**Tio\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} Composite as Photoanode of Photoelectrochemical Water Splitting**

Dian Anggraini\textsuperscript{1}, Pratiwi Kusuma Wardani\textsuperscript{1}, Mutia Agustina\textsuperscript{1}, Amir Awaluddin\textsuperscript{1}, Khuzaimah Arifin\textsuperscript{2,*}

\textsuperscript{1}Department of Chemistry, Faculty of Mathematic and Natural Science, Universitas Riau, Kampus Binawidya, Km 12.5 Simpang Baru, Pekanbaru, Riau, Indonesia
\textsuperscript{2}Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Malaysia

*Corresponding author: khuzaim@ukm.edu.my

**Abstract.** Titanium dioxide is one of the most investigated materials for photoelectrochemical (PEC) water splitting. However, TiO\textsubscript{2} has a wide band gap of approximately 3.2 eV, which limits its absorption energy to UV only, and the photoexcitation products (i.e., electron and hole) easily recombine. Developing a composite with other semiconductor materials is one of the efforts for improving the performance of TiO\textsubscript{2} photoelectrode. In this study, a composite of TiO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} thin films was developed, and its performance in PEC water splitting was investigated. Co\textsubscript{3}O\textsubscript{4} was synthesized using a hydrothermal method, and TiO\textsubscript{2} P25 was used. TiO\textsubscript{2} and Co\textsubscript{3}O\textsubscript{4} were mixed by ball milling before coating on a clean FTO and annealing at 550 °C. Two weight variations of TiO\textsubscript{2}:Co\textsubscript{3}O\textsubscript{4} were used (95:5 and 90:10%). XRD and FESEM analysis were used to investigate crystallinity phase and surface morphology. The optical band gap of the thin films was determined by UV-Vis spectroscopy, where the film with 90:10 weight ratio of TiO\textsubscript{2}:Co\textsubscript{3}O\textsubscript{4} obtained the smallest band gap of 2.9 eV. Co\textsubscript{3}O\textsubscript{4} improved the current density and TiO\textsubscript{2} performance by approximately three times.

### 1. Introduction

At present, the demand for energy, especially from renewable and sustainable resources, increases tremendously. One of the most investigated resources is sunlight energy, which is the source of living on Earth. By mimicking plant photosynthesis, in which sunlight energy is converted into chemical energy, artificial photosynthesis focuses on photoelectrochemical (PEC) water molecule splitting to produce hydrogen and oxygen. Hydrogen is used as fuel in a cell system to produce electricity with pure water as the only by-product. PEC is a safe, clean and environment-friendly technology [1].

PEC water splitting has attracted great attention since Fujishima and Honda (1972) announced their discovery of using TiO\textsubscript{2} as photoanode [2]. To date, TiO\textsubscript{2} remains the most favored candidate for PEC water splitting because it is thermodynamically stable, cheap, non-toxic, and has favorable band edge alignment with water redox potentials. However, TiO\textsubscript{2} has a wide band gap of approximately 3.0 eV, which can only utilize UV light energy; the amount of UV is only 4% of the solar spectrum. In addition,
the photo-excitation products of electrons and holes are prone to recombination given the wide band gap [3].

Several attempts have been conducted to develop TiO$_2$ as an acceptable photocathode for PEC water splitting; strategies tested include doping with other elements, surface modification, and synthesis of nanosized photocatalyst or composites with other materials. These attempts mainly aimed to suppress the charge recombination of the photo-excitation products and enhance the activity and stability of TiO$_2$ photocatalysts [4]. TiO$_2$ efficiency has been improved using combinations of several techniques [5]. Zhang et al. [7] reported that the combination of N-doped TiO$_2$ nanoparticle with reduced graphene oxide exhibits an enhancement of 17.8 times compared with pristine TiO$_2$. Furthermore, the use of CdS quantum dots for sensitizing TiO$_2$ nanotube-array photovoltaic electrodes increased the short-circuit photocurrent of the TiO$_2$ nanotube by 35 times from 0.22 mA/cm$^2$ to 7.82 mA/cm$^2$ [6]. However, CdS is a highly toxic material that is not recommended for use. Dong et al. [8] also reported the rapid activation of Co$_3$O$_4$/TiO$_2$ as photoanodes. Co$_3$O$_4$ treated with Ar-plasma under irradiation resulted in two times higher photo current density (i.e., 2.5 mA/cm$^2$) than the untreated Co$_3$O$_4$/TiO$_2$ (1.25 mA/cm$^2$). Ar plasma treatment is a fast and very efficient strategy for activating Co$_3$O$_4$ to increase the water oxidation reactivity. However, this method requires high voltage and is not cost effective.

In this study, the composite of TiO$_2$ and cobalt oxide thin films was investigated as photoanode of PEC water splitting. Cobalt oxide is another-typically investigated material in various catalytic applications, such as Li-ion batteries, photocatalysis and solar absorbers. In the cobalt oxide phase, Co$_3$O$_4$ is prominent because of its high chemical stability and narrow optical band gap of 1.5 – 2.0 eV in the bulk state [9]. TiO$_2$/Co$_3$O$_4$ composite thin films were prepared by hydrothermal and doctor blading methods assisted by ball-milling to produce a well-mixed composite that can improve the TiO$_2$ thin film performance in PEC water splitting.

2. Experimental

2.1. Preparation TiO$_2$ as a control
In brief, 0.2 g of TiO$_2$ P25 and 0.05 g of poly ethylene glycol were added with 1 mL of ethanol and crushed. The mixture was coated on the FTO surface through blade coating and annealed at 500 °C for 2 h.

2.2. Synthesis of cobalt oxide
Cobalt oxide was synthesized by hydrothermal method according to previous studies [10]. About 1.74 g of cobalt nitrate hexahydrate and 0.72 g of urea were dissolved in 50 mL of deionized water. The homogeneous solution obtained was transferred to a stainless steel autoclave. The autoclave was placed in the furnace at 100 °C for 6 h. The autoclave was cooled to room temperature. The sample was rinsed with deionized water and placed in the oven to dry. Before mixing the cobalt oxide with TiO$_2$, the cobalt oxide synthesized by hydrothermal method was ball-milled for 2 h.

2.3. Mixing of TiO$_2$ and Co$_3$O$_4$ as a sample
TiO$_2$, Co$_3$O$_4$, poly ethylene glycol, and ethanol were ball-milled for 20 min, coated on the FTO surface, and annealed at 550 °C for 2 h (two weight variations of TiO$_2$:Co$_3$O$_4$ (95:5 and 90%:10%). The sample characterized and used as working electrode.

2.4. Characterization
Crystalline phase and size were determined using D8 Advance XRD (Bruker AXS Germany). Surface morphology was observed using a FESEM model Carboxen Polydimethyl Siloxane (Supelco). NIR UV-
Vis reflector spectra were recorded using a Perkin Elmer Lambda 950 spectrophotometer in ‘diffuse reflectance’ mode with a wavelength of 300-800 nm.

2.5. Electrochemical Study

Linear sweep voltammetry analysis was performed using Ametek Versastat 4 under 100 mW/cm² xenon lamp in a three-electrode system with 0.5 M Na₂SO₄ electrolyte solution. The TiO₂/Co₃O₄ thin films were used as the working electrode, platinum wires as the counter electrodes, and Ag/AgCl electrodes as the reference electrodes.

3. Results and Discussion

![Figure 1. XRD pattern of TiO₂, Co₃O₄ and samples (i.e., 95:5 and 90:10)](image)

The crystal structures and phase purity of TiO₂, Co₃O₄, and the two samples were examined using XRD (Figure 1). TiO₂ is consistent with the standard anatase (JCPDS No. 21-1272) and rutile (JCPDS No. 21-1276), but the percentage of anatase is higher (87.3%) than that of rutile (12.7%). The high intensity of the anatase peak indicates the good crystallinity of the formed titania. In the photocatalyst process, the anatase and rutile phases can be used, but the former has higher potential as photocatalyst because it has a lattice structure that is compatible with the photocatalyst activity. In the anatase crystalline phase, TiO₂ exhibits high photocatalytic properties. The XRD pattern of Co₃O₄ shows the orientation of (111), (220), (311), (511) and (440) planes, which are the main characteristics of the Co₃O₄ phase that correspond to the phase of cobalt oxide spinel (JSPD No. 00-042-1467). Hence, cobalt oxide produced from this hydrothermal method successfully produced the Co₃O₄ phase. The good crystallinity of Co₃O₄ also suggests that the energy provided during the reaction is sufficient to react to form crystalline materials. The synthesis approach applied in this study is the same as that reported by Liu et al. [10].

The two samples (95:5 and 90:10) show relatively the same diffraction pattern. The diffraction peak of the sample shows decreased intensity and shifts within the 2θ value lower than that of TiO₂. This shift
occurs because of the addition of a weight ratio of Co$_3$O$_4$, which migrates to the TiO$_2$ crystal structure lattice. The peaks of Co$_3$O$_4$ are weaker than those of TiO$_2$ because the former is coated by the latter. The intensity of the diffraction peak which is quite high and firm for the addition of Co$_3$O$_4$, indicating the good crystallinity of the sample that could lead to rapid electron diffusion. Hence, the electron transfer in the photoelectrode will be high [11], increasing the efficiency of the photocatalytic process. Overall, this property can improve the performance of photoanodes.

The morphologies of TiO$_2$/Co$_3$O$_4$ were determined using FESEM (Figure 2). In general, the morphology of TiO$_2$/Co$_3$O$_4$ is dependent on different factors, such as synthesis method, synthesis condition, post-treatment and precursor used. In Figure 2 (a-c) indicate that the addition of Co$_3$O$_4$ plays a significant role in morphological changes. In Figure 2, the morphology of TiO$_2$/Co$_3$O$_4$ with a weight percentage 90:10 displayed nanospheres; the sample is cubic shaped and has a connection between the nanospheres and cubic. Figure 2 (c) shows that a small fraction of sphere-like particles that appear as bright spots with diameter of 150-450 nm and are homogenously dispersed in the matrix of particles with diameter of 300-450 nm. The tiny particles that appear as bright spots are uniformly distributed in TiO$_2$/Co$_3$O$_4$. According to the XRD results, TiO$_2$ and Co$_3$O$_4$ coexist in the TiO$_2$/Co$_3$O$_4$ composites Figure 2 (d) presents TiO$_2$ without the addition of Co$_3$O$_4$. Figure 2 (a-c) shows that nano spheres are large in size and are homogenous. Ramakrishnan et al. [12] fabricated cobalt oxide nanoparticle on TiO$_2$ nanorods/FTO with varying electrodeposition times of 20, 40 and 60 s followed by annealing at 500 °C; the product displayed a nanorod morphology. TiO$_2$ was synthesized by hydrothermal method on the FTO surface after being deposited with nanorod oxide nanoparticles. The-as deposited cobalt oxide nanoparticles on densely grown TiO$_2$ nanorods have a length of 1-2 µm.

![Figure 2. Morphology of TiO$_2$:Co$_3$O$_4$ (90:10) (a) 1µm (b) 100 nm (c) 200 nm (d) TiO$_2$](image-url)
Figure 3 shows that TiO$_2$ used as a control has a band gap value of 3.25 eV. This finding is consistent with the theory that TiO$_2$ anatase has a band gap value of approximately 3.2 eV. The band gaps of samples 95:5 and 90:10 are 3.125 and 2.9 eV, respectively. Adding lower amount of Co$_3$O$_4$ led to a smaller band gap value. This finding is due to several factors, including the percentage of Co$_3$O$_4$ in the TiO$_2$ film, which significantly change the light absorption of the reflector. However, for higher concentrations of Co$_3$O$_4$, the light absorption of the reflectance decreases because the dark film becomes thinner as more Co$_3$O$_4$ is added. The TiO$_2$:Co$_3$O$_4$ sample with a weight ratio of 90%:10% inhibited light absorption on TiO$_2$/Co$_3$O$_4$ nanoparticles. This result is supported by the appearance of 90:10 samples, which are darker in color than the 95:5 samples. Therefore, light effects contribute significantly to the band gap value.

Prior to adding Co$_3$O$_4$, the current density of the bare TiO$_2$ was also measured for comparison. In addition, the measurement results of TiO$_2$ as a control exhibited the lowest current density in the dark and light reactions among the samples. The comparison of dark and light reaction (current density) is shown in Figure 4. Overall, the current density in the light reaction is higher than that in the dark reaction. This finding indicates that energy can increase the current density produced. The increase in the current density is directly proportional to the increase obtained by the weight of cobalt oxide provided. TiO$_2$/Co$_3$O$_4$ with a weight ratio of 90:10 appeared darker because the added Co$_3$O$_4$ had higher absorption in the visible range. The enhancement in the current density shows the effectiveness of TiO$_2$ and Co$_3$O$_4$. The photogenerated electron will move from the conduction band of cobalt oxide to that TiO$_2$ and then to the FTO substrate, finally reaching the metallic counter electrode (Pt) and hole movement in the reverse direction.
Figure 4. Comparison of dark and light current density-voltage diagrams of TiO$_2$/Co$_3$O$_4$ on FTO in 0.5 M Na$_2$SO$_4$ aqueous solution with a light density of 100 mW/cm$^2$.

4. Conclusion
TiO$_2$/Co$_3$O$_4$ with different weight ratios can improve the photocatalytic properties. The addition of Co$_3$O$_4$ produces small band gap. Co$_3$O$_4$ in TiO$_2$ can change the light absorption of the reflector. The current density in the light reaction is higher than that in the dark reaction. TiO$_2$/Co$_3$O$_4$ with a weight ratio of 90:10 has a high photocurrent density, which is increased by photon energy and contributes to the large band gap.

Acknowledgement
The Ministry of Education, Malaysia, supported this work through the FRGS/1/2015/SG01/UKM/03/1 Research grant and Universiti Kebangsaan Malaysia under Research University Grant GUP-2016-085.

References
[1] Lopes T, Dias P, Andrade L and Mendes A 2014 Solar Energy Materials and Solar Cells. 128 399-410
[2] Chen M, Chen K, Liu S, Zhang L, Zhang J and Wilkinson P 2012 Chemical Society Reviews. 41 5654-5671
[3] Xia H, Hong B, Li B, Zhao Z, Lin M, Savilov V and Aldoshin 2015 Advanced Functional Materials. 25 627-635
[4] Moniz S, Shevlin A, Martin J, Guo X and Tang J Energy & Environmental Science. 8 731-759
[5] Jin Q, Yamamoto H, Yamamoto K, Fujishima M and Tada H 2013 Phys.Chem.Chem.Phys. 15 20313-19
[6] Wang F, Hsieh C, Lee F and Yang M 2013 Applied Catalysis B: Environmental. 142, 626-632.
[7] Zhang G, Huang H, Li W, Yu F, Wu H and Zhou L 2012 Electrochimica Acta. 81 117-122
[8] Dong G, Hu H, Huang X, Zhang Y and Bi Y 2018 Rapid activation of Co₃O₄ cocatalyst with oxygen vacancies on TiO₂ photoanodes for efficient water splitting J.Mater.Chem.A. 6 21003-21009

[9] Fan Y, Zhang N, Zhang L, Shao H, Wang J, Zhang J and Cao C 2013 Electrochimica Acta. 94 285

[10] Liu Z, Ma C, Cai Q, Hong T, Guo K and Yan L 2017 Promising Cobalt Oxide and Cobalt Oxide/Silver Photocathodes for Photoelectrochemical Water Splitting. Solar Energy Materials and Solar Cells. 161 46-51

[11] Lee K, Mazare A and Schmuki P 2014 One-Dimensional Titanium Dioxide Nanomaterials: Nanotubes. Chemical reviews. 114 (19) 9385-9454

[12] Ramakrishnan, Vivek, Kim, Hyun, Park, Jucheol, Yang and Beelyong 2016 Cobalt Oxide Nanoparticles on TiO₂ Nanorod/FTO as a Photoanode with Enhanced Visible Light Sensitization. Royal Society of Chemistry. 1 1-10