SYNTHESIS OF ROBUST BI-COMPONENT Co_3O_4-TiO_2 NANOTUBE ARRAYS

K.A. Khairul[1], S. Ismail[1], F. Budiman[2], M.Z.Z. Abidin[1] and R.F. Munawar[1]

[1]Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]School of Electrical Engineering,
Telkom University, Jl. Telekomunikasi No. 1,
Bandung 40257, Indonesia.

Corresponding Author's Email: [1]syahriza@utem.edu.my

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ABSTRACT: This research work studied the formation of the cobalt oxide nanostructure on the TiO_2 nanotubes. Bi-component Co_3O_4-TiO_2 nanotube arrays were synthesized via wet impregnation of Co_3O_4 onto the surface of TiO_2 nanotube arrays followed by the heat treatment process under air, with varying the precursor molarity of cobalt complex. The morphological and structural of the bi-component nanostructure were characterised by Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-Ray (EDX), X-Ray Diffraction (XRD), and Raman spectroscopy. The deposition of the cobalt oxide nanostructure was shown on the FESEM, EDX, as well as Raman result where there were increased on the cobalt oxide nanostructure with the increased of the precursor molarity. This work provides a simple and cost-effective method to synthesis the bi-component nanostructure of Co_3O_4-TiO_2.

KEYWORDS: *Titanium Dioxide Nanotubes; Bi-Component Material; Wet Impregnation; Cobalt Oxide*

1.0 INTRODUCTION

Titanium dioxide (TiO_2) nanomaterials have received wide attention over the past decades for their performance in photodegradation of pollutants [1-2] and photoelectrochemical water splitting applications

[3-4]. TiO_2 offers several benefits as well, such as low cost, non-toxic, and good chemical and thermal stability [5-6]. In the form of nanotubes, TiO_2 exhibits semiconductor nature with high surface area and aspect ratio [7]. Recently, the anodic oxidation (anodization) process to grow the TiO_2 nanotube arrays have been studied extensively due to its exceptional advantages in controlling the size of nanotubes into desired dimension [8]. However, the wide band gap of TiO_2 (~3.2 eV for anatase phase) limits the absorption of light into the ultraviolet region only, as well as a shorter lifetime of photogenerated charge carriers [9]. These limitations can be resolved by developing an effective solution, such as coupling with another semiconductor [10].

Cobalt oxide, Co_3O_4 has been proposed as the candidate material to be coupling with TiO_2 nanostructure. In facts, Co_3O_4 has a narrow band gap which able to response upon visible light irradiation [11]. The coupling would reduce the band gap of TiO_2, which is due to the insertion of the impurities in the band gap of TiO_2. Thus it would be useful for the photocatalytic activity in the visible region. As the TiO_2 is a n-type semiconductor while Co_3O_4 is a p-type semiconductor, the formation of bi-component material of Co_3O_4-TiO_2 will form heterojunction of p-n semiconductor and expected to increase the photogenerated charge carriers' lifetime [12]. It is reported that the heterounions between semiconductors of type P and type n will enhance the photocatalytic activity.

To the best of our knowledge depositing Co_3O_4 materials in such thin and long tubes is a challenge due to the lack of suitable routes. In this work, Co_3O_4 was deposited onto the TiO_2 nanotube surface via wet impregnation method using $Co(NO_3)_2$ as the precursor solution. The morphological and phase of the bi-component sample is studied in this work upon different precursor molarity of $Co(NO_3)_2$.

2.0 EXPERIMENTAL

Ti foils (Purity 99.9%, Sigma Aldrich) with 0.127 mm thickness were cut into 40 mm x 10 mm size. The foils were ultrasonically cleaned using ethanol and deionised (DI) water for several minutes and dried using air gun. Anodization was performed in a two electrodes system that connected to a DC power supply, with Ti foil as the working electrode and graphite rod as the counter electrode. The electrolyte used was 100 ml of ethylene glycol containing the 0.3 g of ammonium fluoride (NH_4F) and 5% hydrogen peroxide (H_2O_2). The process was carried out under a constant voltage 60 V for 30 min at room temperature. Subsequently, the as anodised sample was rinsed and dried using DI water and air gun, respectively. The deposition of the cobalt oxide was done using a wet impregnation method. The process involved the solution of cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), sodium hydroxide (NaOH), and deionised water for the rinsing purpose. The beakers for the precursor and rinsing water were placed alternately. The as anodised sample was immersed into 0.1 M, 0.3 M, and 0.5 M of $Co(NO_3)_2$ solutions, followed by DI water then 0.1 M, 0.3 M, and 0.5 M of NaOH solution, and finally DI water alternatively for 30 min. Such cycle was repeated 3 times followed by heat treatment in a tube furnace at 500°C for 1 h under air atmosphere.

Surface morphology of the samples was observed FESEM (Jeol JSM-6701F). The energy dispersion X-ray, EDX equipped with FESEM was used as the elemental analysis to determine the Co element on the TiO_2 nanotube arrays. The crystalline phase of samples was identified by X-ray diffraction, XRD (ExpertPro PANalytical). Raman spectroscopy (UniRAM-3500) was conducted to determine the bi-component nanostructure with 532 nm laser excitation.

3.0 RESULTS AND DISCUSSION

Figure 1(a) displays the top view of the pure TiO_2 nanotubes with a regularly aligned pore structure. The average of the inner tube diameter is about 100 nm, and the outer diameter is 130 nm. Upon immersed in the $Co(NO_3)_2$ precursor solution, it embedded on the tip of the nanotube mouth, as can be observed in Figure 1(b). The Co species started to agglomerate and blocked the nanotube structure upon the increased in precursor molarity, as shown in Figure 1(c) and (d). This finding indicates that lower precursor molarity is preferable to be used for the impregnation method, to avoid the blocking of nanotube structure.

The EDX analysis shown in Table 1 identified the presence of Ti, O and Co elements upon wet impregnation process. The data results confirm the depositing material consist of Co and O element. Besides, the Co content on the sample is higher when immersed in higher precursor molarity. These results show the incorporation of cobalt oxide is noticeable with the molarity of the precursor solution.

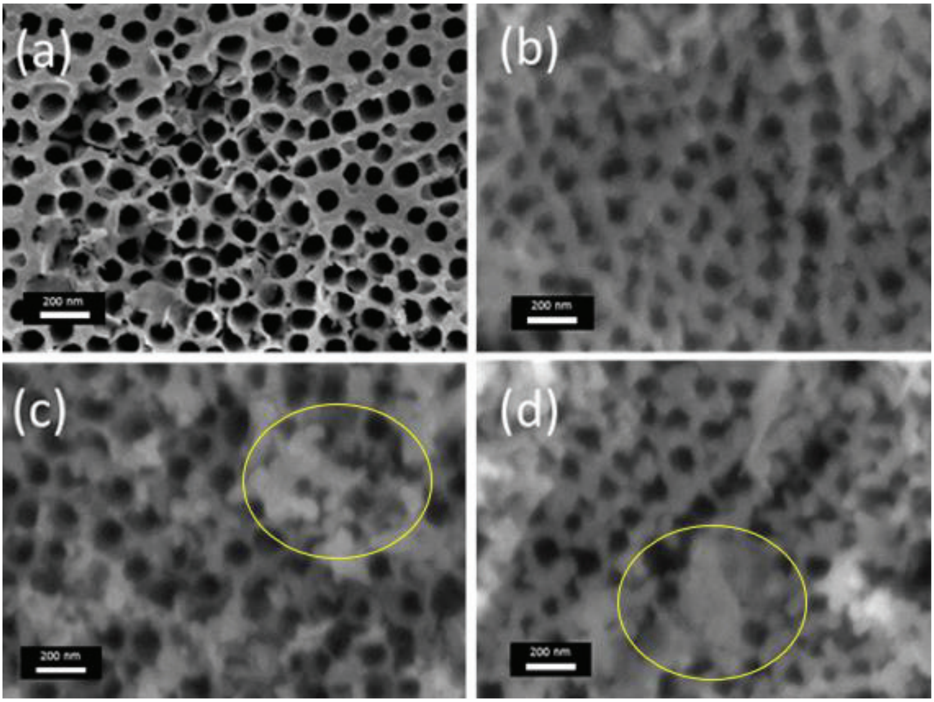

Figure 1: Top view FESEM images of (a) pure TiO_2 nanotubes and bi-component Co_3O_4-TiO_2 nanotubes with different precursor molarity of $Co(NO_3)_2$ with (b) 0.1 M, (c) 0.3 M and (d) 0.5 M (yellow circles show agglomeration of Co species)

Table 1: Elemental composition (at%) of pure TiO_2 nanotubes and Co_3O_4-TiO_2 bi-component

Precursor molarity (M)	Ti (at%)	O (at%)	Co (at%)
0	36.6	63.4	-
0.1	36.2	63.24	0.56
0.3	34.15	64.28	1.57
0.5	24.08	70.68	5.24

The crystalline phase of the pure TiO_2 and Co_3O_4-TiO_2 bi-component was determined by the XRD result, as shown in Figure 2. The XRD pattern of the pure TiO_2 displays diffraction peaks at 25.2°, 37.8°, 48.0°, 53.9°, 55.0° and 62.7°, indexed to the anatase phase (A) of TiO_2 (JCPDS No. 21-1272). Besides, the XRD pattern for the Ti (JCPDS No. 72-4624) can be observed on the pure TiO_2, though the peak slowly decreased as the precursor molarity increased. However, there was no significant XRD pattern associated with metallic Co, CoO or Co_3O_4. This finding shows that the XRD does not detect the cobalt phase formation, particularly on very thin surface, owing to x-ray penetration depth, therefore cannot be utilised to identify the local structure of the cobalt atom on the samples. It is noted that the XRD analysis is not elemental selective aside from sensitive to a long-range ordering [13].

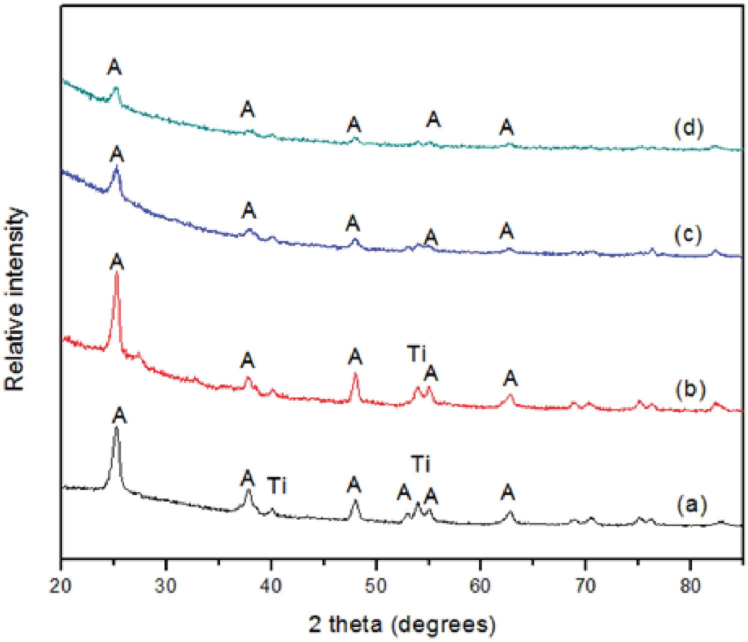

Figure 2: XRD patterns for (a) pure TiO_2 nanotubes and bi-component Co_3O_4-TiO_2 nanotubes with different precursor molarity of $Co(NO_3)_2$ with (b) 0.1 M, (c) 0.3 M and (d) 0.5 M

Raman spectra of the Co_3O_4-TiO_2 nanotubes bi-component immersed in different precursor molarity are shown in Figure 3. In here, Raman analysis was used to identify the phase, since the penetration depth of laser is lower compared to x-ray light. From the measurement results, all samples exhibit the typical Raman peaks assigned for TiO_2 anatase phase, which located at 142, 398, 516 and 639 cm^{-1} respectively [14], also confirmed that by the pure TiO_2 spectrum as the control sample. As for the bi-component sample, there were one new peak at 683 cm^{-1} aside from the anatase peaks. The peak is clearer when the concentration of Co_3O_4 is higher. The new peaks attribute to Ag (687 cm^{-1}), which reflects the vibrational mode from the octahedral cations in the normal spinel of Co_3O_4 [15]. Besides, the TiO_2 peaks of the bi-component sample started to broaden upon high cobalt precursor in which may correspond to the interaction of cobalt species and oxygen sublattice disorder [16-17]. This results confirmed the formation of Co_3O_4 spinel phase on the TiO_2 nanotubes.

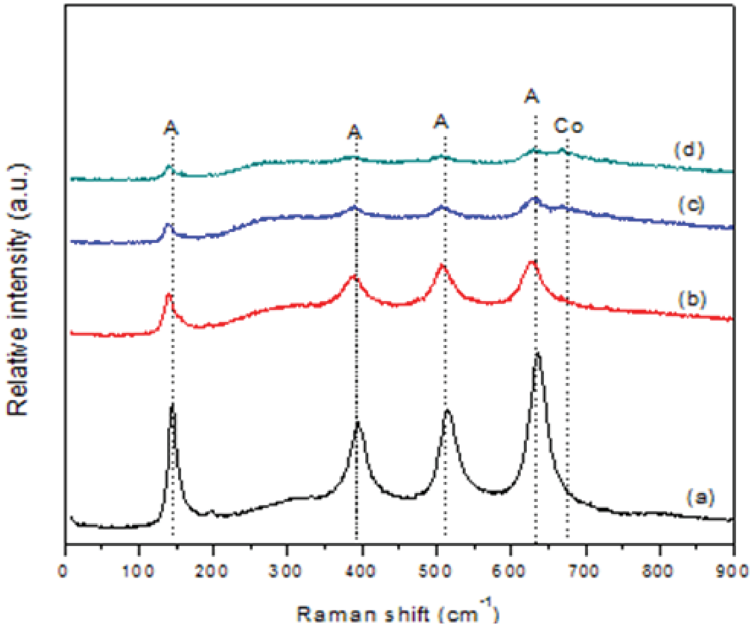

Figure 3: Raman spectra of (a) pure TiO_2 nanotubes and bi-component Co_3O_4-TiO_2 nanotubes with different precursor molarity of $Co(NO_3)_2$ with (b) 0.1 M, (c) 0.3 M and (d) 0.5 M

The application of bi-component Co_3O_4-TiO_2 nanotubes is demonstrated in the degradation of MO dyes under the irradiation of UV light. It is reported that cobalt is a suitable element to enhance the photocatalytic properties of TiO_2 [18-19]. As shown in Figure 4, the pure TiO_2 nanotubes degrade 17.6% of MO dye, which may be attributed to the existence photocatalytic properties of TiO_2 from the raw material. Degradation rate is enhanced to 33.7% by soaking in 0.1 M cobalt chloride precursor. Enhanced degradation rate is due to the cobalt ions, which not only improve absorption rate but also act as shallow traps to separate photo-induced carriers efficiently as well. However, when the concentration of cobalt ions is too high, they may act as recombination centers and decrease the photocatalytic activity. The TiO_2 nanotubes soaked in the precursor solution of $Co(NO_3)_2$ solution with higher molarity of 0.5 M demonstrated poor photodegradation. This is closely related to the TiO_2 nanotubes covered excessively by cobalt and eventually resulted in lower active site of TiO_2 nanotubes for photocatalytic performance. It was believed that this excessive cobalt could create the recombination sites for the charge carriers, thereby reducing the sensitivity to the absorbance. For the wet impregnation process, this findings could be attributed to the diffusion of the loaded cobalt species that reached a saturated condition and started to form an independent layer on the wall surface of nanotubes, which acted as defect sites or recombination sites for the photo-generated charge carriers. This condition can be explained that the transportation of photo-induced electrons to the Ti substrate has been hindered which promoted the poor photocatalytic performances.

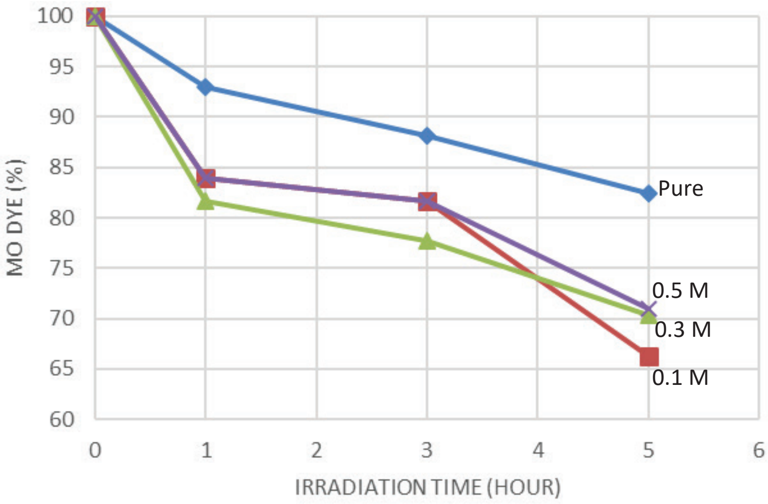

Figure 4: Methyl orange dye degradation versus time of Co_3O_4-TiO_2 nanotubes with different precursor molarity of $Co(NO_3)_2$

4.0 CONCLUSION

In summary, the Co_3O_4-TiO_2 bi-component nanotubes were successfully synthesized using simple anodization and wet impregnation method. The precursor molarity of $Co(NO_3)_2$ solution and NaOH solution plays a vital role in the morphological and content of Co_3O_4 onto the TiO_2 nanotubes. It was found the lower precursor molarity is preferable to be used for the impregnation method, to avoid the blocking of nanotube structure. Here, the optimum concentration of the dopant Co solution that did not block the structure of the nanotubes was 0.1 M. The amount of cobalt coating into TiO_2 nanotubes play an important role in developing an efficient photocatalyst in order to improve the photocatalytic degradation further.

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