PREPARATION OF COBALT DECORATED TITANIUM DIOXIDE NANOTUBES BY ELECTRODEPOSITION

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ABSTRACT: In the present study a cobalt decorated titanium dioxide (TiO_2) nanotube arrays photocatalyst with varying dopant concentration of cobalt chloride (0.01 mM, 0.05 mM and 0.1 mM) and deposition time (1 min, 2 min and 3 min) were synthesized by electrodeposition method. The sample produced were characterized by X-ray Diffraction (XRD), Raman Spectroscopy (RAMAN), Scanning Electron Microscope (SEM), and UV-Vis absorption spectra (UV-Visible) technique. Methyl orange dye was used as the environmental pollutant probe. The photocatalytic performance of the synthesized photocatalysts was evaluated under the UV irradiation sources. The optimum concentration of cobalt chloride of 0.05 mM gives better decoration of cobalt on TiO_2. Furthermore, it reveals that the highest degradation activity under UV irradiation can be up to 60%. While, excess of cobalt (Co) decorated on TiO_2 suppressed the photocatalytic of TiO_2 as well as forming lumps on the TiO_2 due to agglomeration. Hence, these contributed to the reduction of effective surface sites and the degradation of dye become limited.

KEYWORDS: *Titanium Dioxide; Cobalt; Nanotubes; Photocatalytic*

1.0 INTRODUCTION

Environmental problems have become serious issue due to the rapid development of industrialization. The contamination of ground water caused the serious onslaught to aquatic and human life. Several methods have currently been employed for water treatment process such as physical and chemical technique, activated carbon adsorption and photocatalytic reaction via advanced oxidation processes (AOPs). Jantawasu et al. [1] reported that AOPs are a good method in addressing this issue due to its competency in degrading and mineralizing organic pollutants. The metal oxide semiconductor which employed in heterogeneous photocatalysis is one of the AOPs promising methods that widely applied in toxic compound decomposition [2]. TiO_2 is one of the metal oxide semiconductor and has widely used as photocatalyst material since the discovery of its water splitting properties by Fujishima and Honda [3]. Over the past decades, nanoscale TiO_2 has attracted much attention due to the outstanding stability, strategic redox potential, UV-photo activated, non-toxic and low cost [4]. Whereas in nanotubes arrays (NTs), TiO_2 has been widely fabricated by anodization process, which is a self-organized nanotubular oxide and it can be conducted at room temperature. The formation of nanotubes oxide offer more superior properties, as it provides higher surface area with more efficient charge transfer for water photolysis as well as morphology of highly anisotropic geometry. Grimes et al. [5] reported that the highly ordered TiO_2 nanotubes arrays provide an effective pathway for electron percolation compared to TiO_2 nanoparticle films.

However, the lower quantum yield of photo-oxidation reaction of TiO_2 attributed to the fast recombination electrons and holes pairs and intrinsic band gap of TiO_2 (3.2 eV anatase) which alternately limits the photocatalytic performance in optical absorption to the ultraviolet region of the solar spectrum [6]. The efficiency of this material can be improved by doping, heterostructure and co-deposited with other metal oxide to produce composites metal oxide [7]. On the other hands, cobalt is a p-type semiconductor that has superior properties. It has narrow band gap and can be activated by visible light. Therefore, by incorporating these materials, n-p type heterojunction semiconductor can be created. This contemporary n-p type semiconductor can be actuated by visible light. According to Jiang et al. [8], cobalt was verified to be among the most convincing dopants to boost the response of light and TiO_2 photoactivity out of the present transition metals.

In the present work, the aim is to improve the separation of electron-hole which leads to improve photocatalytic performance. Therefore, it is necessary to develop effective solutions to expand their useful range of activation into visible range and minimizing photogenerated electron-hole recombination. Hence, TiO_2/Co photocatalyst was prepared by anodization and electrodeposition and investigated as well as the morphology and structural of the TiO_2/Co. The decomposition of methyl orange by using the produced TiO_2/Co photocatalyst is evaluated by using UV-vis irradiation.

2.0 METHODOLOGY

2.1 Preparation of TiO_2 nanotube arrays

High-purity Ti foil (99.99%) was used as a substrate and was cut into desired shape with dimension of 4.0 x 1.0 cm. Next, the foils were undergoing the degreasing process via sonication in the acetone for 15 minutes and rinsed with distilled water. Then, the cleaned Ti substrate is dried in an air stream. TiO_2 nanotube arrays were synthesis by anodization method in an ethylene glycol solution containing NH_4F and H_2O_2. Anodization is carried out in a two-electrode where Ti foils as the working electrode (WE) and graphite rod as the counter electrode (CE) at a consistent 60 V anodic potential for 30 minutes in room temperature. The anodization ramp was set at 10 vs^{-1} to homogenize the electrolyte and conserve a consistent current during the anodization. Upon anodization process, the TiO_2 nanotubes is then rinse with acetone and distilled water using ultrasonic bath for 1 minutes and air dried with an air gun. This process is to get rid of the residual electrolyte on the nanotubes and $Ti(OH)_4$ precipitate residue of the nanopores opening.

2.2 Preparation of Co-TiO_2 nanotubes

In a typical experiment, cobalt decorated on TiO_2 nanotubes is carried out using electrodeposition process at consistent potential of 1 V. Different molarity of cobalt chloride solution of 0.01 mM, 0.05 mM and 0.10 mM was deposited on TiO_2 nanotubes with deposition time of 1, 2 and 3 minutes. The thickness of Co is controlled by the deposition times. The resulting amorphous TiO_2/Co nanotubes were finally annealed at 400°C for 1 hour and at heating rate of 5°C/min to improve stoichiometry and crystallization.

2.3 Characterization

The samples were characterized by field emission scanning electron microscope (FE-SEM S4800, Hitachi) and X-ray Diffraction (Expert Pro PANalytical) was used to evaluate the morphological and structural characteristic. X-ray diffraction (XRD) patterns were recorded at room temperature with CuKα radiation of 0.15418 nm in a diffractometer using a generator voltage of 40 kV and current of 40 mA. The data were collected for scattering angles (2θ) ranging from 20° to 90° with a step of 0.0136° for 2s per point. While, Raman spectra were recorded at room temperature using the UniRAM-3500 that was performed at a laser wavelength of 523 nm.

2.4 Photocatalytic Reaction

The photocatalytic experiments were conducted by measuring photodegradation of methyl orange (MO) dye solution with TiO_2/Co nanotubes immersed in the dye solution under UV light illumination. The dye solution without samples was used as reference. The surface area of the nanotubes tested was 3 cm^2. The degradation testing was performed using a germicidal UV-C 150 W lamp. The concentration of the MO is prepared at 30 ppm and 30 ml of MO was poured into glass beaker during the illumination. The solution of MO with differences of molarity and time of illumination was kept in the dark for adsorption and desorption equilibrium. The irradiation of dyes was held for 5 hours and 10 ml of MO was taking out every 1 hours during irradiation for examining the absorbance change of MO by UV-Visible spectroscopy (UV-1700) which light of ultra-violet region (200 nm to 400 nm).

3.0 RESULTS AND DISCUSSION

In order to find the suitable conditions for the synthesis of TiO_2/Co nanotube arrays, the effect of cobalt deposited on TiO_2 in different molarity is studied. To verify the formation of the nanotube of TiO_2 and cobalt decorated on the nanostructure, FESEM analysis was performed. It gives direct evidence of Co decorated on TiO_2 nanostructure. Figures 1 (a) – (c) depict the FESEM images with a different molarity of cobalt decorated at deposition time of 1 min. Figures 1 (a)ii – (c)ii are magnified image of Figures 1 (a)i – (c)i. The morphology of Co decorated TiO_2 nanotubes had clearly transformed as the concentration of cobalt chloride solution was increased. This can be seen from Figures 1(a) – (c). The density of deposited Co on the TiO_2 nanotubes surface can be seen as a function of molarity whereby at 0.01 mM, the wall thickness of TiO_2 is thinner and the covered by the Co are only at the top mouth (Figure 1 (a)). As the Co solution is increased to 0.05 mM, the density of Co deposited is increased. Thicker deposition is formed on the surface of the TiO_2 and collection of Co particles can be seen seated on the tube wall. At 0.1 mM, deposition of Co has started to agglomerate due to excessive of Co seated on the surface of nanotube TiO_2 as seen in Figure 1 (c).

The phase composition and crystallinity of Co decorated on TiO_2 nanotubes were characterized by X-ray diffraction (XRD). As shown in Figure 2, the diffraction pattern of the sample was indexed to anatase phase of TiO_2 and CO_3O_4. The main diffraction peaks of anatase phase is 25.2 °, 37.5 °, 48.1 °, 53 °, 62.8 °, 69 °, 70.7 °, 75.5 ° and 76.3 ° can be indexed to the (101), (004), (200), (105), (211), (204), (116), (220), (215) and (301). At 25.2° and 37.5° are strong peaks and assign to anatase crystal structure TiO_2 nanotubes. This result is aligned with Geng et al. [9]. With increasing of Cobalt cloride concentration, the relative intensities of the anatase to cobalt related peaks increase gradually. The Co_3O_4 peak started to clearly present at 37.8° (311) and 56° (422) for 0.05 mM. Additionally, another diffraction peak of Co_3O_4 can be observed when the deposition of Co is done for 3 min (Figure 2 (b)) at 30.5° and 36.6°. There are well consistent with (220) and (311), which demonstrate that the cobalt is well coated over TiO_2 nanotubes surface.

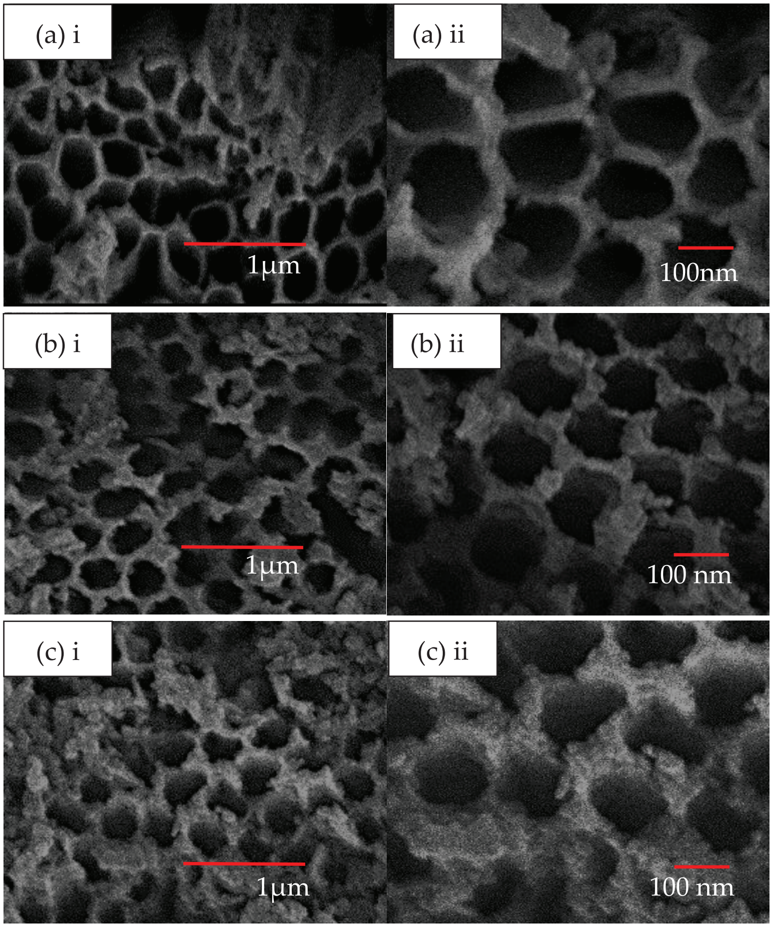

Figure 1: FESEM image of the cobalt decorated on TiO_2 in different molarity of cobalt cloride (a) 0.01 mM, (b) 0.05 mM and (c) 0.1 mM (i-showing low magnification images and ii-showing high magnification images)

However, the intensities of Co_3O_4 has is much lower compares to the anatase is due to the formation of small grains sized as well as less amount of loading supplied during the deposition [10]. As the conclusion, the additional of metal ions into TiO_2 crystal lattice has very negligible influence on the phase of the TiO_2 because the metal ion concentration is very insignificant with respect to TiO_2 [11].

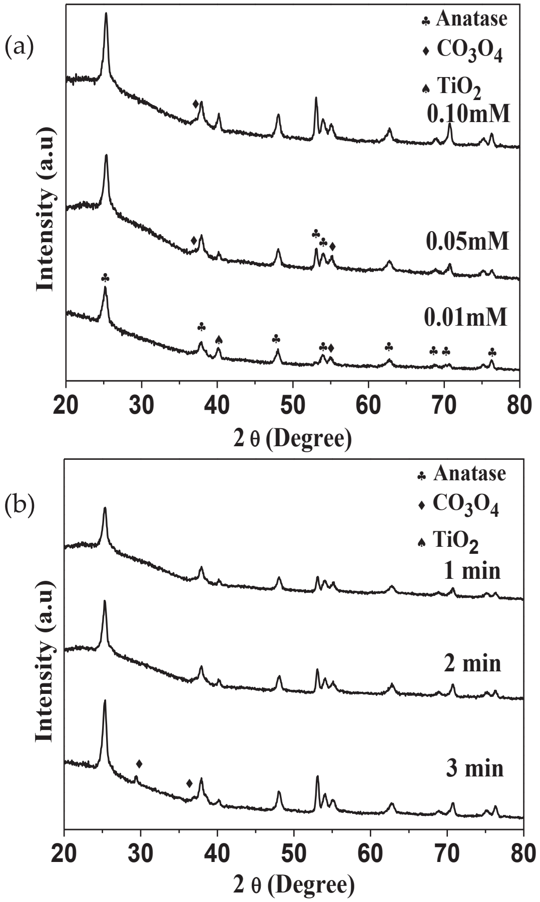

Figure 2: XRD patterns of Cobalt decorated TiO_2, (a) Different of molarity of Cobalt in 1 min and (b) Different of time deposited in 0.05 mM

Raman spectra were further utilized to reveal structural characteristic of Co/TiO_2 nanotubes structure. Figure 3 shows five well-resolved peaks that are observed around 143 cm^{-1}, 194 cm- cm^{-1}, 395 cm^{-1}, 511 cm^{-1} and 633 cm^{-1}. These peaks can be defined as the $Eg_{(1)}$, $Eg_{(2)}$, $B1g_{(1)}$,$B1g_{(2)}$ and $Eg_{(3)}$, respectively. These modes represent the anatase phase. The strongest $Eg_{(1)}$ mode is observed at 143 cm^{-1}. On the other hand, the decorated Co/TiO_2 nanotubes with different molarity and deposition time consist of similar bands (Figures 3 (a) and (b)). However minimal peak shift were observe. It is noticeable the blue shift occurs for 143 cm^{-1} ($Eg_{(1)}$) and red shift of 633 cm^{-1} ($Eg_{(3)}$). The shifting of the Raman bands is due to oxygen vacancies or disorder induced defects and phonon confinement effects [12]. This implies that direct incorporation of Co and well-decorated with TiO_2. The crystalline size in the nanoscale range may affect the frequency shifting and broadening of Raman peaks due to the phonon confinement and along with the phonon confinement, oxygen vacancies play an important role for frequency shifting as well as broadening of Raman modes [13].

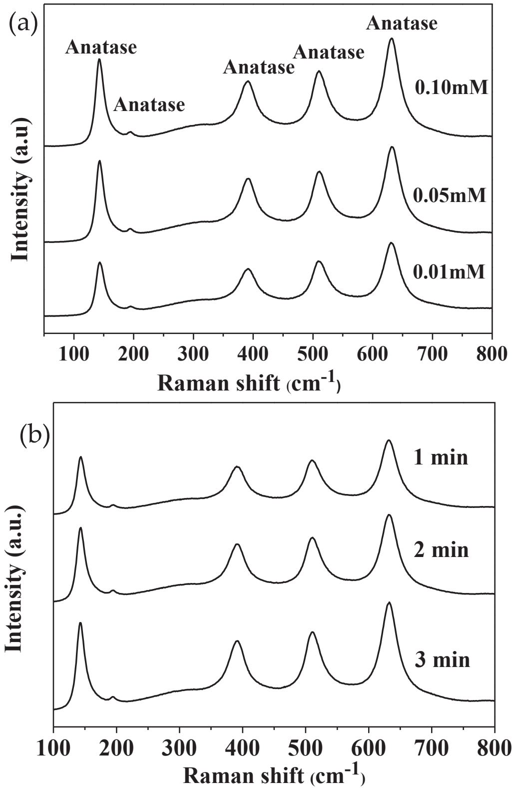

Figure 3: Raman spectra of Cobalt decorated TiO_2, (a) Different of molarity of Cobalt in 1 min and (b) Different of time deposited in 0.05 mM

The catalytic performance of Co/TiO_2 nanotubes are shown in Figures 4 (a) and (b) for different molarity of cobalt at 1 min deposition time and different electrodeposited time with 0.05 mM cobalt chloride solution respectively. For sample with low concentration of 0.01 mM, less degradation efficiency is observed. The highest degradation rate can be seen with samples of 0.05 mM with 60% degradation compares to the 0.1 mM that only give 40% degradation. This indicates that further increase of cobalt solution concentration, will not improve the photocatalytic reaction. This is due to the excessive Co that can reduce the catalytic properties of TiO_2 and Co may as well act as the recombination centers. The usage of Co beyond a certain level and excessive time electrodeposited also lead to accumulation of Co. Thus, tends to the reduction of some effective surface active sites and resists separation and transportation of photogenerated [14]. The molarity of Co solution for 0.05 mM at 1 min shows that the degradation rate of methyl orange in solution can be up to 60% in 5 hours degradation time. Optimum Co concentration makes the space charge thickness layer substantially equals to the depth of light penetration.

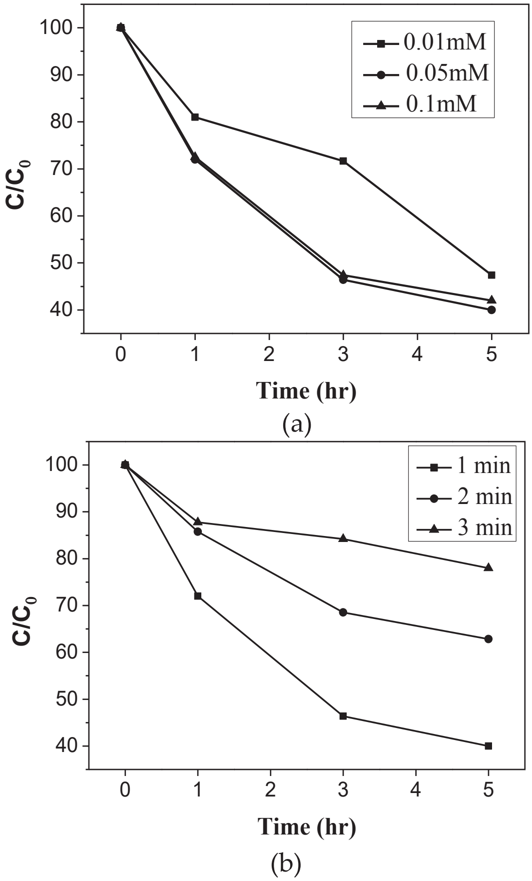

Figure 4: Photocatalytic performance (a) Different molarity of cobalt at 1 min deposition time and (b) Different electrodeposited time with 0.05 mM cobalt chloride solution

4.0 CONCLUSION

In summary, TiO_2 nanotube/Co was successfully fabricated by electrodeposition process, which shows enhanced photocatalytic activity. The TiO_2 nanotube containing 0.05 mM with 1 min exhibits a good performance of methyl orange degradation and a better incorporation of Co in the TiO_2 nanotube lattice without any secondary phase. That was promotes the photoresponse to extend into the visible energy region.

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REFERENCES

[1] P. Jantawasu, T. Sreethawong and S. Chavadej, "Photocatalytic activity of nanocrystalline mesoporous-assembled TiO_2 photocatalyst for degradation of methyl orange monoazo dye in aqueous wastewater", *Chemical Engineering Journal*, vol. 155, no. 1/2, pp. 223-233, 2009.

[2] E. Casbeer, V.K. Sharma and X.Z. Li, "Synthesis and photocatalytic activity of ferrites under visible light: a review", *Separation and Purification Technology*, vol. 87, no. 18, pp. 1-14, 2012.

[3] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode", *Nature,* vol. 238, no. 5358, pp. 37, 1972.

[4] W. Zhao, X. He, Y. Peng, H. Zhang, D. Sun and X. Wang, "Preparation of mesoporous TiO_2 with enhanced photocatalytic activity towards tannery wastewater degradation", *Water Science and Technology*, vol. 75, no. 5-6, pp. 1494-1499, 2017.

[5] C.A. Grimes, "Synthesis and application of highly ordered arrays of TiO_2 nanotubes", *Journal of Materials Chemistry*, vol. 17, no. 15, pp. 1451-1457, 2007.

[6] G. Dai, J. Yu, and G. Liu, "Synthesis and enhanced visible-light photoelectrocatalytic activity of p-n junction BiOI/TiO_2 nanotube arrays", *Journal of Physical Chemistry C,* vol. 115, no. 15, pp. 7339-7346, 2011.

[7] P. Roy, S. Berger, and P. Schmuki, "TiO_2 Nanotubes: Synthesis and applications", *Angewandte Chemie-International Edition*, vol. 50, no. 13, pp. 2904-2939, 2011.

[8] P. Jiang, W. Xiang, J. Kuang, W. Liu and W. Cao, "Effect of cobalt doping on the electronic, optical and photocatalytic properties of TiO_2", *Solid State Sciences*, vol. 46, pp. 27-32, 2015.

[9] H. Geng, H. Ang, X. Ding, H. Tan, G. Guo, G. Qu, Y. Yang, J. Zheng, Q. Yan and H. Gu, "Metal coordination polymer derived mesoporous Co_3O_4 nanorod with uniform TiO_2 coating as advanced anodes for lithium ion batteries", *Nanoscale,* vol. 8, no. 5, pp. 2967-2973, 2016.

[10] Y. Fan, N. Zhang, L. Zhang, H. Shao, J. Wang, J. Zhang and C. Cao, "Co_3O_4- coated TiO_2 nanotube composites synthesized through photo-deposition strategy with enhanced performance for lithium-ion batteries", *Electrochimica Acta*, vol. 94, pp. 285-293, 2013.

[11] S. Bala, I. mondal, A. Goswami, U. Pal and R. Mondal, "Co-MOF as a sacrificial template: manifesting a new Co_3O_4/TiO_2 system with ap-n heterojunction for photocatalytic hydrogen evaluation", *Journal of Materials Chemistry A*, vol. 3, no. 40, pp. 20288-20296, 2015.

[12] B. Santara, B. Pal and P.K. Giri, "Signature of strong ferromagnetism and optical properties of Co doped TiO_2 nanoparticles", *Journal of Applied Physics*, vol. 110, no. 11, pp. 114322-13101, 2011.

[13] W.F Zhang, Y.L He, M.S. Zhang, Z. Yin and Q. Chen, "Raman scattering study on anatase TiO_2 nanocrystals", *Journal of Physics D: Applied Physics,* vol. 33, no. 8, pp. 912, 2000.

[14] M. Hamadanian, A. Reisi-Vanani and A. Majedi, "Sol-gel preparation and characterization of Co/TiO_2 nanoparticle: application to the degradation of methyl orange", *Journal of the Iranian Chemical Society*, vol. 7, no. 2, pp. S52-S58, 2010.