



Synthesis and Characterization of Ag@C-TiO₂ Nanocomposite for Degradation of Sasirangan Textile Wastewater

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Abstract

Carbon-titanium oxide nanocomposite (denoted as @C-TiO₂) was successfully synthesized via hydrothermal method at 150°C for 24 h. The C-TiO₂ nanocomposite was furtherly modified by adding an Ag metal dopant (denoted as Ag@C-TiO₂) to improve and applied to the photocatalytic degradation of Sasirangan textile wastewater. The composite photocatalysts were characterized by XRD and UV-Vis DRS spectroscopies. XRD patterns showed that TiO₂ in @C-TiO₂ mainly consisted of a brookite phase, as indicated by a series sharp diffraction peak at 2θ = 27.2° (111), 31.5° (121) and 55.9° (241). The calculated band gap energy (E_g) derived from UV-Vis DRS spectra for TiO₂, @C-TiO₂, and Ag@C-TiO₂ were 2.95 eV, 2.54 eV, and 2.74 eV, respectively. Ag@C-TiO₂ photocatalyst was found to be active for the photocatalytic degradation of Sasirangan textile wastewater, as indicated by the change of wastewater color from dark to clear. The quantitative photocatalytic activity of Ag@C-TiO₂ was evaluated in the degradation of methylene blue, whereas the conversion of methylene blue was 41.3%. The addition of Ag to @C-TiO₂ is believed to play an essential role in the enhancement of photocatalytic activity.

1. Introduction

Photodegradation is a common method for the treatment of textile dyes before it disposed into the environment using photocatalyst materials, where organic dyes are broken down into smaller compounds in the presence of light (photons), and the reactions are accelerated by using photocatalysts [1, 2]. One of the most widely used photocatalyst material is TiO₂ because it has high photoactivity in the UV region (gap energy of TiO₂ = 3.0 eV (rutile), 3.2 eV (anatase)) and had high chemical stability. TiO₂ performance can be significantly improved by adding additional material (dopant), both metal and non-metal, which will reduce the energy gap so that the response to UV rays or appears to be increased [3]. There are several studies have been reported on the addition of non-metal dopants such as nitrogen (N), sulfur (S), and carbon (C) to improve the sensitivity of TiO₂ towards visible-light resources [4, 5]. For example, carbon-

doped-TiO₂ (C-TiO₂) with the amount of carbon-doped around 5.2 %mol has the lowest bandgap energy 2.3–2.8 eV [4]. Several previous reports have also shown that C-TiO₂ catalysts were effective for the photodecomposition of acid orange 7 (AO7) with 99% conversion [6]. Teng *et al.* [7] also reported the conversion of Rhodamine B using a C-TiO₂ catalyst (with a bandgap energy of 2.91 eV) and 95% conversion Rhodamine B was achieved under visible-light irradiation.

Utilization of palm oil shell has a big challenge as a raw material in the synthesis of activated carbon since Indonesia is the biggest country in the production of crude palm oil (CPO) with around 38.2 million tons of CPO and 3.05 million tons of palm kernel oil (PKO). Every ton of CPO production, around 6.5% of palm kernel oil shells, will be generated. Several previous reports have shown that palm kernel oil shells can be transformed into active carbon using the carbonization method at a relatively

mild temperature [8, 9]. The performances of activated carbon can be improved both in economic value and used-value through combination with other active substances, such as semiconductor materials (TiO_2 , ZnO , Fe_2O_3) produce photocatalyst composite materials that can be used for dye degradation, clean water treatment, and anti-bacterial with the better performance [10]. In addition, active carbon derived-palm oil kernel shell that obtained via chemical activation of $\text{Na}_2\text{CO}_3/\text{ZnCl}_2$ mixture has high specific surface area BET (S_{BET}) $743.71 \text{ m}^2 \text{ g}^{-1}$ and demonstrated high adsorption capacity for the adsorption of hydrogen sulfides (H_2S) 247.33 ppm [11].

Sasirangan is a traditional cloth that originally comes from South Borneo, it is similar to Batik, but it has different making process. The Sasirangan industry in South Kalimantan is generally a home industry with traditional processing. Seeing the nature of these industrial activities, most of the craftsmen have not made efforts to treat the generated waste (e.g., wastewater after the coloring process) and directly dispose of it into water bodies. Therefore, it has an impact on the disruption of the life processes of aquatic organisms, and at the same time, can threaten the sustainability of aquatic ecosystems [11]. Moreover, the presence of textile waste in waters can interfere with sunlight penetration and oxygen diffusion into water bodies.

In this report, we describe the synthesis of silver-doped carbon-titanium oxide nanocomposites (denoted as $\text{Ag}@C\text{-TiO}_2$) using a straightforward hydrothermal method which are producing particles with high crystallinity, high purity, homogeneous particle size distribution, and also use low temperatures below $<300^\circ\text{C}$ for the reaction. The addition of Ag aims to increase the photocatalyst's response to both UV and visible light and to increase the stability of the photocatalyst, while activated carbon is added to increase the active surface area of the photocatalyst. $\text{Ag}@C\text{-TiO}_2$ nanocomposites that obtained will be compared in their characteristics and photocatalytic activity with pure TiO_2 and $@C\text{-TiO}_2$. The photocatalytic reaction will be carried out on the degradation of Sasirangan wastewater in a batch reactor system. As a comparison, photocatalytic reactions of commercial dye c.a. methylene blue (MB) under the same reaction conditions.

2. Methodology

2.1. Materials and Method

The materials used are Sasirangan wastewater, AgNO_3 (99%, Merck), TiCl_4 (99%, Merck), HCl (37%, Merck), ethylene glycol (EG) (99.5%, Merck Millipore), NaBH_4 (95.0%, Tokyo Chemical Industry (TCI)), methylene blue (70.0%, Tokyo Chemical Industry (TCI)), ethanol (96%, Merck) and distilled water. The source of radiation in this work is the HIMAWARI T5-8W UV lamp.

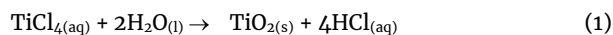
2.2. Synthesis of palm shell charcoal

The crushed palm shell charcoal is acidified first using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ overnight. Giving acid is one of the chemical activation methods of charcoal to enlarge the pores of activated charcoal. The acidified charcoal is then

filtered and reactivated by heating at 500°C for 3 hours to get activated charcoal.

2.3. Preparation of TiO_2 photocatalyst

TiO_2 photocatalyst was prepared using a 99% TiCl_4 solution as a precursor diluted to 2M TiCl_4 by mixing 100 mL of 99% TiCl_4 and 1 mL of 37% HCl in 350 mL of distilled water. This mixing produces a 2M TiCl_4 solution which is turbid white and white precipitate is formed, which is thought to be TiO_2 deposition:



2.4. Synthesis of $@C\text{-TiO}_2$ and $\text{Ag}@C\text{-TiO}_2$ nanocomposite

The $@C\text{-TiO}_2$ nanocomposite was prepared by mixing activated charcoal into a 2 M TiCl_4 solution using a 24-hour hydrothermal reduction method at 150°C . $\text{Ag}@C\text{-TiO}_2$ nanocomposites are made by mixing synthesized $@C\text{-TiO}_2$ powder and adding AgNO_3 . The method used is also the same as the synthesis of $@C\text{-TiO}_2$ nanocomposites.

2.5. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were filed on a Mac Science M18XHF instrument using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The XRD equipment operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed of 4° min^{-1} ($\alpha 1 = 0.1540 \text{ nm}$, $\alpha 2 = 0.1544 \text{ nm}$).

Analysis ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) was performed on a UV-Vis Shimadzu 2450 with a dual-beam system at Affiliation Laboratory of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), University of Indonesia Jakarta BaSO_4 powder was used as standard material. The calculation of bandgap energy (E_g) was derived from the obtained spectra using a formula of $E_g = h \cdot c / \lambda_c$, whereas h is Planck constant ($4,136.10^{-15} \text{ eV}\cdot\text{s}$), c is light velocity ($2,997.10^8 \text{ m}\cdot\text{s}^{-1}$), λ_c is cut-off wavelength (nm). λ_c was derived from plotted data of absorbance versus wavelength with linear cross-section on the spectra.

2.6. Photocatalytic degradation of Sasirangan wastewater and methylene blue

A typical procedure for the photodecomposition of methylene blue (MB) over the $\text{Ag}@C\text{-TiO}_2$ catalyst is described as follows. A solution of MB (5.0 ppm, 30 ml) and 0.15 g $\text{Ag}@C\text{-TiO}_2$ were mixed in the glass-tube reactor (50 ml) then immersed in water batch at 60°C under UV or visible irradiations (UV or visible lamp sources are $4 \times 8 \text{ W}$). The reaction mixture was stirred at 310 rpm for 30 min to reach the equilibrium point of adsorption-desorption. The reaction mixture was irradiated for 120 min at a reaction temperature of 60°C and sampled every 30 min and analyzed by using Perkin Elmer UV-Vis double beam spectroscopy.

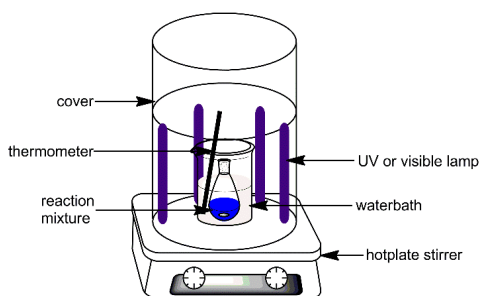


Figure 1. Schematic diagram of the reactor for the photodegradation of methylene blue Ag@C-TiO₂ nanocomposites [12].

3. Result and Discussion

The synthesized TiO₂, @C-TiO₂, and Ag@C-TiO₂ photocatalysts were characterized by using X-ray diffraction, UV-Vis Diffuse reflectance spectroscopy, and the physicochemical properties are summarized in Table 1.

3.1. X-ray diffraction (XRD)

Figure 2 shows the XRD patterns of the synthesized TiO₂, @C-TiO₂, and Ag@C-TiO₂ nanocomposites. XRD pattern for TiO₂ rutile compared to JCPDS card No. 21-1276, for TiO₂ brookite, compared to JCPDS card No. 29-1360, and for TiO₂ anatase compared with JCPDS card No. 21-1272. It can be observed that the brookite phase was predominantly formed in the TiO₂ sample. A serial diffraction peak at 2θ = 25.78°, 26.86°, 31.24°, 40.32°, 44.94°, 53.4°, 55.98°, 63.2°, 67.1°, and 68.7° which can be recognized as TiO₂ brookite (120), (111), (121), (022), (032), (320) dan (241), respectively (Figure 2a). Anatase phase was also observed at 2θ = 53.4°, which also can be assigned as TiO₂ anatase (105). A single diffraction peak at 2θ = 28.10° that characteristic peaks of TiO₂ rutile (110) (Figure 2a). In the case of C-TiO₂ nanocomposite, the main phase of formed-TiO₂ in @C-TiO₂ was brookite which can be easily recognized at 2θ = 31.24°, 45.61°, and 55.98° as TiO₂ brookite (121), (032), and (241), respectively (Figure 2b). Xie *et al.* [13] also reported that the use of glucose as a precursor of carbon inhibited TiO₂ brookite formation.

In the case of Ag@C-TiO₂ sample, series new diffraction peaks of TiO₂ anatase are clearly observed which can be easily recognized at 2θ = 24.48°, 36.94°, 46.81° and 53.48° as TiO₂ anatase (101), (103), (201) and (105), respectively. A small peak at 2θ = 9.70° was also observed in @C-TiO₂, which can be attributed to C(001) phase with tiny crystallite sizes. Moreover, a series diffraction peaks at 2θ = 37.82°, 64.20°, and 77.16° which can be assigned as Ag(111), Ag(220), and Ag(311), respectively. The crystallite sizes of Ag(111) metal in Ag@C-TiO₂ nanocomposite were 52.8 nm, and the crystallite sizes of the anatase TiO₂ (101) phase in Ag@C-TiO₂ was 11.8 nm.

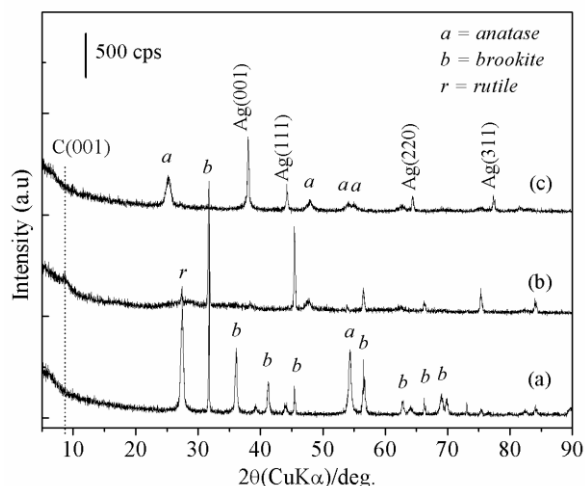


Figure 2. XRD patterns of the synthesized (a) TiO₂, (b) @C-TiO₂, and (c) Ag@C-TiO₂

Table 1. Physico-chemical properties of TiO₂, @C-TiO₂, and Ag@C-TiO₂ nanocomposites

Entry	Catalysts	Identified phases of TiO ₂ ^a	D ^b /nm	λ _c (nm)	E _g ^d (eV)
1	TiO ₂	Brookite, rutile	37.8	419	2.95
2	@C-TiO ₂	Brookite, rutile, anatase	35.3	483	2.54
3	Ag@C-TiO ₂	Anatase	5.0 ^e & 52.8 ^f	n.d.	2.74

^aIdentified main phases of TiO₂ compared with JCPDS card. Rutile (JCPDS card No. 21-1276), brookite (JCPDS card No. 29-1360), and anatase (JCPDS card No. 21-1272). ^bAverage crystallite sizes of TiO₂, calculated by using the Scherrer equation. ^cObserved cross-section of wavelength (nm), derived from UV-Vis DRS spectra data. ^dBand gap energy derived from UV-Vis DRS spectra data. ^eCrystallite sizes of anatase (TiO₂(101)) at 2θ = 25.3°. ^fCrystallite sizes of Ag(111) at 2θ = 38.1°.

3.2. UV-Vis DRS Analysis

Figure 3 displays the UV-Vis DRS spectra of each synthesized catalysts. The bandgap energy (E_g) was estimated from the plotting of absorbance (A) versus wavelength (nm) using Tauc equation $\alpha \cdot h \cdot c / \lambda c = B_d (h \cdot c / \lambda c - E_g)^n$ for allowed transitions (n = 2 for indirect transition, n = 1/2 for direct transition), h is Planck's constant, c is light velocity, and B_d is the absorption constant [14, 15]. The reflectance spectrum profile shows that TiO₂, @C-TiO₂, and Ag@C-TiO₂ have absorption regions in visible light areas (λ > 400nm), indicating the doping process that has been carried out was successfully achieved. The values of λ_c for each TiO₂, @C-TiO₂, and Ag@C-TiO₂ are 420 nm, 487 nm, and 451 nm. The bandgap energy of Ag@C-TiO₂ (2.74 eV) produced is relatively small compared to the pure TiO₂ (2.95 eV). These results are a good agreement with the previous report of Wang and Lewis [16], who reported the synthesis of @C-TiO₂ photocatalysts, which have E_g of 2.3 to 2.8 eV. Hence, it can be confirmed that the addition of C material and co-catalyst in the form of Ag can shift the gap energy of the TiO₂ band to the visible light region. These results indicate that the addition of dopant Ag significantly shifted the absorption band of TiO₂ to the visible region, as indicated by the E_g.

3.3. Photocatalytic degradation

The Ag@C-TiO₂ nanocomposite photocatalytic activity test was carried out through the photocatalytic reaction of waste Sasirangan. The reaction is accomplished in a reactor that has been designed and carried out under UV light and visible light for 120 minutes with stirring at 60°C. Stirring is done so that both UV and visible light can hit all parts of the photocatalyst evenly. Photocatalyst samples were weighed at 0.15 g, then added to 30 mL of Sasirangan waste. Before irradiation is done (dark), the photocatalyst mixture and the Sasirangan waste are stirred for 30 minutes so that the

molecules of the substances in the waste can be absorbed on the surface of the catalyst. Then the test is carried out for 120 min. The results of the reaction are then compared with Sasirangan waste before being reacted. Methylene blue was also tested by catalytic activity to see the comparison of the degradation results. The photo images of the de-coloration of Sasirangan and methylene blue waste before and after photocatalytic degradation are shown in Figure 4. The color produced after the reaction is quite bright. This indicates that the concentration in the solution decreases. After irradiation, the solution is centrifuged to separate the solution with a photocatalyst and analyzed using a UV-VIS spectrophotometer.

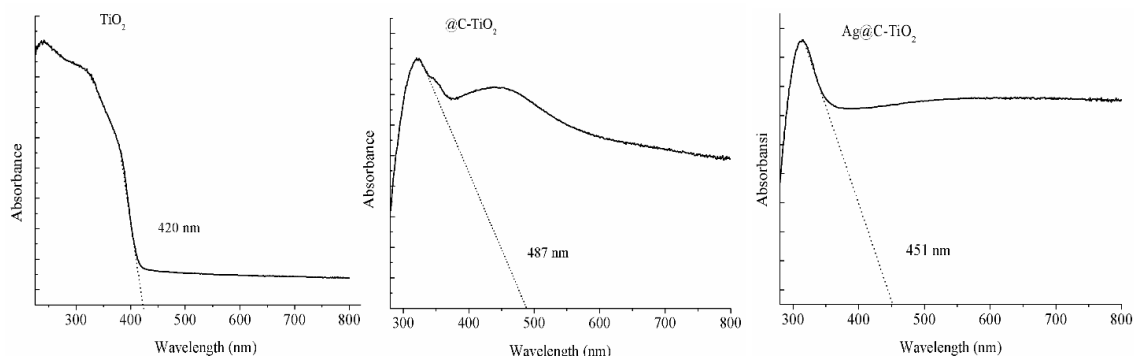


Figure 3. UV-Vis DRS spectra for TiO₂, @C-TiO₂, and Ag@C-TiO₂.

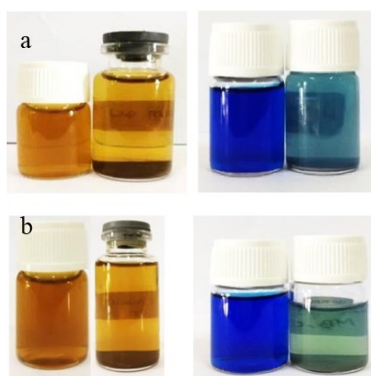


Figure 4. Photo images of photocatalytic reactions of Sasirangan wastewater and methylene blue (MB) using Ag@C-TiO₂ under irradiation of (a) UV light and (b) Visible light.

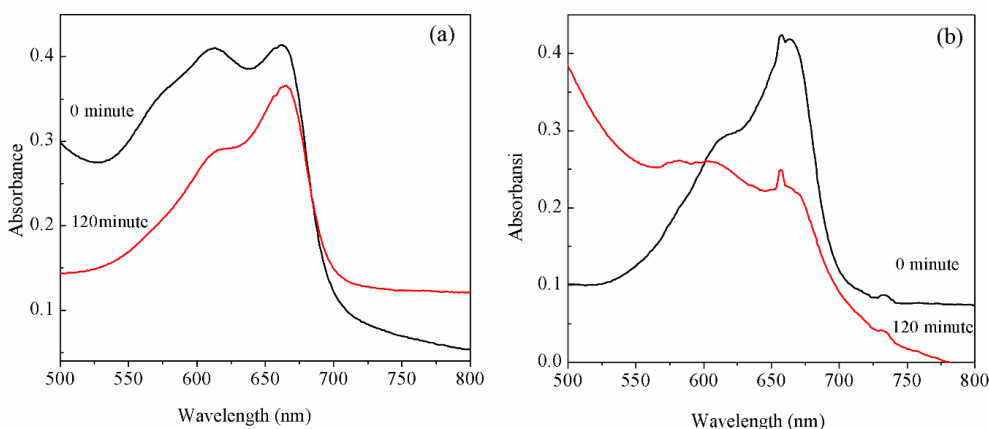


Figure 5. UV-Vis spectra of methylene blue under (a) UV light and (b) visible light after 0 minutes and 120 minutes.

Based on UV-Vis analysis data, spectra results (Figure 5) show a decrease in absorbance, which indicates that there is a change in the concentration of the MB

solution when reacted with Ag@C-TiO₂ photocatalysts and the results are summarized in Table 1.

Table 2. Results of Photodegradation of MB over Ag@C-TiO₂ nanocomposite

Radiation	Initial concentration (ppm)	Final concentration (ppm)	Conversion (%)
Uv light	3.30	2.92	11.11
Visible light	3.40	1.98	41.28

The results of the qualitative analysis showed that the addition of Ag dopants to the @C-TiO₂ nanocomposite could degrade Sasirangan waste and methylene blue waste. While the results of quantitative analysis can only be done on a blue methylene solution and cannot be done on Sasirangan waste, as there are many Sasirangan wastes dyes and organic substances, so it is less supportive in quantitative analysis using UV-Vis. Photocatalytic reactions also produce better degradation when done under visible light. This can be seen from the more transparent color changes in the blue methylene solution. This result is also due to the bandgap energy decreasing, where Ag@C-TiO₂ has a smaller E_g value compared to TiO₂. This can be seen from the results of UV-DRS characterization.

4. Conclusion

Based on the results of research and data processing, it can be concluded that the Ag@C-TiO₂ nanocomposite has been successfully synthesized using the hydrothermal method at 150°C for 24 hours. The XRD pattern of the TiO₂ and @C-TiO₂ nanocomposite shows that the TiO₂ that appears is dominated by the brookite phase (121) while in Ag@C-TiO₂, the primary identified TiO₂ phases were anatase. The bandgap energy values of TiO₂, @C-TiO₂, and Ag@C-TiO₂ are 2.95 eV, 2.54 eV, and 2.74 eV, respectively. Ag@C-TiO₂ nanocomposite is active in degrading Sasirangan and methylene blue waste under visible light with a conversion of 41.28%.

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