*Journal of Advanced Research in Micro and Nano Engineering*, 23, Issue 1 (2024) 49-60

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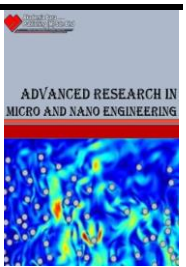
Journal of Advanced Research in
Micro and Nano Engineering

Journal homepage:
https://www.akademiabaru.com/submit/index.php/armne/index
ISSN: 2756-8210



# Mechanism of $Co_3O_4$-$TiO_2$ Nanocomposite Formation with Enhanced Photocatalytic Performance

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**ARTICLE INFO**

***Article history:***
Received 1 June 2024
Received in revised form 9 July 2024
Accepted 17 August 2024
Available online 30 September 2024

**ABSTRACT**

$TiO_2$ nanotubes are tubular structures that have garnered significant attention in materials science and engineering due to their unique properties and diverse applications. In this study, highly ordered and well aligned $TiO_2$ nanotubes were successfully synthesized through anodization of Ti foil in ethylene glycol ($C_2H_6O_2$) containing ammonium fluoride ($NH_4F$) and hydrogen peroxide ($H_2O_2$) at 60 V for 30 minutes. The effectiveness of $TiO_2$ as a photocatalyst under solar light is limited by its wide band gap and high recombination rate of charge carriers. To address these limitations, $TiO_2$ nanotubes were modified with cobalt oxide. The resulting $Co_3O_4$-$TiO_2$ nanocomposite was synthesized using a wet impregnation technique, aiming to enhance the photocatalytic performance of $TiO_2$ nanotubes across a broader range of the solar spectrum. The formation of $Co_3O_4$-$TiO_2$ nanocomposite is by immersing the $TiO_2$ nanotubes in the metal salt precursor solution of $Co(NO_3)_2$ for a certain soaking period. The soaking cycle was repeated a few times to ensure the deposition of cobalt oxide nanostructures on the $TiO_2$ nanotube samples. This diffusion interstitial process via wet impregnation was time dependent, which altered the amount of cobalt loaded on the nanotube's surface. The addition of cobalt significantly improved the photodegradation activity of the nanotubes under visible light, outperforming bare $TiO_2$ nanotubes. This enhancement is likely due to the cobalt acting as shallow traps, which effectively promote the separation of photogenerated charge carriers.

***Keywords:***
Anodization; wet impregnation; photocatalytic; nanotubes

## 1. Introduction

Titanium dioxide ($TiO_2$) is a remarkable semiconductor material widely used as a photocatalyst. This abundant transition metal oxide stands out for its environmental compatibility, being non-toxic and non-flammable. In nano-size dimensions, $TiO_2$ is more advantageous compared to their larger, bulk equivalents. For example, $TiO_2$ nanoparticles are particularly prized across diverse applications, largely due to their increased surface area that gives rise to distinctive properties and behaviors. In

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https://doi.org/10.37934/armne.23.1.4960

addition, these $TiO_2$ nanoparticles can be synthesized through a variety of physical, chemical, and environmentally friendly methods [1]. Recently, $TiO_2$ nanotubes have emerged as a promising candidate for semiconductor photocatalysis which is able to eliminate organic pollutants via heterogeneous photocatalysis [2]. It has several unique properties that make them well-suited for photocatalysis. $TiO_2$ nanotubes have a high surface area due to their tubular structure, which allows for increased contact area with reactants in water. This property enhances catalytic activity and promotes efficient reactions, making $TiO_2$ ideal for use as a photocatalyst in wastewater treatment. Besides that, the main component of $TiO_2$ nanotubes, is a relatively low-cost material compared to other catalysts. This cost-effectiveness makes $TiO_2$ nanotubes attractive for commercial applications in environmental remedies such as wastewater. The fabrication techniques such as the hydrothermal and anodization methods, are relatively simple and robust. This simplicity in fabrication makes $TiO_2$ nanotubes more accessible for widespread use in various applications [3].

$TiO_2$ nanotubes, despite promising as photocatalysts, face several limitations that hinder their extensive efficiency. The primary drawback is their wide bandgap (3.2 eV for anatase phase), which restricts their light absorption mainly to the UV range, utilizing only about 5% of solar radiation [4]. This, coupled with rapid electron-hole recombination, leads to low quantum yield and poor visible light performance. The potential for photocorrosion under certain conditions affects long-term stability and reusability [5]. Despite their high surface area, $TiO_2$ nanotubes may have limited adsorption capacity for certain pollutants and can be challenging to recover from treated water, potentially causing secondary pollution. The synthesis of uniform, high-quality $TiO_2$ nanotubes can be complex, often requiring specialized equipment [6]. Certain methods require careful control of reaction parameters to ensure the formation of uniform nanotubes. Additionally, nanotubes may agglomerate, reducing effective surface area and catalytic activity [7]. The active sites on the surface that are responsible for catalyzing reactions may become less accessible. This reduction in effective surface area can hinder the efficiency of the photocatalytic process, as fewer active sites are available for interactions with reactant molecules. To mitigate the negative effects of agglomeration, strategies such as surface modification, dispersion techniques, and the use of support materials can be employed to prevent or minimize agglomeration of nanotubes. Various approaches to nanotube treatment are aimed to maintain their dispersion, preserving their high surface area, and enhance their catalytic activity for diverse applications. Regarding the mechanism of photocatalyst-driven pollutant degradation, valuable insights have been reported in the literature. For instance, Eleen Dayana Mohamed Isa *et al.*, have contributed to our understanding of this process [8].

To address these issues, researchers often modify $TiO_2$ nanotubes through doping, sensitization, or the creation of heterojunctions to enhance visible light absorption and reduce electron-hole recombination [9]. One of the common strategies is coupling $TiO_2$ with another material which can alter the electronic state of the $TiO_2$ resulting in a change in the optical properties [10]. The incorporation of other materials such as cobalt oxide ($Co_3O_4$) into the $TiO_2$ photocatalyst structure has gained interest in the works of literature recently due to the exciting features of the bi-component system. In this context, the incorporation of cobalt oxide ($Co_3O_4$) into the $TiO_2$ matrix has emerged as a viable approach to improve the photocatalytic efficiency of the material [11]. Cobalt oxide is known to act as an efficient co-catalyst, facilitating the separation of photogenerated electron-hole pairs and promoting the transfer of charge carriers to the surface of the photocatalyst, where they can participate in the oxidation of organic pollutants [12]. For instance, the indirect all-solid-state Z-scheme system composed of $TiO_2$ and cobalt oxide has been shown to exhibit significantly improved photocatalytic degradation of methylene blue under visible light irradiation, with the cobalt oxide component acting as an electron acceptor and facilitating the separation of charge carriers [13]. The synergistic effect between the two components leads to improved light absorption, charge carrier separation, and surface redox reactions, making this a promising approach for environmental remediation applications.

In this research, the synthesis of $Co_3O_4$-$TiO_2$ nanocomposite semiconductor oxide by anodization and wet impregnation method is investigated as well as the morphology and structural of the structures. The prepared $Co_3O_4$-$TiO_2$ nanocomposite were thoroughly characterized using a selection of analytical techniques to elucidate their structural, morphological, and optical properties. The evaluation of photocatalytic properties was done by degradation of organic dyes using visible light irradiation. Cobalt oxide ($Co_3O_4$) is a p-type semiconductor material with a bandgap around 2.0-2.2 eV, allowing for visible light absorption and enhanced photocatalytic activity [14]. Moreover, the combination of $Co_3O_4$ and $TiO_2$ can lead to the formation of heterojunctions that promote the separation of photogenerated electron-hole pairs, consequently improving the overall photocatalytic performance.

## 2. Methodology

In this study, Titanium foils were used as the substrate for growing the $TiO_2$ nanotubes by anodization. The materials used in the anodization process were ethanol, ethylene glycol, ammonium fluoride ($NH_4F$), and hydrogen peroxide ($H_2O_2$). As for the deposition of $Co_3O_4$ on the $TiO_2$ nanotubes, the materials used were cobalt nitrate hexahydrate ($Co\ (NO_3)_2.6H_2O$), and sodium hydroxide (NaOH).

Anodization was performed in a two-electrode configuration with the Ti foils as the working electrode (anode) and the graphite rod as the counter electrode (cathode). This configuration was connected to a DC power supply to supply a constant potential of 60 V for 30 minutes at room temperature. This study used constant voltage mode and the current change (current density) was monitored and recorded. This data is needed to study the formation mechanism of the $TiO_2$ nanotubes. Throughout the anodization, the electrolyte was stirred continuously to maintain a uniform current.

For the deposition of $Co_3O_4$ into the $TiO_2$ nanotubes, the as-anodized $TiO_2$ nanotubes were immersed first in the metal salt precursor solution of $Co(NO_3)_2$. Then, the samples were rinsed in deionized water to remove excess adsorbed ions. The samples were then immersed in the hydroxide precursor solution of NaOH. This is followed by rinsing again in deionized water to remove excess and unreacted ions as well as the reaction byproduct. The immersion process is done for a specific duration in each beaker. Such immersion cycle was repeated according to the parameter studied. After the chemical modification, these samples were heat-treated for 1 h at 400 ◦C with a heating rate of 10 ◦C/min and a cooling rate of 5 ◦C/min.

The photocatalytic activity of the samples was evaluated by the degradation of methyl orange (MO) solution. In this study, 30 ppm methyl orange was used and prepared by dissolving 0.03 g of solid methyl orange in 1000 ml of distilled water. All the samples were immersed horizontally in the beaker containing 30 ppm methyl orange solution. The samples were left in the dark for 30 minutes to establish adsorption equilibrium between the solutions and the samples. 100-watt light (CFL) was used as the light source for the photocatalytic reaction. The distance between the treated solution and the light source is fixed at 5 cm. The degradation of the methyl orange concentration was monitored by filtering out 3 ml methyl orange solution after 1, 2, 3, 4, and 5 hours of interval during irradiation of light. Subsequently, the UV-vis adsorption spectra of the filtered solution were measured using a UV-vis spectrophotometer PerkinElmer Lambda 35.

## 3. Results

The general morphology of $TiO_2$ nanotubes shown in Figure 1 is clearly seen by both cross section and the top surface of the nanotubes. The typical surface morphology of this structure consists of nanotubes of open tubular structure about 80 nm in diameter and the cross section with tubular tubes about a micron in length. The distinctive features exhibited by $TiO_2$ nanotubes are highly ordered structures as anodization typically results in vertically aligned, highly ordered arrays of $TiO_2$ nanotubes. The tubular structure provides a significantly higher surface area compared to flat $TiO_2$ films and post-anodization annealing can be used to control the crystalline phase (anatase, rutile, or mixture) of the $TiO_2$ nanotubes. These features have made them attractive for various applications.

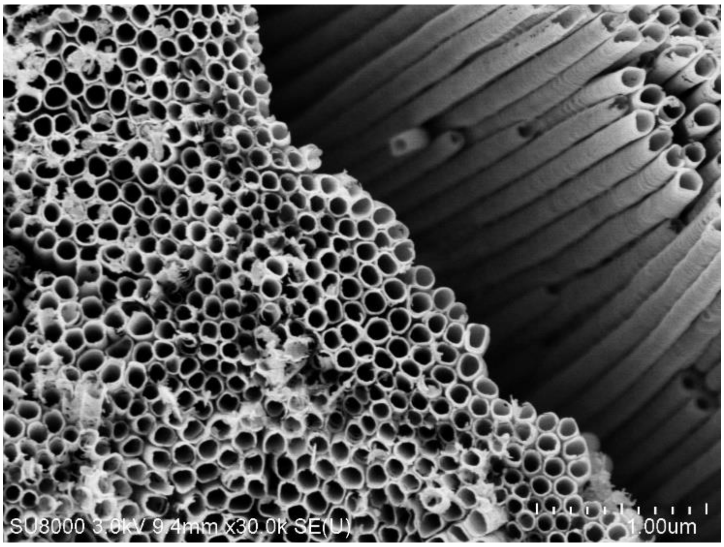
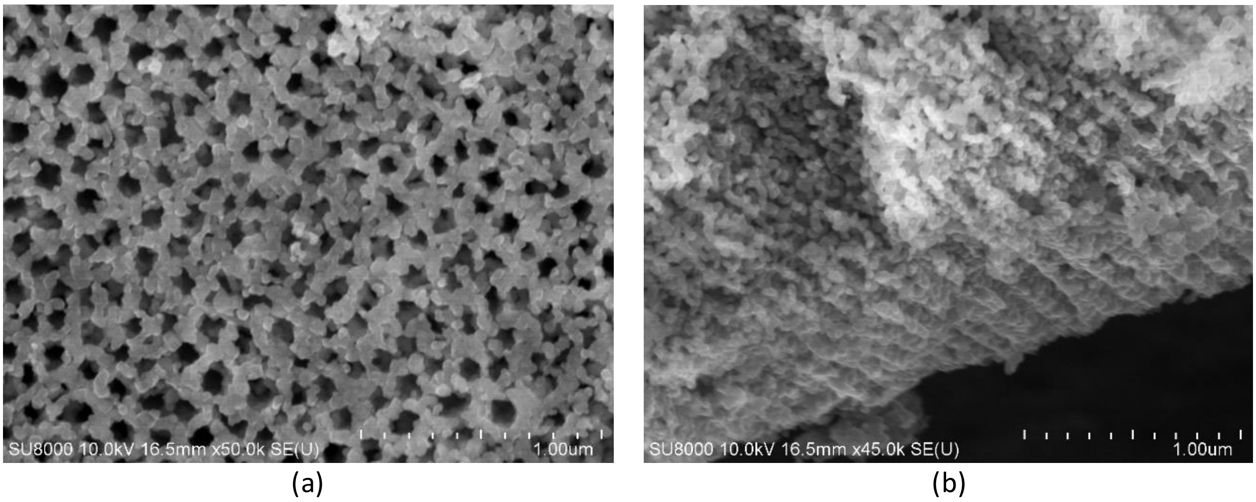


**Fig. 1.** FESEM images of the $TiO_2$ nanotubes produced by the anodization of Ti in ethylene glycol

To study the effect of $Co_3O_4$ loaded on $TiO_2$ nanotubes, $Co_3O_4$-$TiO_2$ nanocomposite were fabricated using the wet impregnation method. The aim is to improve the solar irradiation absorption and further minimize the recombination loss of photo-induced charge carriers. Figure 2 shows the morphology of the desired $Co_3O_4$-$TiO_2$ nanocomposite produced by the wet impregnation method. As in Figure 2(a), the top surface of $TiO_2$ nanotubes was fully covered by the deposition of $Co_3O_4$ nanoparticles. The cross section of the $Co_3O_4$-$TiO_2$ nanocomposite is shown in Figure 2(b). The homogenous distribution of $Co_3O_4$ on the top surface of $TiO_2$ indicates that the wet impregnation method does not disrupt the morphology of the $TiO_2$ nanotubes.



(a) (b)

**Fig. 2.** FESEM images showing the $Co_3O_4$-$TiO_2$ nanocomposite by using wet impregnation method (a) top view, (b) cross sectional view

Figure 3 shows the XRD pattern of crystalline pristine $TiO_2$ nanotube arrays and $Co_3O_4$-$TiO_2$ nanocomposite. It is clear from the pattern that both the produced $TiO_2$ nanotubes and nanocomposite showed characteristic diffraction peaks which were very well matched with the standard pattern of JCPDS (01-084-1286) of anatase $TiO_2$ crystals. No characteristic peaks of any impurities were detected, which demonstrates that the nanotubes had high phase purity, and the sharpness of the peaks indicates the high crystallinity of the $TiO_2$ nanotube arrays. There is no cobalt oxide detected due to the small crystallite size. If cobalt oxide particles are extremely small, their diffraction peaks may be too broad and weak to detect. Cobalt oxide peaks might overlap with stronger $TiO_2$ peaks, making them difficult to distinguish [15].

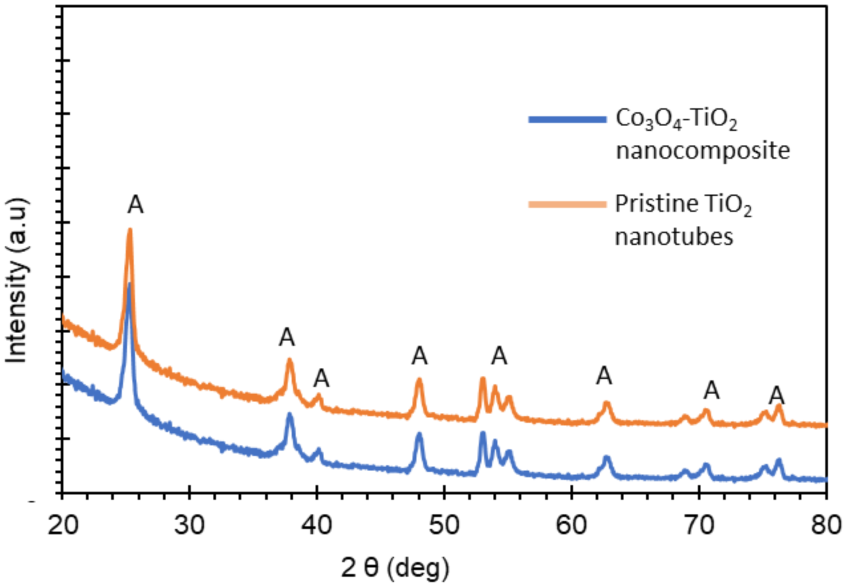


**Fig. 3.** XRD patterns of $TiO_2$ nanotubes and $Co_3O_4$-$TiO_2$ nanocomposite

The Raman spectra of the $TiO_2$ nanotubes and $Co_3O_4$-$TiO_2$ nanocomposite are shown in Figure 4. This analysis is done to confirm the presence of cobalt oxide in the samples. The Raman bands of all the $TiO_2$ nanotubes obviously appeared at 148.3, 201.2, 394.7, 513.5, and 632.9 $cm^{-1}$, which are assigned to the anatase phase of $TiO_2$. Raman bands of cobalt were difficult to detect because the typical Raman bands of cobalt are very similar and overlapped by strong, broad bands of the anatase phase. However, there are some unobvious small peaks that exist as shown in the $Co_3O_4$-$TiO_2$ nanocomposite plot. For the Raman bands of cobalt oxide, the peaks are located at 477, 675 and 682 $cm^{-1}$ [16]. In here only peak 697 $cm^{-1}$ were noticeable and those other peaks become unnoticeable when plotted in the wide range of Raman shift.

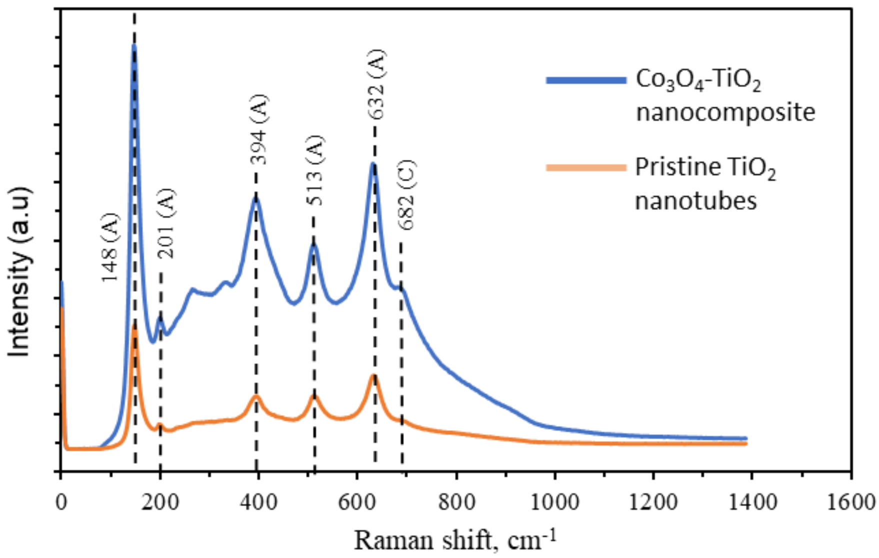


**Fig. 4.** Raman spectra of $TiO_2$ nanotubes and $Co_3O_4$-$TiO_2$ nanocomposite

The formation mechanism for the $Co_3O_4$-$TiO_2$ nanocomposite is illustrated in Figure 5. The wet impregnation method consists of contacting a solid with a liquid containing the components to be deposited on the surface. The diffusion of cobalt species takes place at different rates. This is influenced by selective adsorption of species (charged or not) by coulomb force, van der Waals forces or H-bonds as well as the ion exchange between the charged surface and the electrolyte [17]. The type of product depends on (i) the nature of both reactants (the liquid and the solid surface), and (ii) the reaction conditions. The main parameters affecting the liquid are the time, the nature of the solvent, and the nature and concentrations of the dissolved substances. According to Zhang *et al.,* [18], wet impregnation involves several key steps which are (1) Contacting the solid with the impregnating solution: for a specific period. (2) Drying the solid to remove the absorbed liquid. This drying step is crucial to ensure that the species are securely attached to the solid surface. Finally activating the catalyst by heat treatment induces chemical and physical changes, such as crystallization and phase transformations, which enhance the photocatalytic activity of the nanocomposites.

During this process, a certain volume of solution containing the precursor of the active phase $Co(NO_3)$ solution is contacted with the $TiO_2$ nanotubes (immersion). Then, the nanotubes are soaked in sodium hydroxide to make sure Co species are diffused and attached to the nanotubes. The process is repeated until the required thickness deposition of Co species is achieved. Later the nanotubes are dried and heat treated to ensure the cobalt oxide is strongly deposited and diffused into the $TiO_2$ nanotubes. Besides that, it is also to transform the amorphous $TiO_2$ into crystallite structures. This resulted in the formation of $Co_3O_4$ nanostructures on $TiO_2$ nanotubes. The chemical reactions involved are as follows

$$Co(NO_3)_2.6H_2O + 2NaOH \rightarrow Co(OH)_2 + 2NaNO_3 + 6H_2O \quad (1)$$

After heat treatment

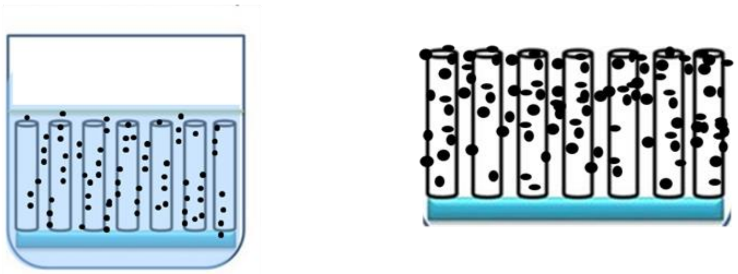
$$Co(OH)_2 \rightarrow CoO + H_2O \quad (2)$$

$$6CoO + O_2 \rightarrow 2Co_3O_4 \quad (3)$$

For this method, an excess of solution is used. After a certain time, the solid is separated, and the excess solvent is removed by drying. In the overall impregnation process, the following important facts should be noted: the equilibrium between liquid and solid is slow to establish and even the distribution of attached species inside the pores is not easy to attain. The deposition involves many different types of interaction. The deposition of the active element is never quantitative as the quantity deposited depends on the solid/liquid ratio. Despite the deposition is slow, requiring several hours and cycles, however, the method allows the distribution of the species to be very well controlled and high dispersions may be obtained. The wet impregnation method gains a great advantage when compared to other methods used in the preparation of nanocomposite materials, namely that it is easy to prepare a layer of active matter on the oxide surface. This could be attributed to a diffusion process, which is much slower. Besides that, it is inexpensive and allows the final property and configuration to be controllable in advance [19].

(A) Beaker with $Co(NO_3)$ solution

(B) $TiO_2$ nanotube structures



(C) $TiO_2$ nanotube immerse in $Co(NO_3)$ solution

(D) Co species deposited to the $TiO_2$ nanotube

**Fig. 5.** Mechanism of the $Co_3O_4$-$TiO_2$ nanocomposite formation by wet impregnation method

The optical properties of the pristine $TiO_2$ nanotubes by anodization and $Co_3O_4$-$TiO_2$ nanocomposite were studied using UV-vis diffuse reflectance spectroscopy. The data of the spectra was analyzed and the band gap energy was calculated using Eq. (4).

$$(\alpha hv)^{1/\gamma} = B(hv - E_g) \quad (4)$$

where *h* is the Planck constant, *v* is the photon's frequency, $E_g$ is the band gap energy, and *B* is a constant. The γ factor depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition band gaps, respectively [20]. The data of the spectra was plotted and analyzed as shown in Figure 6 and 7. Figure 6(a) shows the highest absorption band at 380 nm in which a similar absorption band of bulk anatase (~390 nm). The absorption of spectra decreases upon the visible light wavelength range. The visible light region shows a broad absorption band which might be due to the scattering effect caused by the pore or cracks in the nanotube arrays [21]. From Figure 6(b), the band gap was estimated by extrapolating the straight line to the X-axis intercept. It was found that the band gap energy for the $TiO_2$ nanotubes is 3.25 eV which is reflected in the optical absorbance results. From this finding, the band gap value is still large despite the modification made on the nanostructures.

Figure 7 shows the optical absorption spectra of the $Co_3O_4$-$TiO_2$ nanocomposite. The optical absorption of the $Co_3O_4$-$TiO_2$ presents enhancement in the visible light absorption range from 390 nm to 620 nm. This is indicated in Figure 7(a) where the increment of the absorption at about 20%. The introduction of cobalt species into the $TiO_2$ nanotubes might contribute to the extension of the absorption range to the visible light range. Figure 7(b) shows the straight line extrapolated from the plotted graph representing the band gap for the $Co_3O_4$-$TiO_2$ nanocomposite sample. The estimated band gap was found to be ~2.4 eV which is lower than the band gap of a pristine $TiO_2$ nanotube. Hence, the evaluated optical properties of the $Co_3O_4$-$TiO_2$ nanocomposite are in correspond to better visible light absorption compared to the pure $TiO_2$ nanotubes.

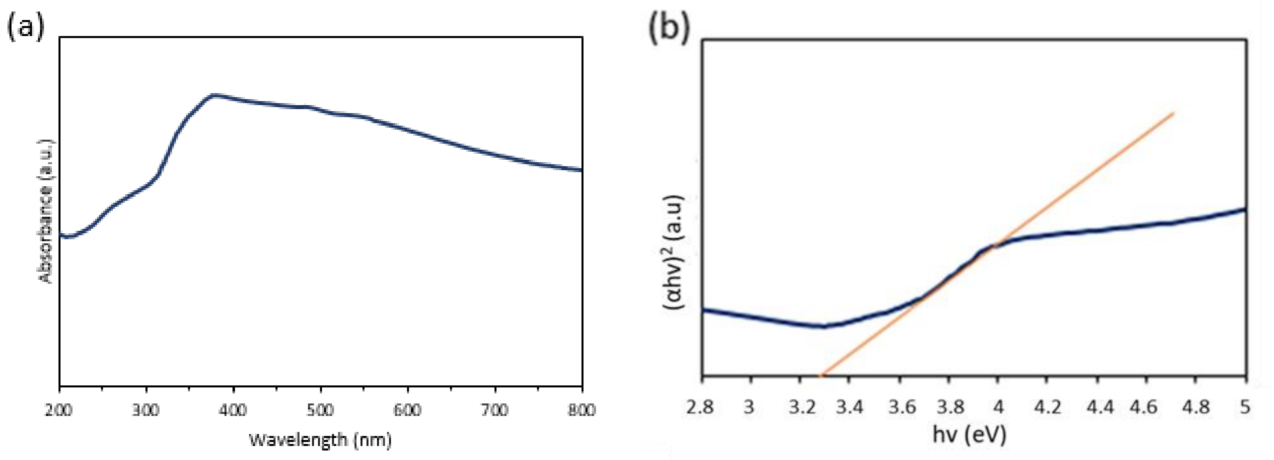


**Fig. 6.** band gap energy of pristine $TiO_2$ nanotubes (a) Optical absorbance spectra and (b) Estimated band gap energy

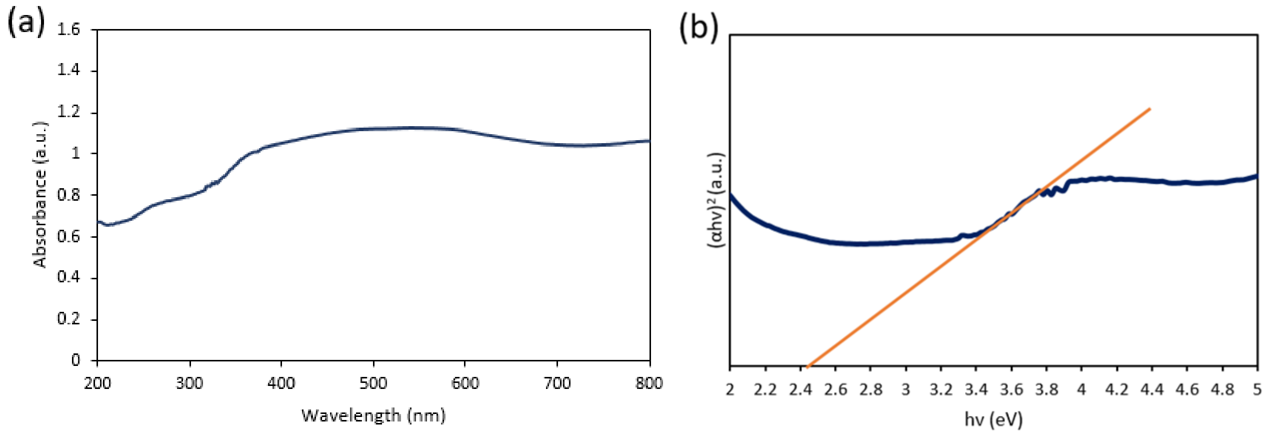


**Fig. 7.** Band gap energy of $Co_3O_4$-$TiO_2$ nanocomposite. (a) Optical absorbance spectra and (b) calculated band gap energy

Photocatalytic activities of the prepared $Co_3O_4$-$TiO_2$ nanocomposite samples were evaluated by degrading methyl orange (MO) solution under visible light (320 - 700 nm). The optimized sample produced in the previous section is used to endure the photocatalytic test for 5 hours. To study the photodegradation of MO dye solution, visual observation of the colour of MO dye changes should be recorded and proceed with the UV-vis spectroscopy analysis. There are obviously prominent colour changes in the MO dye degradation for the samples degraded after 1, 3 and 5 hours. The relative intensity of the absorption peak of MO dye solution at 464 nm is recorded for the anodized $TiO_2$ nanotubes and the $Co_3O_4$-$TiO_2$ nanocomposite sample as a function of visible light exposure time. Table 1 presents the data of the absorption peak value at 464 nm absorbance spectra. The data were then plotted into the graph as shown in Figure 8. The degradation of the MO dye solution was examined in order to understand the effect of cobalt addition on the photocatalytic activity of $TiO_2$ nanotubes.

**Table 1**
Highest peak of each sample for different time of UV light exposure

| Samples | Highest peak (at wavelength 464nm) | | | | |
|---|---|---|---|---|---|
| | Absorbance (a.u) | Absorbance (a.u) | Absorbance (a.u) | Absorbance (a.u) | Absorbance (a.u) |
| | 1 hour | 2 hours | 3 hours | 4 hours | 5 hours |
| $TiO_2$ nanotubes | 1.7313 | 1.6884 | 1.6724 | 1.6642 | 1.6487 |
| $Co_3O_4$-$TiO_2$ nanocomposite | 1.6617 | 1.5618 | 1.4998 | 1.483 | 1.4342 |

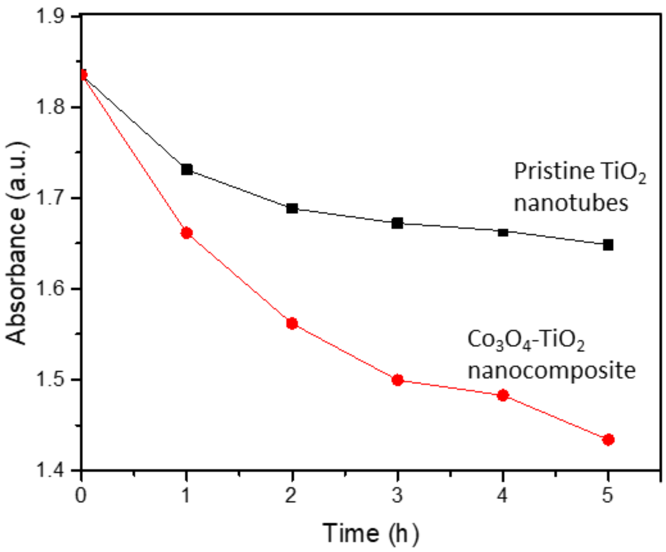


**Fig. 8.** Absorbance peak at 464 nm wavelength for $TiO_2$ nanotubes and $Co_3O_4$-$TiO_2$ nanocomposite samples against time

From Figure 8, there was a decrease in the absorbance peak over time for both $TiO_2$ and $Co_3O_4$-$TiO_2$ nanocomposite samples. The reduction of absorbance for the $Co_3O_4$-$TiO_2$ nanocomposite is much lower than the $TiO_2$ nanotubes. This can be correlated with the lower band gap of $Co_3O_4$-$TiO_2$ nanocomposite that makes this sample become better photocatalyst. Hence the decrease in absorption is due to the reduction of the dye solution concentration. Thus, it can be observed that the rate of degradation was greater for the $Co_3O_4$-$TiO_2$ nanocomposite sample. This indicates that the introduction of cobalt oxide on the $TiO_2$ nanotube structure improved the photocatalytic activity. The key factors contributing to the enhanced photocatalytic performance of the $Co_3O_4$-$TiO_2$ nanocomposite are due to factors such as the interaction between $Co_3O_4$ and $TiO_2$ nanotubes results in matched energy levels, facilitating efficient separation of photogenerated electron-hole pairs [22]. Besides, the introduction of $Co_3O_4$ enhances the light absorption ability of $TiO_2$ in the visible light range, leading to better utilization of light energy for photocatalysis. Finally, superior efficiency in separating and transferring photogenerated carriers are demonstrated, particularly electrons, to the solution for photocatalysis. These factors collectively contribute to the superior photocatalytic performance observed when using $Co_3O_4$-$TiO_2$ nanocomposite as a photocatalyst.

## 4. Conclusions

Anatase $TiO_2$ nanotubes were synthesized through the anodization of a Ti foil in a fluoride-organic based electrolyte solution. Subsequently, the $TiO_2$ nanotubes were modified with $Co_3O_4$ to create a $Co_3O_4$-$TiO_2$ nanocomposite. The photocatalytic property using these hybrid materials was evaluated through a degradation test under visible light. The reduction of absorbance for the $Co_3O_4$-$TiO_2$ nanocomposite is much lower than the $TiO_2$ nanotubes due to the lower band gap of the $Co_3O_4$-$TiO_2$ nanocomposite.

## Acknowledgement

This research was funded by a grant from the Ministry of Higher Education of Malaysia (FRGS /2/2014/TK04/FKP/F000241).

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