodization voltage and time, electrolyte composition, post treatment temperature etc. are affecting the properties of TiO_2 NTs. It is reported that anodization voltage is one key parameter that effect the formation of TiO_2 nanotube arrays on the foil surface and straight channels against the foil [4]. The applied voltage can strongly influence the various properties of TiO_2 NTs namely, pore diameter, inter pore distance and film thickness [1]. Numerous research groups have investigated the effect of anodization voltage on the properties of TiO_2 NTs. However, there is limited literature related to the effect of anodization voltage on the photodegradation of environmental pollutants, especially formaldehyde (HCHO) removal from waste air streams.

The present study is aimed to fabricate TiO_2 NTs using glycerol mediated ionic liquid as the electrolyte. The IL electrolyte used in this study is greener, less toxic, has favourable electrochemical properties and more importantly it is cheaper and display high biocompatibility [5, 6]. The electrolyte was obtained by mixing choline chloride and glycerol in 1:2 molar ratio where glycerol acts as a complexing agent and hydrogen bond donor while choline chloride as hydrogen acceptor [7]. The formation of choline chloride-glycerol eutectic ionic liquid (EIL) was confirmed by the determination of its melting point which is lower than the melting point of the starting materials, mainly due to the formation of intermolecular hydrogen bonds during synthesis [8]. Different voltages from 5 to 50 V were applied for the fabrication of TiO_2 NTs via anodization and the properties including surface morphology and structural properties of the obtained TiO_2 NTs were determined using field emission scanning electron microscopy (FESEM) and X-ray diffraction

(XRD). The photocatalytic performance of the fabricated TiO_2 NTs was evaluated for the removal of gaseous HCHO under visible light irradiation.

2 Materials and Methodology

2.1 Synthesis of Chloride-Based Electrolyte

Choline chloride (ChCl, 98%, Sigma Aldrich) and glycerol ($C_3H_8O_3$, 98%, Fischer Scientific) were mixed at 1:2 molar ratio and heated for 30 min at 80 °C to form a colorless eutectic ionic liquid (EIL) [8, 9]. The EIL was used as the electrolyte for the anodization process of Ti foil to form TiO_2 NTs.

2.2 Synthesis of TiO_2 NTs

The substrate used for anodization process was technical grade titanium foil with thickness of 0.1 mm (Titanium, Ti Gr5/Tc4 Grade 5 ASTM B265 Thin Plate Sheet), was cut into 2 cm × 1 cm. The Ti substrate were ultrasonically washed in acetone for 10 min, followed by thorough rinsing with deionized water and dried in air. Anodization process was conducted using electrochemical set up and the details can be found in our previous work [10]. Briefly, the set up consisted of platinum rod as cathode and Ti substrate as anode 2.5 cm was the distance fixed between cathode and anode. The electrode was immersed in 35 mL of choline chloride-glycerol eutectic ionic liquid (ChCl-Gly EIL) as the electrolyte and the experiment was carried out at anodization voltages of 5, 10, 15, 20, 30, 40 and 50 V (DC power supply) for a fixed period of 1 h under ambient temperature and pressure. After anodization process, the obtained samples were removed instantly from the electrolyte solution and rinsed with deionized water. The samples were air-dried in ambient atmosphere. The as-synthesized TiO_2 NTs were further studied without undergoing any calcination process.

2.3 Characterization of TiO_2 NTs

In order to investigate the surface morphology of the synthesized TiO_2 NTs, the samples were characterized by Field emission scanning electron microscopy (FESEM) using Carl Zeiss instrument (SUPRA 55VP). The images were captured at 50 kX magnification at an acceleration voltage of 30 kV. The fabricated NTs were further analyzed using X-ray diffractometer (XRD, PANalytical X'Pert^3 Powder) with Cu Kα radiation (40 kV, 40 mA). The scanning was carried out at 2θ angle between 10° and 80° with the step size of 0.01°.

2.4 Photocatalytic Degradation of Formaldehyde

The photocatalytic activity for the removal of HCHO was evaluated in a batch mode. The titanium foil containing TiO_2 NTs was positioned in the 250 mL quartz photoreactor attached with a holder. HCHO (37% in aq. solution, Sigma Aldrich) of 3.22 ppm was stored in a tightly sealed stainless-steel container. HCHO vapor filled the quartz photoreactor by diffusion when the valves were opened. After 30 min of equilibration in the dark, the quartz photoreactor was illuminated with a halogen lamp (150 W) as the visible light source. The photocatalytic activity of HCHO was monitored by sampling at a regular interval of 30 min for a total of 120 min. A HCHO sensor meter (Hal Tech) connected at the outlet to measure the HCHO vapor concentration. The sensor can measure the HCHO concentration up to 10 ppm. During the experiments, the temperature of the photoreactor was maintained at 25 ± 1 °C using a cooling fan. At the end of the reaction, the remaining HCHO was purged with He. The photodegradation performance, X was investigated and calculated using Eq. (1):

$$X = \frac{C_o - C_t}{\mathrm{m}} \tag{1}$$

where, X denotes the concentration of HCHO (mg L^{-1}) removed per gram of TiO_2 NTs, C_o is the initial HCHO concentration (mg L^{-1}), C_t represents HCHO concentration at sampling time, t (mg L^{-1}) and m represents the mass of the TiO_2 NTs photocatalyst used (g).

3 Results and Discussion

3.1 Characterization of TiO_2 NTs

3.1.1 Morphology of TiO_2 NTs

The NTs morphology and structure are strongly influenced by the anodization condition, particularly the anodization voltage, as it is the important factor controlling the tube diameter [11]. Generally, NTs growth occurs proportional to the anodization voltage up to a voltage where dielectric breakdown of the oxide occurs. The effect of anodization voltage on the TiO_2 NTs formation was investigated with the objective to fabricate NTs with optimum pore diameter for improving photodegradation of HCHO under visible light illumination.

Figure 1 shows the FESEM images of anodized Ti foil in ChCl-Gly EIL at various anodization voltages. The evolution morphologies for TiO_2 NTs as a function of voltage are shown in Fig. 1a–h. No NTs formation was observed at a lower anodization voltages of 5 and 10 V as depicted in Fig. 1a, b. The results suggest that lower voltages are incapable of initiating NTs formation and growth in ChCl-Gly EIL electrolyte. Increasing the anodization voltage to 15 V produced a few poor-ordered TiO_2 NTs structures concentrated at one place on the surface of the Ti foil as can be seen in Fig. 1c. This is because the formation of oxide layer is too thin which retards the possibility of oxide layer dissolution to form the tubular structure [12].

Increasing the anodization voltage to 20 V, led to increased coverage of irregular shaped TiO_2 NTs on the surface of Ti foil as illustrated in Fig. 1d. Compared to the sample prepared at 20 V, the sample prepared at 30 V showed the formation of denser clusters of the TiO_2 NTs as presented in Fig. 1e. Nevertheless, it is important to note that further increase in anodization voltage beyond 30 V led to NTs rupture, disintegration, and less dense distribution of the tubular structure of the TiO_2 NTs which can be observed in Fig. 1f–h. The results suggest that anodization voltages of 30 V could produce TiO_2 NTs with well-defined pore structure and evenly distributed NTs on the surface of Ti foil. Apparently, the average inner tube diameter increased from 23.62 ± 3.52 nm to 35.31 ± 3.87 nm when the voltage was raised from 15 to 50 V as tabulated in Table 1. The results are consistent with those reported by Omidvar et al. [13].

In the present work, the NTs diameter was observed to increase with increasing anodization voltage which may be due to the severe electrical field dissolution which accelerates the formation of pore-like structures during the initial stage of anodization process [14]. Studies suggested that the difference in anodization voltage determines the strength of electrical field developed across the oxide layer and thus affects the tube diameter. Consequently, larger NTs were obtained at higher voltage [15]. Previous studies reported that NTs with diameter ranging between 30 and 90 nm can be produced by anodization in 0.25 wt% (NH_4F + ethylene glycol) solution + 2 vol% water at voltages between 30 and 60 V [4]. In addition, Gong et al. showed that an increase in TiO_2 NTs diameter could be obtained, ranging from 25 to 65 nm for anodization voltage ranging from 10 to 40 V where Ti foils were anodized in 0.5 wt% HF solution [16]. These studies showed that the NTs diameter was greatly influenced by the anodization voltage. In this work, the TiO_2 NTs with diameter from 23.62 ± 3.52 nm to 35.31 ± 3.87 nm were synthesized depending on the anodization voltage.

3.1.2 XRD Analysis

X-ray diffraction analysis was carried out to investigate the effect of anodization voltage on structural properties of the synthesized TiO_2 NTs. The XRD patterns of the TiO_2 NTs synthesized at various anodization voltages for 1 h duration are shown in Fig. 2. All the NTs samples were prepared without post-heat treatment or calcination process. In Fig. 2, all samples represent characteristic diffraction peaks

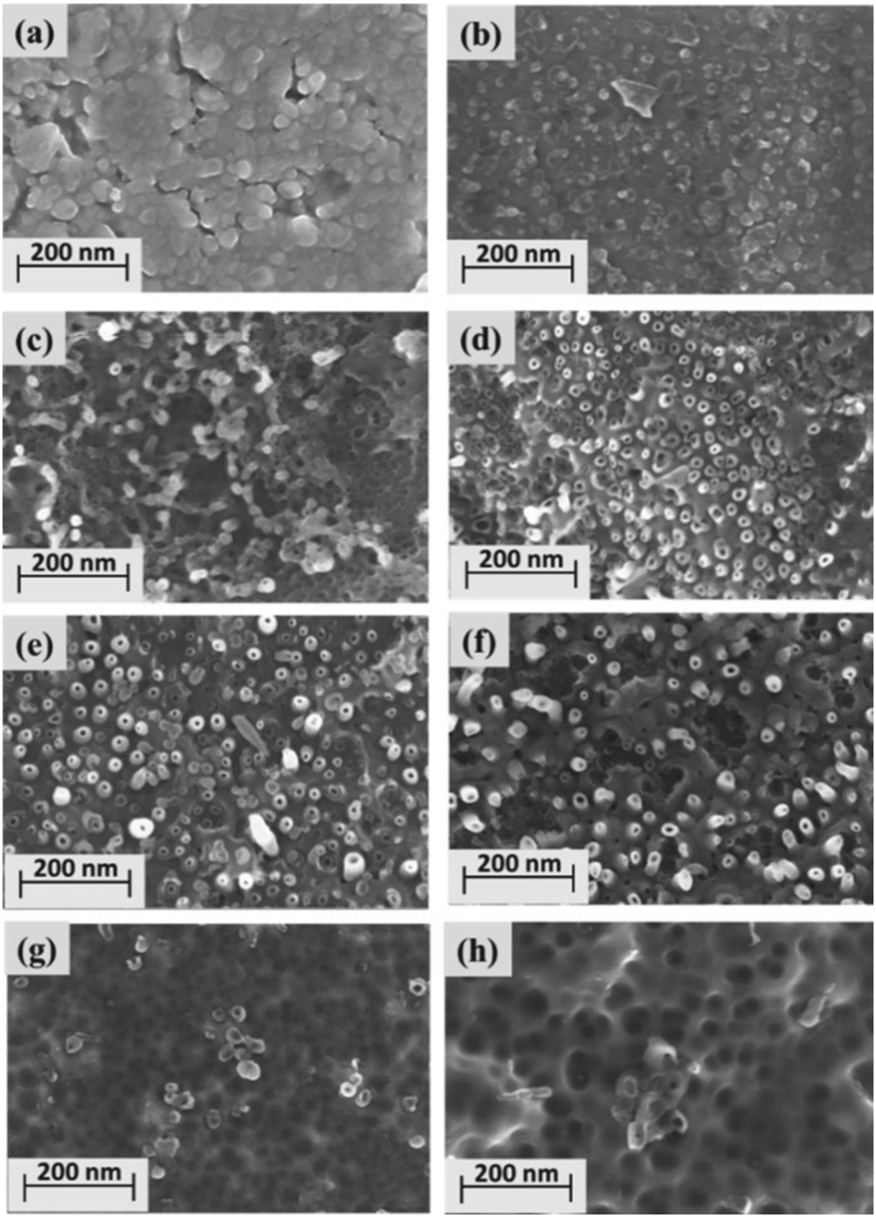

Fig. 1 FESEM images of TiO_2 NTs observed for 60 min at different anodization voltages: **a** 5 V, **b** 10 V, **c** 15 V, **d** 20 V, **e** 30 V, **f** 35 V, **g** 40 V and **h** 50 V at 50 kX magnification

Table 1 Average inner tube diameter of TiO_2 NTs anodized for 60 min at different anodization voltage

Sample	Anodization voltage (V)	Average inner tube diameter (nm)
(a)	5	–
(b)	10	–
(c)	15	23.62 ± 3.52
(d)	20	27.15 ± 4.69
(e)	30	33.87 ± 7.28
(f)	35	34.46 ± 6.11
(g)	40	35.72 ± 3.95
(h)	50	35.31 ± 3.87

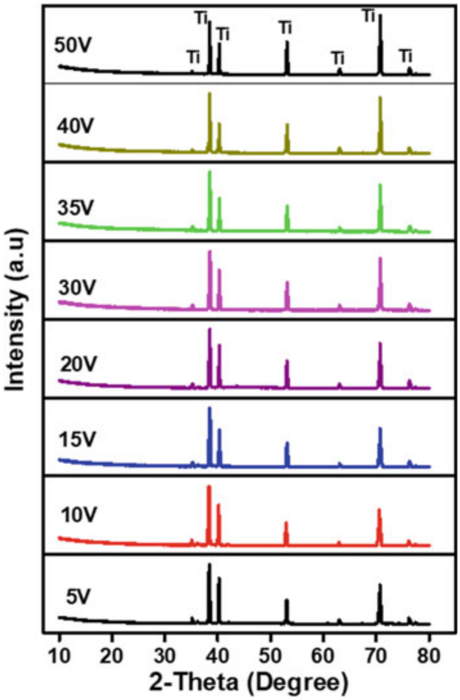

Fig. 2 XRD patterns of TiO_2 NTs anodized at different anodization voltages

for Ti metal. The diffraction peaks at 2θ of 34.9°, 35.8°, 40.3°, 52.9°, 62.9°, 70.6° and 76.3° correspond to (100), (002), (101), (102), (110), (103) and (112) planes, respectively [17, 18]. None of the diffraction peaks represent any of the crystalline structures of TiO_2. It can be observed that the anodization voltage has no significant effect on the structural properties of the synthesized TiO_2 NTs. The position and the intensity of the diffraction peaks showed no clearly observable change with the anodization voltage confirming the synthesis parameters have no significant effect on the structural properties especially the crystalline structure of the synthesized

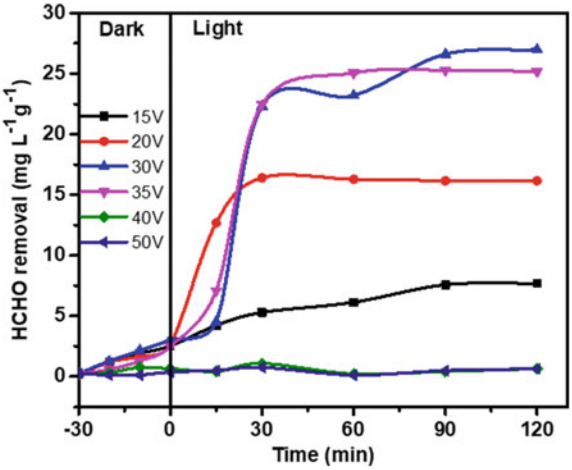

Fig. 3 Effect of anodization voltage on the photodegradation of formaldehyde

TiO_2 NTs. Based on previous work, TiO_2 NTs existed in amorphous phase without heat treatment process [19] but in this work the amorphous TiO_2 NTs were able to displayed photocatalytic property.

3.2 Photocatalytic Activity

The photocatalytic performance of the TiO_2 NTs photocatalyst synthesized at different anodization voltages was evaluated for the removal of gaseous HCHO under visible light irradiation. Figure 3 shows the removal of HCHO by TiO_2 NTs anodized at 15, 20, 30, 35, 40 and 50 V of anodization voltage for 1 h duration. Reaction without light irradiation but the presence of photocatalyst showed only ~3 mg L^{-1} g^{-1} of gaseous HCHO removal and was compared with the HCHO removal under visible light irradiation. The performance clearly shows that HCHO removal was enhanced under visible light irradiation. The HCHO removal without irradiation can be due to the adsorption of HCHO molecules on the in-wall of the reactor and/or on the photocatalyst [20].

The photodegradation ability of the TiO_2 NTs is strongly correlated to the average tube diameter and surface area. It can be seen from Fig. 3, sample anodized at 15 V showed only 7.70 mg L^{-1} g^{-1} of HCHO removal after 120 min of irradiation duration. However, further increase in the anodization voltage to 20 V led to an increment in the HCHO removal (16.17 mg L^{-1} g^{-1}). A noticeable improvement of HCHO removal can be seen for sample anodized at 30 V with 26.99 mg L^{-1} g^{-1} of removal after 120 min of reaction duration in the presence of light radiation, suggesting significant photocatalytic activity of the synthesized TiO_2 NTs. Nevertheless, further increase in the anodization voltage to 35, 40 and 50 V, the HCHO removal showed a decreasing trend which resulted in only 25.18, 0.65 and 0.64 mg L^{-1} g^{-1}, respectively. Overall, HCHO removal shows increasing trends with increasing anodization voltage (15–35 V) from 29.37 to 75.94% of removal and decreases significantly to 11.25 and 10.94% for sample anodized at 40 and 50 V, respectively.

On the other hand, an increase in the anodization voltage led to production of larger average inner tube diameter. This further increased the surface area of the TiO_2 NTs, which facilitates in enhanced photodegradation of HCHO [17, 21]. Nonetheless, samples anodized at 35, 40 and 50 V result in decreased HCHO removal despite having large inner tube diameter. This could be due to the poor-ordered NTs structures which were unable to maintain the integrity of the tubular structure of the TiO_2 NTs synthesized at higher anodization voltages. The results suggest that the tubular structure integrity of the TiO_2 NTs is strongly correlated to the performance of HCHO removal. The TiO_2 NTs synthesized at 30 V displayed the highest performance towards HCHO removal due to their better ordered structure and large tube diameter.

4 Conclusion

TiO_2 NTs were successfully synthesized via electrochemical anodization of Ti foil in glycerol-mediated EIL based electrolyte. The effect of the anodization voltage on the surface morphology, structural properties and subsequent photocatalytic performance of the TiO_2 NTs for photodegradation of HCHO was investigated. The anodization voltage was found to greatly affect the surface morphology, pore size and distribution of the nanotubes on the surface of the Ti foil. At low anodization voltage, higher density and uniformly distributed TiO_2 NTs were formed while at higher anodization voltage the rupture and disintegration of the tubular structure was observed. All the synthesized photocatalyst maintained amorphous phase without heat treatment process. The optimum anodization voltage of 30 V was found to be the most effective for the removal of gaseous HCHO. The TiO_2 NTs fabricated at 30 V anodization voltage displayed 26.99 mg L^{-1} g^{-1} of removal of HCHO after 120 min of reaction duration in the presence of visible light radiation.

Acknowledgements The authors would like to thank the Centre of Research in Ionic Liquids (CORIL), Centre of Innovative Nanostructures and Nanodevices (COINN), and Photocatalyst Laboratory at Catalyst Research (CARE) Laboratory in Universiti Teknologi PETRONAS for providing the facilities. Research Grants awarded by the Ministry of Higher Education Malaysia (FRGS/1/2016/STG01/UTP/02/1), Yayasan Universiti Teknologi PETRONAS (YUTP 015LC0-276) and financial support from UTM-UTP CRG (015MC0-019) are greatly acknowledged.

References

1. Indira, K., Mudali, U.K., Nishimura, T., Rajendran, N.: A review on TiO_2 nanotubes: influence of anodization parameters, formation mechanism, properties, corrosion behavior, and biomedical applications. J. Bio Tribo Corros. **1**(4), 28 (2015)

2. Sreekantan, S., Saharudin, K., Wei, L.C.: Formation of TiO_2 nanotubes via anodization and potential applications for photocatalysts, biomedical materials, and photoelectrochemical cell. IOP Conf. Ser. Mater. Sci. Eng. **21**(1), 012002 (2011)
3. Regonini, D., Clemens, F.J.: Anodized TiO_2 nanotubes: effect of anodizing time on film length, morphology and photoelectrochemical properties. Mater. Lett. **142**, 97–101 (2015)
4. Qin, L., Chen, Q., Lan, R., Jiang, R., Quan, X., Xu, B., Zhang, F., Jia, Y.: Effect of anodization parameters on morphology and photocatalysis properties of TiO_2 nanotube arrays. J. Mater. Sci. Technol. **31**(10), 1059–1064 (2015)
5. Ju, Y.J., Lien, C.H., Chang, K.H., Hu, C.C., Wong, D.S.H.: Deep eutectic solvent-based ionic liquid electrolytes for electrical double-layer capacitors. J. Chin. Chem. Soc. **59**(10), 1280–1287 (2012)
6. Baokou, X., Anouti, M.: Physical properties of a new deep eutectic solvent based on a sulfonium ionic liquid as a suitable electrolyte for electric double-layer capacitors. J. Phys. Chem. C **119**(2), 970–979 (2015)
7. Zaidi, W., Boisset, A., Jacquemin, J., Timperman, L., Anouti, M.: Deep eutectic solvents based on N-methylacetamide and a lithium salt as electrolytes at elevated temperature for activated carbon-based supercapacitors. J. Phys. Chem. C **118**(8), 4033–4042 (2014)
8. Jaihindh, D.P., Fu, Y.P.: Facile synthesis of deep eutectic solvent assisted BiOCl/$BiVO_4$@AgNWs plasmonic photocatalysts under visible light enhanced catalytic performance. Catal. Today **297**, 246–254 (2017)
9. Shaabani, A., Afshari, R.: Magnetic Ugi-functionalized graphene oxide complexed with copper nanoparticles: efficient catalyst toward Ullman coupling reaction in deep eutectic solvents. J. Colloid Interface Sci. **510**, 384–394 (2018)
10. Sahrin, N.T., Nawaz, R., Chong, F.K., Lee, S.L., Wirzal, W.D.H.: Visible light photodegradation of formaldehyde over TiO_2 nanotubes synthesized via electrochemical anodization of titanium foil. Nanomaterials **10**(1) (2020)
11. Zhang, W., Liu, Y., Guo, F., Liu, J., Yang, F.: Kinetic analysis of the anodic growth of TiO_2 nanotubes: effects of voltage and temperature. J. Mater. Chem. C **7**(45), 14098–14108 (2019)
12. Ismail, S., Khairul, K.A., Hisham, N.A.A.N., Mamat, M.S., Azam, M.A.: Effect of voltage on TiO_2 nanotubes formation in ethylene glycol solution. Jurnal Teknologi **79**(5–2), 117–120 (2017)
13. Omidvar, H., Goodarzi, S., Seif, A., Azadmehr, A.R.: Influence of anodization parameters on the morphology of TiO_2 nanotube arrays. J. Superlattices Microstruct. **50**(1), 6–39 (2011)
14. Lai, C.W., Sreekantan, S.: Effect of applied potential on the formation of self-organized nanotube arrays and its photoelectrochemical response. J. Nanomater. 1–7 (2011)
15. Kapusta-Kołodziej, J., Syrek, K., Pawlik, A., Jarosz, M., Tynkevych, O., Sulka, G.D.: Effects of anodizing potential and temperature on the growth of anodic TiO_2 and its photoelectrochemical properties. J. Appl. Surf. Sci. **396**, 1119–1129 (2017)
16. Gong, D., Grimes, C.A., Varghese, O.K., Hu, W., Singh, R.S., Chen, Z., Dickey, E.C.: Titanium oxide nanotube arrays prepared by anodic oxidation. J. Mater. Res. **16**(12), 3331–3334 (2001)
17. Li, H., Wang, G., Niu, J., Wang, E., Niu, G., Xie, C.: Preparation of TiO_2 nanotube arrays with efficient photocatalytic performance and super-hydrophilic properties utilizing anodized voltage method. J. Results Phys. **14**, 102499 (2019)
18. Ng, S., Yam, F.K., Beh, K., Hassan, Z.: Titanium dioxide nanotubes in chloride based electrolyte: an alternative to fluoride based electrolyte. Sains Malaysiana **43**(6), 947–951 (2014)
19. Li, G., Liu, Z.Q., Lu, J., Wang, L., Zhang, Z.: Effect of calcination temperature on the morphology and surface properties of TiO_2 nanotube arrays. J. Appl. Surf. Sci. **255**(16), 7323–7328 (2009)
20. Yu, L., Wang, L., Sun, X., Ye, D.: Enhanced photocatalytic activity of rGO/TiO_2 for the decomposition of formaldehyde under visible light irradiation. J. Environ. Sci. China **73**, 138–146 (2018)
21. Yu, J., Wang, B.: Effect of calcination temperature on morphology and photoelectrochemical properties of anodized titanium dioxide nanotube arrays. J. Appl. Catal. B Environ. **94**(3), 295–302 (2010)