Chapter 8

A WO_3 Sensitized Hollow TiO_2 Nanoarray for Solar Energy Conversion

Nur Farah Atikah Harun[a], Yusairie Mohd[a], Lim Ying Pei[b] &
Lim Ying Chin[a*]

[a]*School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*
[b]*Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*

Abstract

Modified titania nanotubes (TNT) has been widely used in the solar-energy conversion application, however, the surface modification itself is still insufficient to lead to commercialization of TNT due to some drawbacks. In addressing the high electron-hole pair recombination and limited light spectrum utilization possessed by TiO_2, deposition of the narrow band gap and visible light reactive WO_3 has been a good option. Hence, this study aims to investigate the solar-energy conversion performance of the resulted WTNT and its charge-recombination behaviour which is less reported, as well as the study of the photochromic effect by WTNT. This study provides the feasibility of WTNT as potential material for solar-energy conversion and for photochromic application as well as the idea of simple fabrication of WTNT via electrodeposition method.

Introduction

TNT is one of the current oxide semiconductors extensively studied for solar energy conversion application. Superior properties such as having a suitable band gap energy of ~3.0-3.2eV with its band edges surpass the thermodynamic potential for water oxidation and reduction (Zhao *et al.*, 2016) and high chemical stability (Sampaio *et al.*, 2013) renders TiO_2 as a promising candidate. The fabrication of nanotubes has been a popular alternative of architectural designation due to their high surface area resulted from the inner and outer wall (Wang *et al.*, 2007) that potentially maximizes the light absorption. Unfortunately, the TNT itself is insufficient to address the major drawbacks of high electron-hole pair recombination rate and limited utilization of light spectrum due to its wide band gap and thus only responsive towards UV light. Therefore, sensitizing TNT with a visible light reactive material will be an alternative to overcome this issue.

Tungsten trioxide (WO_3) is a promising dopant due to its narrow band gap of 2.5-2.8 eV, visible light reactivity (Murata *et al.*, 2012) and good stability (Liu *et al.*, 2013). Besides being a potential photoanode material, WO_3 is also well-known for its photochromic effect, giving it a possible solution for photochromic applications. Since this study involves the photo-induced application PEC, it is interesting to study the photochromic behavior of the resulted tungsten trioxide loaded titania nanotubes (WTNT) in concurrent with the study of the photoelectrochemical behavior. Hence, this study aims to investigate the effect of solution pH towards the electrodeposition behavior of WO_3 into TNT and its influence towards the solar-energy conversion application, as well as to investigate the photochromic effect introduced by WTNT.

Problem statement

The wide band gap possessed by TiO_2 exerts certain drawbacks that limit the application of TiO_2. For instance, the band gap of 3.2 eV for anatase; 3.0 eV for rutile (Roy *et al.*, 2011) makes TiO_2 only active upon UV light illumination (Sampaio *et al.*, 2013) whereby UV light is only accounted for about 4-5% of solar spectrum. Thus, acquiring UV light for the photo-induced application may be costly or less cost-efficient. Besides that, the wide band gap also leads towards fast recombination rate between the electron-hole pairs (Benjwal & Kar, 2015). This consequently results in low quantum efficiency (Sreekantan *et al.*, 2014) especially in bulk TiO_2 which has a low surface area.

Objectives

1) To investigate the effect of pH on the electrodeposition of WTNT
2) To examine the morphology and chemical species of the resulted WTNT via FESEM and XPS analyses
3) To determine the solar-energy conversion performance of the resulted WTNT

Novelty

The study of deposition time towards the electrodeposition of WO_3 into TNT has been reported (Martins *et al.*, 2016) whom studied its resulting photocatalytic degradation of organic matter. In contrast, this study elaborates the effect of solution pH towards the electrodeposition process and its influence in the solar-energy conversion application with evidence from the charge recombination behaviour. An extensive study was made on the photochromic behavior of the resulted samples; providing a possible reference to the photochromic application.

Benefits to user and society

1) WTNT as a potential robust material for solar cell with a greater light-to-energy conversion performance and as tunable photochromic material
2) By using an environmental friendly and simple fabrication method, WTNT can be produced more cost-efficiently and creating less harmful to the environment

Results and discussion

TNT substrate was fabricated via a two-electrode anodization process where titanium foil was connected to anode whereas a high-density graphite was connected to the cathode. The process was conducted for 1 h in the mixture of 0.5 wt.% NH_4F in 90% ethylene glycol: 10% water. The deposition of WO_3 was carried out by electrodeposition process where the three-electrode system was used: TNT as the working electrode, a Ag/AgCl as the reference electrode and Pt as the counter electrode. The electrolyte used was a mixture of 2.5 mM Na_2WO_4, 1.4 mL H_2O_2 and adjusted to pH 3.0 with HNO_3 added drop-wisely. A deposition potential of -0.75V was supplied and the electrodeposition process was conducted for 15 minutes. The resulted WTNT was labeled as WTNT/pH3.0.

Blank TNT and WTNT were successfully fabricated via anodization and electrodeposition process respectively and the images were as observed in Fig. 1. The nanotubes have an outer diameter of 151 nm as observed in the TEM image. The successful deposition of WO_3 can be proven from the FESEM and TEM images in Fig.1 and XPS analysis (Fig. 2 (b)). From Fig. 2 (a), two Ti 2p peaks at 465.3 and 459.3 eV were observed in both WTNT/pH3.0 before and after the PEC attributed to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ components. Interestingly, shifting was observed towards lower binding energies after PEC test which was at 463.9 and 458.2 eV respectively, close to the reported value of Ti^{3+} peak (Hantusch *et al.*, 2017), suggesting the transition of Ti^{4+} to Ti^{3+} upon light irradiation during the PEC test which is attributed to the photogeneration of electron (Lai *et al.*, 2012).

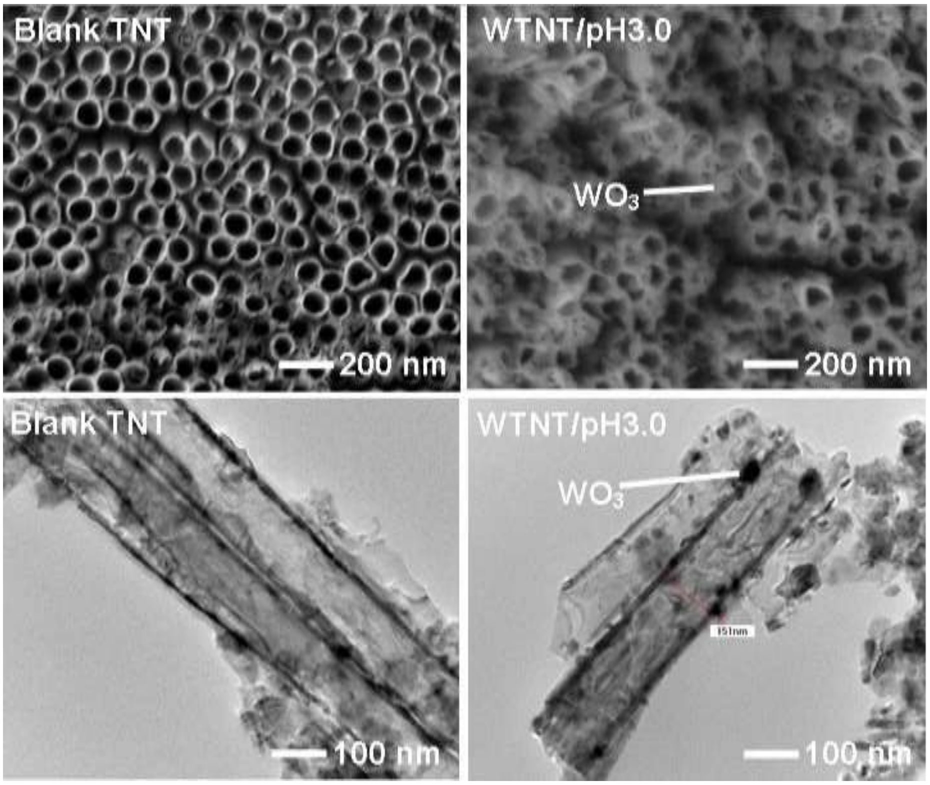

Fig. 1. FESEM images and TEM images of blank TNT and WTNT/pH3.0

At the same time, shifting of W 4f peaks (Figure 2 (b)) were also observed after PEC which could also be attributed to the excitement of electrons from W^{6+} to W^{5+}, supported by similar shifting behaviour reported by other researchers (Leghari *et al.*, 2014; Zhou *et al.*, 2017). These confirm the photochromic behavior of the resulted WTNT. Furthermore, the colour change from the bluish grey of WTNT/pH3.0 before PEC to blue-black colour after PEC as shown in Fig. 2 (b) signified the possible electronic transition during the PEC test. Hence, XPS analysis was made on the spectrum for W species. From Fig. 2 (c), WTNT/pH3.0 shows an enhanced photoresponse and photo-energy conversion efficiency from 1.9 ± 0.4% of blank TNT to 6.5 ± 0.4%. Such PEC enhancement was due to the introduction of WO_3 which acts as charge carrier trap (Sun *et al.*, 2015) as proven via lower arc magnitude of Nyquist plot of WTNT/pH3.0 as compared to blank TNT (Fig. 2 (d)) and lower charge transfer resistance, R_{ct} as shown in Fig. 2 (e).

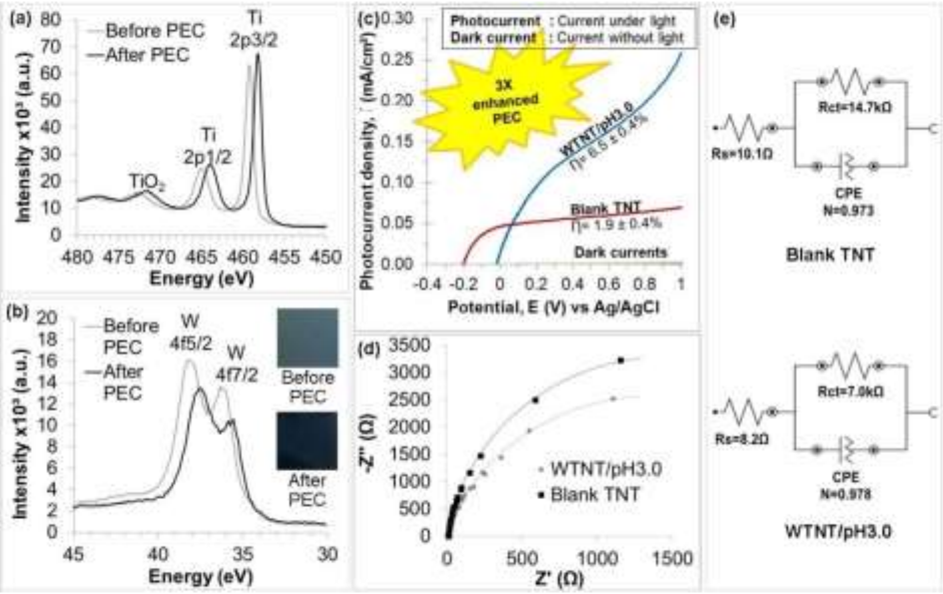

Fig. 2. XPS narrow scan of (a) Ti 2p and (b) W 4f; (c) I vs. V; (d) Nyquist plots scanned from 10 kHz to 0.02 Hz at +0.2 V under light illumination and (e) equivalent circuits of blank TNT and WTNT/pH3.0

Conclusion

WTNT shows three times enhancement of PEC performance as compared to blank TNT due to the charge trapping effect introduced by WO_3 as proven by a lower charge transfer resistance. The observation on photochromic effect shown by physical colour change and shifting of photoelectron spectra after PEC shows that WTNT can serve as a potential tunable photochromic material as well as exhibits good solar-energy conversion performance.

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