

Effect of Photoelectrochemical Electrolyte Additives on the Photoconversion Efficiency of Tungsten Trioxide Loaded Titania Nanotubes Prepared Via Electrodeposition

Lim Ying Chin, Nur Farah Atikah Harun, Asmaa Kadim Ayal, Yusairie Mohd, Lim Ying Pei

Abstract: This study aims to investigate the effect of additives (sulfuric acid and ethanol) in sodium sulfate as photoelectrochemical (PEC) electrolyte on the photoconversion efficiency of tungsten trioxide loaded titania nanotubes (WTNT). Titania nanotubes (TNT) were first fabricated via anodization while the deposition of tungsten trioxide onto the titania nanotubes (WTNT) were successfully carried out via electrodeposition at various potentials. Assessing the PEC performance of WTNT fabricated at pH 1.5 in solely sodium sulfate was not adequate to enhance the PEC performance of WTNT compared to blank TNT. A similar result was obtained when sulfuric acid was added or when fabricating WTNT at pH 0.8. Adding ethanol into sodium sulfate electrolyte has successfully improved the PEC performance of WTNT with observable inclining photoconversion efficiency trend upon increasing electrodeposition potentials of WTNT from -0.45 V to -0.75 V.

Keywords : additives, photoconversion efficiency, photoelectrochemical cell, titania nanotubes.

I. INTRODUCTION

Titanium dioxide nanotubes (TNT) have been widely used in various photoinduced applications which include the photoelectrochemical (PEC) application. The good chemical stability [1], suitable band gap energy and location of band edges that surpass the thermodynamic potential of water redox reactions [2], as well as the high surface area offered by the nanotubular structured TNT, renders TNT as promising photoanodes. With their one-dimensional architecture, TNT permit the movement of electrons in unidirectional and hence prevent the recombination of electron-hole pairs. The limitation of TNT is that their wide band gap energy of ~ 3.0 eV have resulted in their only-UV-light reactivity [1], hence lower utilization of light spectrum from the sunlight; and lower quantum efficiency [3], [4]. Therefore modification of TNT such as hybridizing or doping it with various dopants

from non-metal, metal, metal oxide, to metal chalcogenide [5]–[9] have been made in order to counter the problem. WO_3 has a band gap energy range of 2.4–2.8 eV [10] and possesses visible light reactivity, making WO_3 as one of the promising dopant candidates that can widen the light spectrum utilization and narrow down the band gap energy of TNT to reduce the electron-hole recombination. Quite a number of reports had claimed an improved visible light reactivity and various photo-induced applications upon using WO_3 as a dopant onto TNT [10]–[17]. However, several considerations should be taken into account when using WO_3 as dopant onto TNT for PEC application. First, WO_3 suffers from self-oxidation or anodic photocorrosion [18] due to the accumulation of holes on the surface. Besides that, incomplete water oxidation also tends to occur in a PEC cell where hydrogen peroxide would be generated instead of oxygen gas [19]. Hence, the accumulated hydrogen peroxide molecules on the surface would hinder the photoreactivity of WO_3 .

Sodium sulfate is widely used as PEC electrolyte when assessing the PEC performance of photoanode. Sun and co-workers [10] studied WTNT as photoanode in PEC cell and found out that WO_3 nanomaterials exhibited fast degradation of photocurrent densities with time in 0.1 M Na_2SO_4 electrolyte during visible light illumination. Therefore, an alteration on the PEC electrolyte is required in order to address the problem. Since it is understood that WO_3 is stable in acidic condition, it might be worthwhile to study the PEC performance in an acidic electrolyte with different pH value. However, Das and co-workers [17] who studied the photoresponse of WTNT reported that only a small photocurrent (~ 2 μA) was generated in 0.1 M H_2SO_4 . Nevertheless, adding organic solvent such as methanol has enhanced the photoresponse of WTNT to approximately three times compared to when H_2SO_4 was solely used which could be attributed to the enhanced hole capturing and current doubling.

Therefore, it is interesting to investigate the PEC performance of electrodeposited WTNT prepared at different conditions (pH and potentials) in Na_2SO_4 with the addition of H_2SO_4 and organic solvent (ethanol) and their photoconversion efficiency performance.

Revised Manuscript Received on October 30, 2019.

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II. METHODOLOGY

Ordered TNT on Ti substrates were prepared according to a procedure described previously [20] Briefly, TNT were prepared via an electrochemical anodization method where smooth Ti foil of $1 \times 2 \text{ cm}^2$ dimension was used as a free-standing anode while a graphite rod was used as the cathode. The two electrodes were immersed into a mixed electrolyte of 0.5 wt.% NH_4F in 90:10 (ethylene glycol: water) and 40 V potential were supplied to the system for 60 minutes with continuous stirring to ensure homogeneity. The blank TNT were then calcined in air at 500°C for 2 h with $2^\circ\text{C}/\text{min}$ temperature ramping to induce crystallinity. WTNT were prepared via electrodeposition technique where a three-electrode system was used, consisting of a platinum wire as the counter electrode, Ag/AgCl as the reference electrode and the earlier prepared TNT as working electrode where the deposition of WO_3 would take place. The electrodeposition was conducted in a 50 mL of 2.5 mM $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ electrolyte. The solution was adjusted to pH 1.5 (for Condition I and II) and pH 0.8 (for Condition III and IV) by adding 1.4 mL H_2O_2 and HNO_3 dropwise. The deposition potential was varied from -0.45V , -0.55V , -0.65V to -0.75V while fixing the deposition time to 15 minutes for each sample.

FESEM morphological analysis was conducted on blank TNT and selected WTNT using Carl Zeiss SUPRA 40VP operating at 5kV. To determine the elemental composition, an EDX (Oxford Instruments) attached to the FESEM was used. XRD analysis was conducted to examine the crystalline structure of the samples using X'Pert Pro-MPD, PAN analytical operating at 40 kV and 30 mA with a scanning range of $2\theta=10-90^\circ$ using $\text{Cu K}\alpha$ ($\lambda=1.504\text{\AA}$). The photoelectrochemical test was conducted to determine the photoconversion efficiency performance of blank TNT and WTNT in 0.1M Na_2SO_4 electrolyte. The test was conducted in a three-electrode cell equipped with a flat quartz window. A platinum wire was used as the counter electrode, Ag/AgCl as the reference electrode and the prepared sample was used as the working electrode. The three electrodes were immersed into Na_2SO_4 electrolytes with different additives as listed in Table I.

Table I: Samples preparation condition and PEC electrolyte composition used during PEC test assessment

| Conditions | I | II | III | IV |
|------------------------------|--|---|---|--|
| Sample preparation condition | WTNT, pH 1.5, -0.45 to -0.75V | WTNT, pH 1.5, -0.45 to -0.75V | WTNT pH 0.8, -0.45 to -0.75V | WTNT pH 0.8, -0.45 to -0.75V |
| PEC electrolyte composition | 0.1M Na_2SO_4 | 0.1M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ | 0.1M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ | 0.1M $\text{Na}_2\text{SO}_4 + 2\text{M C}_2\text{H}_5\text{OH}$ |

The current was obtained by using a potentiostat (AUTOLAB) with scanning a potential sweep from +1 to -1 V at a rate of 50 mV/s . A 300 W halogen lamp was used as the light source. The photocurrent was obtained upon the irradiation of light whereas dark current was obtained during the absence of light. Intermittent irradiation was supplied towards the cell and hence both photo and dark currents could be assessed in a single experiment. UV-DRS analysis was

conducted on blank TNT and selected WTNT to investigate the optical properties of WTNT using the UV-Vis-NIR spectrophotometer (UV 3600, Shimadzu Corporation, Kyoto, Japan) at a wavelength range of 200–800 nm and barium sulfate was used as the reflectance standard.

III. RESULTS AND DISCUSSION

Fig. 1(a) and 1(b) shows the FESEM images of blank TNT and selected WTNT. The nanotubes (Fig. 1(a)) were uniformly aligned with the smooth wall, opened top and closed bottom as shown in the inset figure, having an outer diameter of 107 - 143 nm, inner diameter of 78 - 104 nm and an average wall thickness of $16.4 \pm 2.8 \text{ nm}$. The length of the nanotubes is about $2.2 \mu\text{m}$.

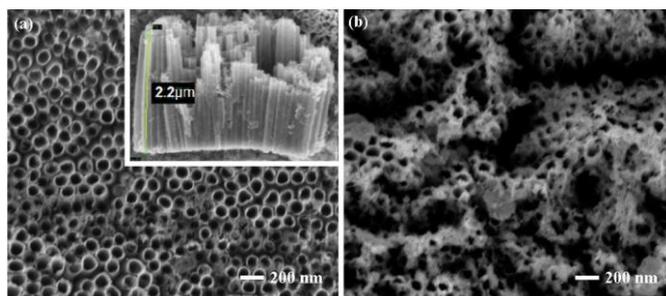


Fig. 1: FESEM images of (a) blank TNT and (b) WTNT/-0.75V prepared at pH 0.8. Inset figure in (a) shows the cross-sectional FESEM image of blank TNT

WO_3 nanoparticles were successfully deposited on the top mouth of the nanotubes upon electrodeposition, as shown by the visible irregular small clumps in Fig. 1(b). The well-aligned and ordered nanotubes of blank TNT had turned into clumped nanotubes which might, in turn, contribute towards improved PEC performance due to increased surface roughness. The presence of WO_3 was confirmed by the presence of W species detected in EDX analysis as illustrated in Fig. 2, which is in the form of monoclinic structured WO_3 as proven via XRD analysis as shown in Fig. 3. Both Ti and O were originated from TNT and no other impurities were detected.

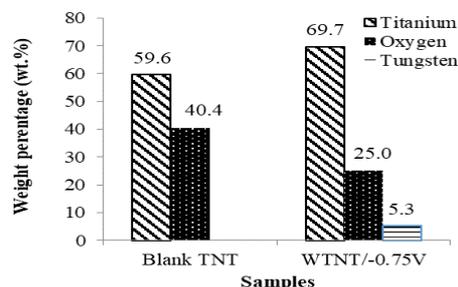


Fig. 2: EDX elemental composition for blank TNT and WTNT

Based on the diffractograms in Fig. 3, TNT as well as WTNT/ -0.75V exhibited diffraction peaks of Ti (JCPDS 44-1294) at $2\theta=35.2^\circ, 38.4^\circ, 40.3^\circ, 53.1^\circ, 62.9^\circ, 70.7^\circ, 74.1^\circ, 77.2^\circ, 82.3^\circ, 86.8^\circ$ corresponding to (100), (002), (101), (102), (110), (103), (112), (201), (004), and (202), respectively.

The prominent characteristic anatase peak (JCPDS 21-1272) at $2\theta=25.4^\circ$ corresponding to (101) was also observed in both samples, followed by other anatase peaks at $2\theta=48.0^\circ, 53.7^\circ, 55.1^\circ, 68.7^\circ$ which correspond to (200), (105), (211) and (116) respectively. A small rutile peak at $2\theta=27.4^\circ$ was also observed which corresponds to (110) (JCPDS 21-1276). These show that the TNT substrates obtained majorly consist of anatase and a minor rutile structure. The crystallite size (D) of the prominent anatase TiO_2 at (101) plane was calculated using the Scherer equation as follow:

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where λ =X-ray radiation wavelength, β =full width at half maximum intensity, θ =Bragg angle in radian. The calculated crystallite size of anatase TiO_2 at $2\theta=25.4^\circ$ in blank TNT and WTNT/ -0.75V was 27 nm and 28 nm, respectively, indicating no discernible change in crystallite size of anatase TiO_2 upon WO_3 deposition. However, prominent characteristic peaks belong to monoclinic structured WO_3 ($m\text{-WO}_3$) could be observed in WTNT/ -0.75V at the doublet peaks of $2\theta= 23.2^\circ$ and 23.5° corresponding to (002) and (020), respectively (JCPDS 43-1035). The presence of monoclinic WO_3 structure could be attributed to the post-calcination process conducted at 500°C as reported by Djaoued and co-workers [22].

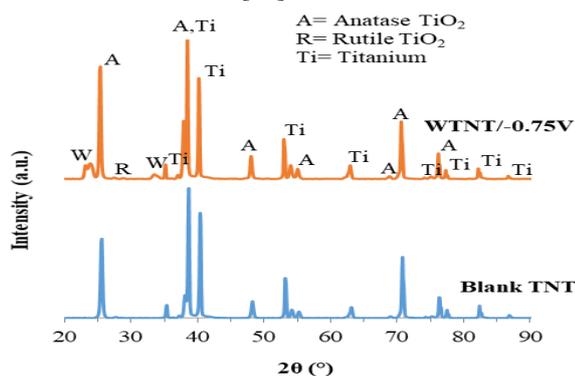


Fig. 3: XRD diffractograms of blank TNT and WTNT/ -0.75V prepared at pH 0.8.

The PEC performance of blank TNT and WTNT was assessed via photoconversion efficiency performance (η) which could be calculated using equation (2) where I_0 (mA/cm^2) refers to the photocurrent density obtained by subtracting the photocurrent with dark current as shown in Fig. 4 and dividing the value to the surface area of the sample. V_{bias} refers to the selected potential bias to calculate I_0 as shown in Fig. 2(a). J_{light} (mW/cm^2) refers to the light irradiance power.

$$\eta = \frac{I_0 (1.23 - V_{bias})}{J_{light}} \quad (2)$$

The photoresponse and photoconversion efficiency performance was illustrated in Fig. 4. Fig. 4(a) and 4(b) shows the photoresponse of blank TNT and WTNT/ -0.75V fabricated at pH 1.5 under intermittent irradiation, assessed in 0.1 M Na_2SO_4 (Condition I) and in 0.1 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (Condition II), respectively. The Na_2SO_4 solution has a pH ~ 6 and with the addition of H_2SO_4 , the solution pH reduced to pH ~ 3 .

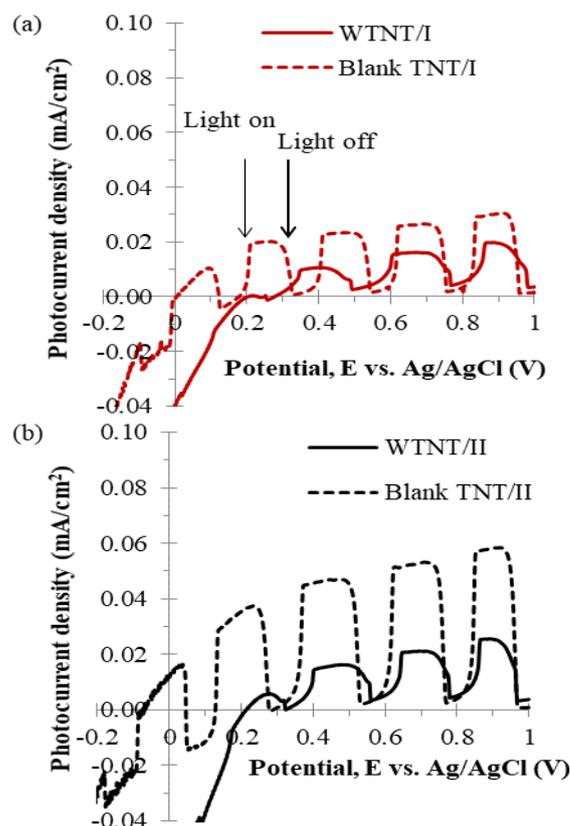


Fig. 4: I-V Curve for blank TNT and WTNT/ -0.75V assessed in PEC electrolyte of (a) condition I and (b) condition II.

From the I-V graph, it was observed that WTNT/ -0.75V exhibited a lower photoresponse compared to blank TNT in both conditions I and II. This shows that the photoresponse of WTNT could not be enhanced when using solely Na_2SO_4 and even with the addition of H_2SO_4 . This could be supported by the declining photoconversion efficiency performance of WTNT shown in Fig. 5 as compared to blank TNT.

However, it is interesting to note that the overall photoconversion efficiencies of blank TNT and all WTNT in Condition II were slightly higher as compared to those in Condition I, showing that PEC performance of blank TNT and WTNT was slightly enhanced upon reducing the electrolyte pH as shown in Fig. 5, suggesting that electrolyte pH does has an effect on the PEC performance of photoanode in this study. This could be attributed to higher H^+ ions concentration in the electrolyte with a lower pH (pH ~ 3 in this study). With higher H^+ concentration, the electrolyte medium tends to donate H^+ ions on the TNT or WTNT surface, making the electrode positively charged [23]. Therefore, the anions including OH^- ions from the electrolyte would be attracted towards TNT or WTNT and be oxidized into oxygen gas ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) hence the high electron flow into the photoanode would be detected as high photocurrent. Therefore this explains the higher photocurrent of blank TNT and WTNT/ -0.75V at positive potentials (more water oxidation and flow of electrons) was observed (Fig. 4) and higher overall photoconversion efficiency (Fig. 5) in Condition II as compared to Condition I.

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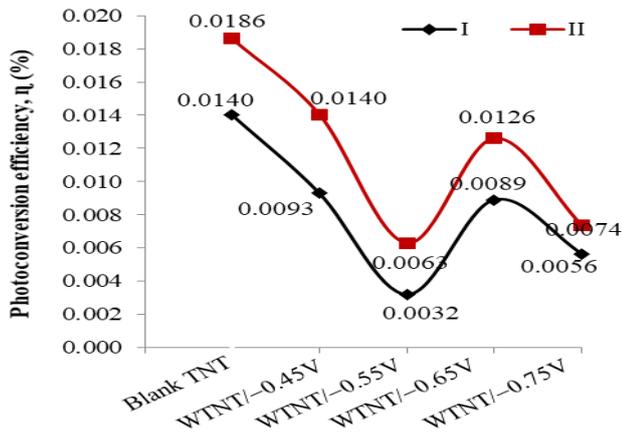


Fig. 5 Photoconversion efficiency trend of WTNT of various deposition potentials prepared at pH 1.5 assessed in PEC electrolyte of condition I and II

It is hypothesized that more WO_3 deposited will result in an enhancement of PEC performance for WTNT. As such, an attempt was carried out to deposit WO_3 onto TNT at lower pH (pH~0.8) as deposition rate increases with increasing H^+ concentration. Nevertheless, WTNT/-0.75V fabricated at pH 0.8 shows a lower photoresponse compared to blank TNT in $\text{Na}_2\text{SO}_4+\text{H}_2\text{SO}_4$ (pH~3) (Condition III) as shown in Fig. 6(a). If comparing the WTNT' fabricated in pH 1.5 (Condition II) and pH 0.8 (Condition III) where both PEC performances were evaluated using the same electrolyte ($\text{Na}_2\text{SO}_4+\text{H}_2\text{SO}_4$), the PEC performance for those WTNT at pH 0.8 was even lower than that of pH 1.5 (Fig. 4 (b) and 6(a)). While it is understood that lower electrodeposition pH leads to a faster electrodeposition rate and therefore more WO_3 will be introduced onto TNT, the PEC performance of WTNT still could not be enhanced if the same electrolyte composition was used. Furthermore, the PEC performance of WTNT in Condition III (Fig. 6a) was still lower compared to blank TNT, indicating that the modification of TNT with WO_3 which act as dopant in this study could not enhance the PEC performance as hypothesized in our study.

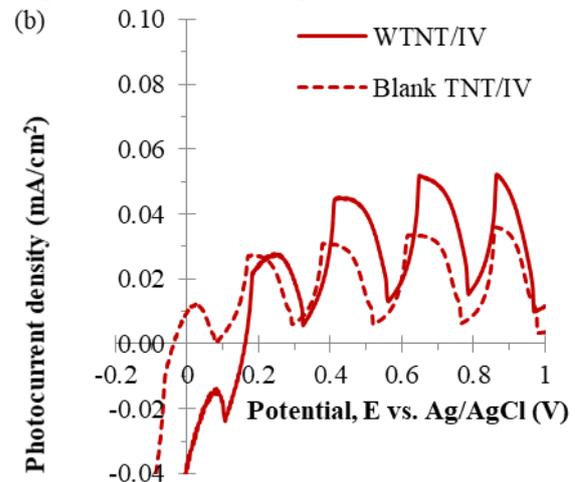
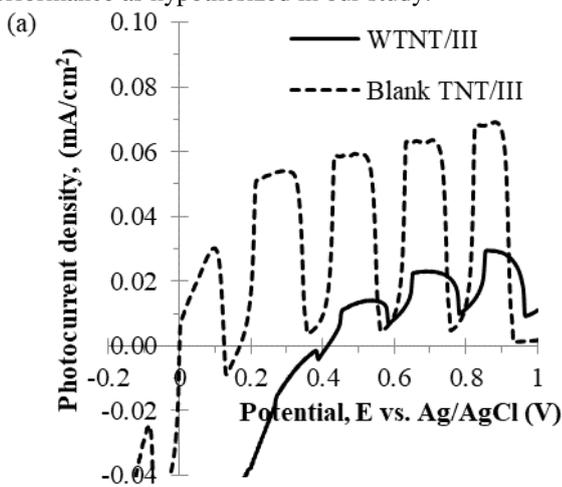


Fig. 6: I-V Curve for blank TNT and WTNT/-0.75V assessed in PEC electrolyte of (a) condition III and (b) condition IV

Nevertheless, the photoresponse of WTNT/-0.75V was observed to enhance as compared to blank TNT upon the addition of $\text{C}_2\text{H}_5\text{OH}$ into the PEC electrolyte (Condition IV) as illustrated in Fig. 6(b). This could be supported by the higher overall photoconversion efficiency performance of all WTNT as compared to blank TNT as shown in Fig. 7. Furthermore, the enhancement of PEC performance was observed to incline upon increasing deposition potentials from -0.45V to -0.75V which could be attributed to the increasing amount of WO_3 upon increasing deposition potentials. The PEC enhancement of WTNT upon adding ethanol into PEC electrolyte could be attributed to the organic molecule species which could serve as a hole scavenger. It is known that WO_3 suffers from incomplete water oxidation and also self-oxidation due to the accumulation of hole on its surface. Therefore, introducing ethanol would be a great solution to this problem where the organic molecule would scavenge the accumulated holes and hence enhances the photoreactivity and PEC performance of the photoanode.

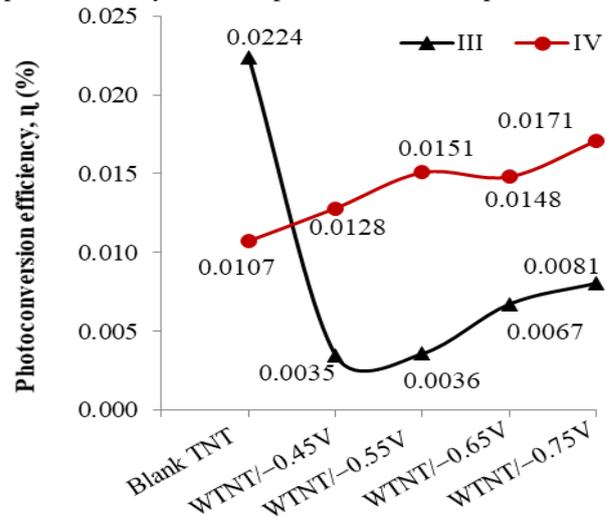


Fig. 7: Photoconversion efficiency trend of WTNT of various deposition potentials prepared at pH 0.8 assessed in PEC electrolyte of condition III and IV

Fig. 8 shows the UVDRS spectra and Kubelka Munk-Tauc plots of blank TNT and WTNT/-0.75V fabricated at pH 0.8. From Fig. 8, it was shown that both blank TNT and WTNT/-0.75V exhibited strong UV light absorption at $\lambda < 380$ nm which was due to intrinsic band gap absorption of TiO_2 [23]. Upon deposition of WO_3 , a slight red shift occurred where the absorption edge slightly shifted towards visible light region (inset of Fig. 8) due to the visible light reactivity of WO_3 .

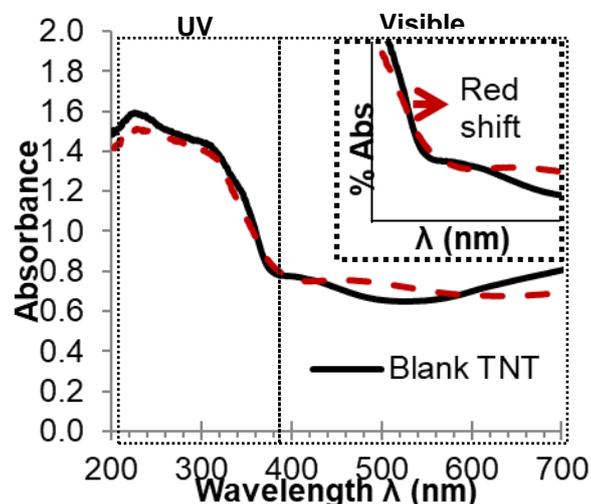


Fig. 8: UV DRS spectra with inset figure of enlargement at pointed wavelength region

The band gap energy (E_g) of blank TNT obtained from Kubelka Munk-Tauc plot as observed in Fig. 9 was 3.0 eV which was due to the presence of rutile structure in the TiO_2 nanotubes [20]. The red shift exhibited by WTNT as observed in Fig. 8 has consequently resulted in a narrower band gap energy of WTNT/-0.75V ($E_g = 2.6$ eV) as compared to blank TNT ($E_g = 3.0$ eV). The successful band gap narrowing effect could be attributed to the introduction of WO_3 onto TNT. Hence, the enhanced photoconversion efficiency performance of WTNT as compared to blank TNT when using PEC electrolyte of Condition IV could be explained from the narrowed down band gap energy which consequently resulted in visible light reactivity and possibly suppressed charge recombination [15].

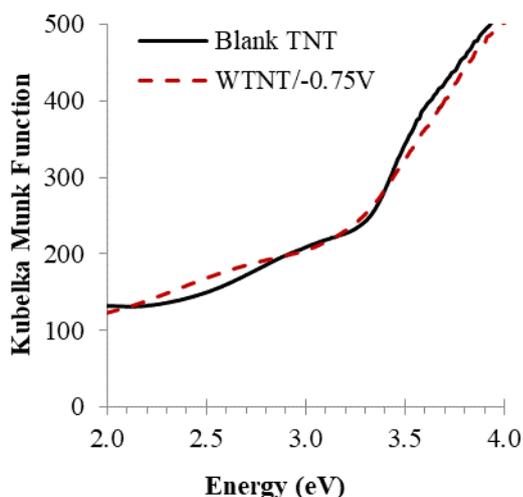


Fig. 9: Kubelka Munk-Tauc plots of blank TNT and WTNT/-0.75V

IV. CONCLUSION

Blank TNT were successfully fabricated via electrochemical anodization of Ti whereas WTNT of various deposition potentials were fabricated via electrodeposition at both pH 1.5 and 0.8 successfully. The nanotubes were uniformly aligned and upon electrodeposition of WO_3 , small clumps of WO_3 were visible with some clumping of nanotubes. The presence of WO_3 was confirmed via EDX and XRD analyses. Introducing ethanol into PEC electrolyte has successfully enhanced the photoconversion efficiency performance of WTNT and inclined PEC performance with increasing deposition potentials from -0.45 V to -0.75 V. The PEC enhancement of WTNT was due to a narrower band gap energy of WTNT in addition with ethanol that served as hole scavenger that counters the accumulation of holes on the surface of WO_3 . With the right selection of electrolyte composition, WTNT can be used as a potential photoanode for PEC application.

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