



## Green synthesis of Ag/TiO<sub>2</sub> Nanocomposite Assisted by Gambier Leaf (*Uncaria gambir* Roxb) Extract

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### Abstract

Studies of green synthesis of nanoparticles mediated by plants extract is extensively explored and studied in recent time due to eco-friendliness, cost-effectiveness, and use a minimum amount of toxic chemicals in the process of inorganic material synthesis. In this study, the immobilization of silver nanoparticles on the surface of titanium dioxide (TiO<sub>2</sub>) was carried out using *Uncaria gambir* Roxb. leaf extract as a silver ion (Ag<sup>+</sup>) reducing agent. The synthesized Ag/TiO<sub>2</sub> nanocomposite was characterized by UV-Vis spectroscopy, X-ray diffraction (XRD), and Diffuse Reflectance Spectroscopy (DRS). The formation of silver nanoparticles was confirmed through UV-Vis spectroscopic analysis, which showed a silver surface plasmon resonance (SPR) band at 426 nm. The X-ray diffraction pattern shows that Ag can inhibit the transition of the anatase into rutile phase. The presence of Ag particles in TiO<sub>2</sub> can increase the absorption ability from an initial wavelength of 407 nm to 438 nm. Based on the results of Rhodamin B degradation, it can be seen that Ag/TiO<sub>2</sub> has a higher photocatalytic activity than bare TiO<sub>2</sub> with 99% percent degradation at 120 minutes of irradiation time.

## 1. Introduction

The use of plant extracts as a substitute for chemical reduction agent in nanoparticle synthesis using chemical reduction methods has received plenty of attention recently. It is because the use of bioreductors is able to overcome one of the problems found in conventional chemical reduction methods, namely the use of toxic and environmentally unfriendly chemical reducing agents. On the other hand, chemical reduction methods are widely used in the synthesis of nanoparticles on a large scale because of their simplicity and relatively low costs [1].

Gambier plant (*Uncaria gambir*.Roxb) is one of the distinctive plants of West Sumatra considered as one of the superior regional commodities used as a herbal plant because of its phytochemical content. The phytochemical content in this plant has the potential to be a reducing agent in the synthesis of metal nanoparticles and metal oxides. Some metal nanoparticles, such as Ag and Au, have successfully been synthesized by metal reduction method using gambier leaf extract bioreductor [2]. Some plants have been reported to reduce Ag ions to form Ag

nanoparticles such as *Butea monosperma*, *Melissa officinalis* leaf extract, *Padina tetrachromatic* seaweed extract, and many other plants [3, 4, 5].

The titania compound (TiO<sub>2</sub>) has been one of the most widely investigated and used materials for the last many decades due to its chemical and thermal stability, non-toxic, corrosion-resistant, environmental friendly, and relatively low in price. Because these advantages make this semiconductor appealing to be applied in various fields, such as hazardous waste remediation, medical, cosmetics, energy, industry, and other fields [6]. However, the applicability of TiO<sub>2</sub> have been limited because of two inherent properties: on the one hand, with a large bandgap that only absorb in the UV (ultraviolet) region and the fast recombination of electron-hole pairs [7]. Thus, in recent years, a variety of strategies have been employed to improve the photocatalytic performance of TiO<sub>2</sub>, such as doping with metal or nonmetal elements [8, 9], coupling with semiconductors with smaller bandgaps [10], and surface modification with noble metals [11]. he use of noble metal nanoparticles in modifying the surface of TiO<sub>2</sub> is interesting to study and develop because the

presence of noble metals in TiO<sub>2</sub> has been widely reported to increase the photocatalytic activity of TiO<sub>2</sub>. Noble metal nanoparticles have a surface plasmon resonance (SPR) effect, the absorption of the photocatalyst was largely increased to visible light region, this is a benefit to the enhancement of the photocatalytic effect and the utilization of the solar light [12]. Additionally, when noble metal contacted with n-semiconductor TiO<sub>2</sub>, it might form a Schottky barrier and the noble metal act as a trap of photogenerated electrons, electron can transfer from TiO<sub>2</sub> to noble metal, which is favorable to the separation of electron-hole pair and subsequently effectively inhibited the recombination of photoinduced electrons and holes. Compared to noble metals such as Pt, Au, and Pd, Ag is more interesting to study because of its relatively low price and higher abundance than other noble metals mentioned [13].

Ag/TiO<sub>2</sub> nanocomposite can be synthesized by several methods such as hydrothermal, microemulsion, ultrasonication, sol-gel photo-deposition, and sol gel-reduction methods [14]. In this study, a combination of the sol gel-reduction method assisted by gambier leaf extract as a silver ion reduction agent and distilled water as a solvent in the synthesis of TiO<sub>2</sub>. The main secondary metabolites contained in the gambier leaf is catechin and catechu tannin compounds; they are flavonoid group, which are expected to reduce Ag<sup>+</sup> to form Ag<sup>0</sup> [15]. The use of gambier leaf extract has never been reported in Ag/TiO<sub>2</sub> synthesis, and utilization distilled water in TiO<sub>2</sub> synthesis using Titanium (IV) isopropoxide as a precursor is not many reported before. Therefore, through this research, we expect that this study can be one of the alternative methods to Ag/TiO<sub>2</sub> synthesis that is environmentally friendly.

## 2. Research Methodology

The synthesis of Ag/TiO<sub>2</sub> nanocomposite in this study uses a combination of chemical reduction and sol-gel methods.

### 2.1. Equipment and Materials

**Equipment** used in this study were glassware, magnetic stirrers, ovens, furnaces, centrifuges, UV-Vis Thermo Scientific Evolution Spectrophotometer 201, X-ray diffraction (XRD) Shimadzu XRD-7000S, and diffuse reflectance spectrophotometer (DRS) JASCO V-570.

**Materials** Fresh gambier leaves (*Uncaria gambier* Roxb.) collected from Andalas University, AgNO<sub>3</sub> (Merck), Titanium tetra isopropoxide (TTIP) (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>) (Sigma-Aldrich ≥97%), triethanolamine (TEA) (Merck), Rhodamine B (Sigma-Aldrich), and distilled water.

### 2.2. Synthesis of halogen-free TiO<sub>2</sub> nanoparticles

A measured quantity of TTIP was added to TEA with a molar ratio of Ti: TEA is 1: 1. The mixture solution stirred for 2 hours under constant rate. The obtained yellowish solution was added with distilled water to achieve a concentration of titanate is 0.5 M. The solution was continued stirred for 24 hours until the sol titanate solution was formed, which is indicated by the appearance of Tyndall effect of the titanate sol [16]. As a

control of Ag/TiO<sub>2</sub> nanocomposite, bare TiO<sub>2</sub> was synthesized by calcining the titanate sol at 500°C for 2 hours.

### 2.3. Synthesis of Ag nanoparticles

The prepared of gambier leaf extract (4%, 2 mL) and 2 mL 0.5 M TEA solution were added to 45 mL distilled water and stirred at 400 rpm under room temperature. 1 mL of 0.1 M AgNO<sub>3</sub> solution was added to the mixture with a volume ratio of 0.1 M AgNO<sub>3</sub>: 0.5 M TEA: 4% gambier leaf extract is 2: 2: 1. The mixture was stirred to continue for 4 hours, and the changes in color will appear. The stability of formed silver nanoparticles was periodically monitored by measuring the wavelength and absorbance using a UV-Vis spectrophotometer in the range of 200–700 nm [17].

### 2.4. Synthesis of Ag/TiO<sub>2</sub> nanocomposites

A measured quantity of 0.5 M titanate sol solution was added to the Ag sol solution with a molar ratio of Ag: TiO<sub>2</sub> is 2: 100. The mixture was stirred under constant rate and room temperature for 24 hours. The sol mixture was dried at 110°C until a dry gel was obtained. The dry gel was calcined using a furnace at 500°C for two hours. The Ag/TiO<sub>2</sub> powder obtained was washed with distilled water using the decantation method. The precipitate was dried at 110°C for 4 hours to obtain dry Ag/TiO<sub>2</sub> powder.

### 2.5. Photocatalytic Activity Test in Rhodamine B Degradation

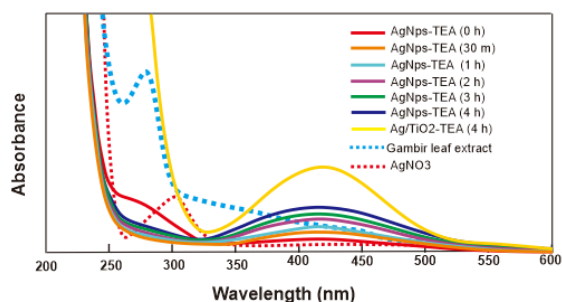
Degradation of Rhodamine B was carried out under solar light irradiation. 20 mL of 20 ppm Rhodamine B solution was added with 10 mg Ag/TiO<sub>2</sub> nanocomposite in 100 mL Pyrex beaker glass. The suspension kept on stirring during irradiation. Photodegradation was carried out in 0–2 hours with time intervals of 15, 30, 45, 60, and 120 minutes. After solar irradiation, the photocatalyst was centrifuge at 4600 rpm for 10 minutes to separate photocatalyst and degraded solution. Percent degradation of Rhodamine B was monitored by UV-Vis spectrophotometer (wavelength of 554 nm) of the samples at regular intervals.

## 3. Results and Discussions

### 3.1. UV-Vis Spectrophotometer Analysis

Ag nanoparticles have been synthesized using the reduction methods mediated by gambier leaf extract as a reducing agent and TEA as a capping agent. The synthesis of Ag using gambier leaf extract as a reducing agent has been previously reported by Labanni *et al.* [17] using diethanolamine (DEA) as a capping agent and obtained the optimum of molar ratio of AgNO<sub>3</sub>: DEA is 1:10. This molar ratio was also used in this study, with an Ag formation reaction time of 4 hours. The addition of AgNO<sub>3</sub> solution to a mixture of distilled water, TEA, and gambier extract changes the color of the solution from light yellow to grayish brown, which indicates the reduction of Ag<sup>+</sup> to Ag<sup>0</sup> attributed to surface plasmon resonance (SPR) phenomenon. In addition to observing the color changes that occur, the process of synthesis of Ag sol was also observed using a UV-Vis spectrophotometer to determine the formation of a typical absorption peak (SPR) of Ag at

$\lambda$  400–450 nm [18]. The intensity of spectra SPR increased gradually with the increase of time reaction, which shows a continues formation of silver nanoparticles during the reaction.

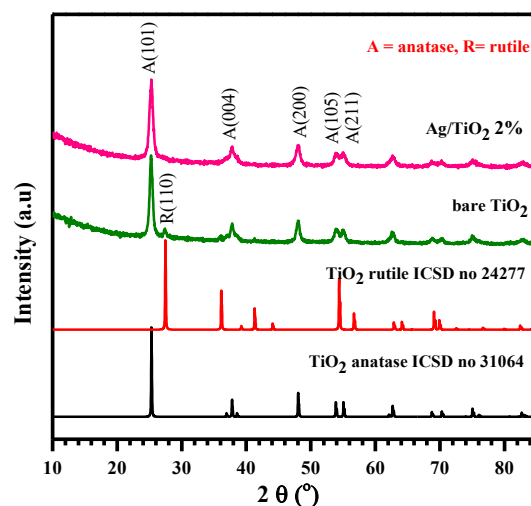


**Figure 1.** UV-Vis absorption spectrum of Ag/TiO<sub>2</sub> sol, Ag nanoparticles, gambier extract, and AgNO<sub>3</sub> solution

Based on the results of measurements of several samples in Figure 1, the spectra of Ag-TEA synthesized at 0 h has the same absorption peak with the absorption peak of gambier leaf extract in the region of 278 nm identical to catechin compounds [19]. The peak absorption of the AgNO<sub>3</sub> solution appears in the 301 nm region. Spectrum of Ag<sup>0</sup> shown in the 426 nm region, which indicated as typical absorption peaks of the spherical Ag nanoparticles. The absorbance value of the Ag absorption peak increases with longer reaction time, which revealed the increasing formation of silver nanoparticles. Some similar results are previously reported that colloidal spherical silver nanoparticles absorb light in approximately 400–450 nm. The peak of silver nanoparticles absorption at 418 nm has been reported using synthesis for 4 hours using *Gmelina Arborea* fruit extract within 4 hours synthesis reaction. In the UV-Vis spectroscopy study, noble metal nanoparticles provide an absorption band based on the SPR phenomenon, which is strongly influenced by the size and shape of nanoparticles. In this study, there is no peak absorption shifting silver nanoparticles spectrum to smaller or larger wavelengths [20].

### 3.2. XRD Analysis

Figure 2 exhibit the results of the analysis of XRD measurements that have been carried out on the TiO<sub>2</sub> compound and Ag/TiO<sub>2</sub> nanocomposite. The standard used as a comparison was ICSSD numbers 24277 and 31064 for rutile TiO<sub>2</sub> and anatase TiO<sub>2</sub>, respectively.



**Figure 2.** Diffractogram of TiO<sub>2</sub> and Ag/TiO<sub>2</sub>

Diffraction peaks for anatase TiO<sub>2</sub> crystals appear in Ag/TiO<sub>2</sub> and bare TiO<sub>2</sub> at  $2\theta$  25.1° (101), 37.9° (004), 48.0° (200), 54.0° (102), 55.2° (211), 62.7° (204) for each of its crystal planes. On the diffractogram for bare TiO<sub>2</sub>, the peak, which indicated the formation of the rutile phase shown at  $2\theta$  27.2° with a low intensity indicating the crystal plane 110. The diffractogram revealed that the presence of Ag in TiO<sub>2</sub> could inhibit the phase transition from anatase to rutile. Quantification of phase proportions can be determined through XRD measurements. Using the Spurr equation, the percentage of rutile and anatase in its heterojunction structure can be determined [21]. The percentage of anatase and rutile in its heterojunction structure obtained from bare TiO<sub>2</sub> is 77:23. Based on the Scherrer equation, the crystal size of TiO<sub>2</sub> decreased from 16 nm to 14 nm, which indicates that the presence of Ag can inhibit the growth of TiO<sub>2</sub> crystals. Because of the amount of Ag added to TiO<sub>2</sub> was only 2%, the peak of Ag in the nanocomposite Ag/TiO<sub>2</sub> does not appear on diffractograms due to the limitation of the XRD instrument in detecting the presence of elements or compounds in small amounts [22].

### 3.3. Optical Properties Analysis using DRS

The diffuse reflectance spectra of bare TiO<sub>2</sub> and Ag/TiO<sub>2</sub> composites are demonstrated in Figure 3. While the bare TiO<sub>2</sub> strongly absorbs light in 407 nm, outstanding an absorption in the visible region and a redshift of the absorption edge can be observed for Ag/TiO<sub>2</sub> composites (438 nm).

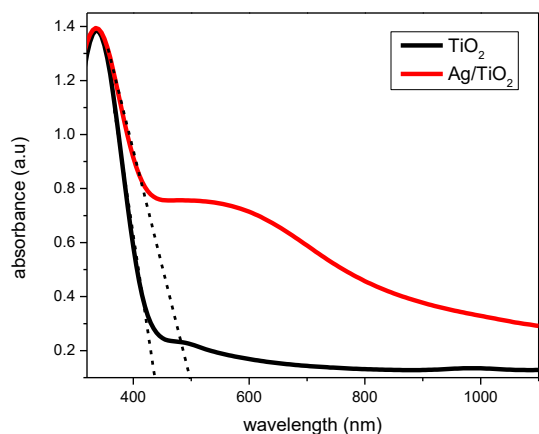


Figure 3. Absorption spectra of TiO<sub>2</sub> and Ag/TiO<sub>2</sub> powders

A broadened absorption of Ag/TiO<sub>2</sub> composites should be attributed to the SPR effect of silver nanoparticles. Furthermore, another peak is shown in 600 nm, which also indicated by the SPR phenomenon of silver nanoparticles. By shifting the absorption ability to a greater wavelength, it is expected to increase the light-harvesting and using capacities and then promote the enhanced photocatalytic activity of Ag/TiO<sub>2</sub> under visible light. [23].

### 3.4. Rhodamine B Photodegradation

Photocatalytic activity was evaluated by monitoring its characteristic absorption band at 554 nm to measure the percentage of degradation of Rhodamine B dye under solar light irradiation. Figure 5 showed the photocatalytic activity of bare TiO<sub>2</sub> and Ag/TiO<sub>2</sub> composites after the irradiation of solar light at room temperature. Ag/TiO<sub>2</sub> composites exhibited a faster degradation rate than bare TiO<sub>2</sub>. At 30 minutes of radiation using Ag/TiO<sub>2</sub>, the Rhodamine B solution was degraded with 85% degradation value, while for TiO<sub>2</sub> in the same of irradiation time, the percent degradation obtained is only 55%. This indicates that the presence of silver nanoparticles on the surface of TiO<sub>2</sub> can enhance the photocatalytic performance of TiO<sub>2</sub>.

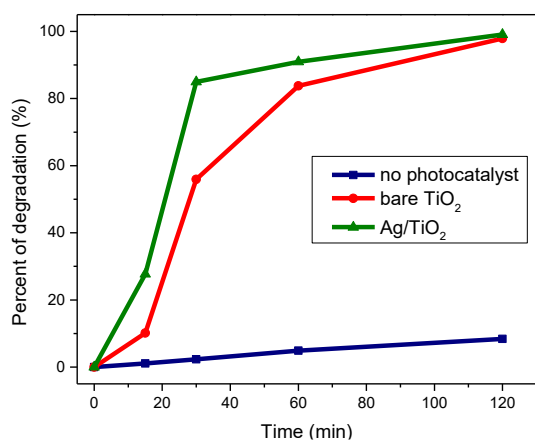
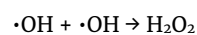
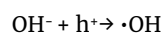
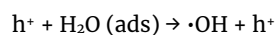
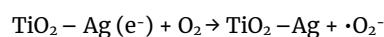
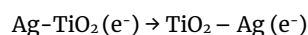
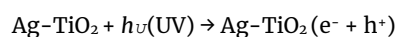


Figure 5. Photodegradation results of Rhodamine B under solar light irradiation

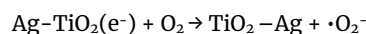
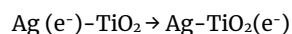
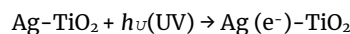
Silver nanoparticles on the surface of TiO<sub>2</sub> can act as an electron trapping agent, while the SPR effect can increase the photocatalytic activity of Ag/TiO<sub>2</sub> both under

UV and visible lights due to broadening of light absorptivity of TiO<sub>2</sub>.

Generally, under UV irradiation, a photocatalyst will react with photons (photogeneration reaction) to create pairs of electrons and holes that have different charges. This reaction carries out if the photon energy that irradiated to the photocatalyst is greater or equal to the bandgap energy of photocatalyst. The presence of silver nanoparticles on TiO<sub>2</sub> surfaces will form a Schottky barrier in the interphase of the surface of Ag and TiO<sub>2</sub> [24]. In the photogeneration process, electrons that are excited in the conduction band can be transferred to silver nanoparticles that are attached to TiO<sub>2</sub> surfaces. These electrons will be temporarily localized around silver nanoparticles before returning to the valence band (recombination process). It is able to retain the charge separation of electron-hole pairs that will increase the probability of a reaction of charge carrier with organic species adsorbed on the surface of TiO<sub>2</sub>, which will increase the photocatalytic activity of Ag/TiO<sub>2</sub>. Under visible light, electrons in the conduction band will not be transferred to the silver nanoparticles. In contrast, electrons which are excited on the silver nanoparticles due to the SPR effect will be transferred to the conduction band of TiO<sub>2</sub>. The mechanism of the reaction of Ag/TiO<sub>2</sub> activity under UV light can be seen below [12]:



Meanwhile, the mechanism of Ag/TiO<sub>2</sub> reaction activity under the visible light can be seen below:



These electrons can react with species adsorbed on the surface of TiO<sub>2</sub> to form reactive species [25]. The reactive species formed will degrade Rhodamine B dye into non-toxic compounds.

## 4. Conclusion

Based on the results obtained, it can be concluded that gambir leaf extract can reduce Ag ions into Ag<sup>0</sup> in Ag/TiO<sub>2</sub> nanocomposite synthesis. Silver nanoparticles on TiO<sub>2</sub> surfaces can inhibit the transition of the anatase into the rutile phase and increase the absorption ability at higher wavelengths. The photocatalytic activity of TiO<sub>2</sub> increases with the presence of Ag in the degradation of Rhodamine B from 55% to 85% under solar light for 30 minutes irradiation.

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