The innovation of antimicrobial and self-cleaning using Ag/TiO$_2$ nanocomposite coated on cotton fabric for footwear application

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Abstract. The Innovation of antimicrobial and self-cleaning material using Ag/TiO$_2$ in a cotton fabric is undertaken to develop capabilities of footwear application. The nanocomposite of Ag/TiO$_2$ was made by using Photo-Assisted Deposition (PAD) method. Ag/TiO$_2$ treated cotton fabrics were impregnated by modified dip coating process with the addition of Tetraethyl Orthosilicate (TEOS) as precursors of SiO$_2$. The addition of TEOS precursors is used to improve TiO$_2$ multifunctional performance in hydrophilic and self-cleaning ability. The synthesized sample of Ag/TiO$_2$ characterized by UV-Visible diffusion reflectance spectrum (UV-Vis DRS) to investigate the gap energy value, X-Ray Diffractometer (XRD) to investigate phase of a crystalline material and crystal size, and Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX) to investigate the morphology and recognize the type of atom on the surface of a material. The effects of Ag/TiO$_2$ coated cotton fabrics for footwear application on microbial disinfection have been assessed by Total Plate Count (TPC) method, using Escherichia Coli and Candida albicans as a model microorganism of skin bacteria and fungi, respectively. It was found that the optimum loading of Ag at 3wt% is evidenced by the effectiveness in disinfecting Escherichia Coli and Candida albicans up to 100%, the ability to self-cleaning and the ability in hydrophilicity will be described further in this paper.

1. Introduction

In the footwear industry, foot odours generated, in particular, in shoes are a big issue that remains unsolved because of the difficulties to destroy odours and bacteria at the same time. High humidity and sanitary conditions that are not hygienic, causing footwear to be an environment suitable for the growth of bacteria and fungi [1]. The unpleasant odour in the foot area is an important issue where it shows that the foot skin is infected with microorganisms. Rodriguez et al. [1] studied antibacterial effects of TiO$_2$ coated polyester fabric for footwear application. In addition, they found that antibacterial activity has been observed under UV-A irradiation. Titanium dioxide (TiO$_2$) is the most commonly used semiconductor photocatalyst, because of its physical and chemical stability, high catalytic activity, high oxidative power, low cost and ease of production. TiO$_2$ photocatalysts have been found to disinfection bacteria, viruses, and fungi under UV illumination [1]. TiO$_2$ has an energy and gap (Eg~3.2 eV) for a crystal anatase and (Eg~3 eV) for rutile so it is only responsive to light which has ($\lambda$ <400 nm) [2-4]. However, the high rate of photo generated electron-hole recombination in TiO$_2$ particles results in a low efficiency of photocatalysis [5-9].

In order to improve photocatalytic activity, it require transition metal doping. Metal doping has long been known to be one of the most effective ways reduce band gap of TiO$_2$ and to improve its visible
light sensitivity [10-16] as well as increase its photocatalytic activity under UV irradiation and then silver particles enable to activate visible light excitation of TiO$_2$ [16]. As we know Ag$^+$ can bind proteins by combining the –SH groups of enzymes, leading to protein inactivation to bacterial cell wall membrane damage it and so alter its functionality [17-19].

Nowadays, Ag/TiO$_2$ is the most commonly used photocatalyst as an antibacterial agent because Ag nanoparticles under UV radiation enhances photocatalytic activity of TiO$_2$ by lowering recombination rate of its photoexcited charge carriers so that the degradation of organic compounds is more optimal because of the hydroxyl radicals formed from more holes [20, 21].

In the present study, Ag/TiO$_2$ nanoparticles were prepared through photo-assisted deposition synthesis. Nanosized Ag can be highly deposited on TiO$_2$ under 6 hours UV-light irradiation. Synthesis Ag sources from AgNO$_3$ compound which is irradiated by UV-A light without any variation of radiation duration. Ag/TiO$_2$ nanocomposites which have been developed in footwear applications. Ag loading will be varied to get optimal loading in disinfecting E. coli and Candida albicans. The manufacturing of footwear samples is prepared by using a modified dip coating method. To keep the composite Ag/TiO$_2$ in nanosized it will need sonication procedure in a repeat. The addition of TEOS as a silica precursor that will make Ag/TiO$_2$ nanocomposite deposited on cotton fabrics so will improve the hydrophilicity and self-cleaning capabilities.

2. Experimental

2.1. Material
The TiO$_2$ powder is Evonik P25, silver nitrate (Merck, P.A), methanol (Merck, P.A), nitric acid (Merck 65%), tetraethyl orthosilicate (Merck, P.A), cotton fabric 100% and distilled water (Wiloso) was used for all experiment.

2.2. Methods
Ag/TiO$_2$ nanocomposite was prepared by PAD (Photo-Assisted Deposition) method. TiO$_2$ P25 was dissolved on distilled water then added HNO$_3$ to be sonicated and AgNO$_3$ solution was made. Sol TiO$_2$ and AgNO$_3$ solution were combined to be irradiated with UV light with the addition of methanol. After that, the solution was dried in a hot plate then calcined in a furnace and ground to obtain Ag/TiO$_2$ nanoparticles. After the Ag/TiO$_2$ nanocomposite ready then prepare the fabric to be coated with Ag/TiO$_2$. The cotton fabric with 5 x 5 cm$^2$ dimension is prepared to be coated with Ag/TiO$_2$ sol. The sol was made Ag/TiO$_2$ nanocomposite to a distilled water and with the addition of 1 mL TEOS then it was sonicated that put the cotton fabric into the solution to be sonicated again. Then dried the fabric with a hair dryer for several minutes.

2.3. Characterization
UV-Vis DRS characterization was carried out to determine the gap energy value of the photocatalyst. Determination of the photocatalyst gap energy value was carried out using a CARY 2415 UV / Vis NIR Spectrophotometer type spectrophotometer equipped with an integrated sphere. Characterization of SEM is used to determine the morphology, porosity, and thickness. SEM is used to characterize materials because electrons have a higher resolution of light using Inspect F50 Scanning Electron Microscopy and for EDX is used to characterize the types of atoms on the surface of materials containing multi-atoms using EDAX TSL AMETEK Energy Dispersive X-Ray. While the purpose of XRD characterization is to determine lattice parameters, crystal size, and identify the phase of a crystalline material. The type of material can also be known by comparing the results of XRD characterization with diffraction peaks using Shimadzu XRD 7000 X-Ray Diffractometer.

2.4. Antimicrobial Activity
The antimicrobial effects of the synthesized Ag/TiO$_2$ initially investigated through controlled experiments in photoreactors. In the controlled experiments, bacterial cultures were first incubated in a
nutrient BHI solution for a day, after that 0.02g Ag/TiO₂ dissolved into 20 mL distilled water and then 10µ bacterial cultures inserted into solution Ag/TiO₂, the obtained solution was continuously stirred with magnetic stirrer at room temperature for 120 min to ensure bacteria does not settle at one point, at the same time the solution was irradiated in photoreactor to evaluate the antibacterial effect of Ag/TiO₂, the number of bacterial colonies remaining on plates was counted with a total plate count (TPC) method.

2.5. Self-Cleaning Activity
The experiment of self-cleaning properties was done by comparing the differences in the colour of the liquid sludge stains on Ag/TiO₂/TEOS coated and non-coated TiO₂ (blank) fabrics. Four samples the cotton is dipped in liquid sludge for 5 minutes, after 5 minutes the sample is dipped in clean water and then it can be seen which fabric the colour of the fabric matches the initial colour.

2.6. Hydrophilicity Activity
The experiment of hydrophilicity properties was done by comparing differences in water absorption capability of Ag/TiO₂, Ag/TiO₂/SiO₂ coated on cotton fabrics and non-coated catalyst (blank). the cotton samples were measured in the initial mass then dipped in water as much as 50 mL for 2 min, after 2 mins of cotton fabric in the mass measurement after water dyed then can be seen which fabric has the best hydrophilic properties.

3. Result and Discussion

3.1. Characterization
The form of material can be known by comparing the results of XRD characterization with catalogue diffraction peaks. The catalyst characterized was 5wt% Ag/TiO₂. In this characterization, Ag/TiO₂ catalysts that have been synthesized will be compared with commercial TiO₂ catalysts, namely TiO₂ P25. Fig.1 shows the XRD TiO₂ P25 pattern and 5% Ag/TiO₂ composite powder loaded. The crystalline structure of the powder is clarified into an anatase and rutile phase with XRD measurements. Ag metal peaks are not seen in the characterization results because the percentage of TiO₂ is much greater than loading Ag, it can also indicate that Ag is attached to the crystal matrix of TiO₂ so it is coherent that the XRD data show similar peaks on Ag/TiO₂ catalysts and TiO₂ P25. Composite powder TiO₂ P25 and Ag/TiO₂ are crystallized well. The crystal size calculated using the Scherrer equation is anatase 20 nm and rutile 23 nm for TiO₂ P25, anatase 34 nm and rutile 39 nm for Ag/TiO₂. Ag will function as a trapper electron then if the position of Ag in the possible matrix to prevent recombination is more accurate than its existence being a crystal.

![Figure 1. XRD patterns of TiO₂ P25, Ag/TiO₂.](image)

Fig. 2 shows SEM images of loading variation of Ag/TiO₂ composites prepared by the photo-assisted deposition method. Fig. 2a, 2b, and 2c indicate SEM images of the surface of the composite with the x20,000 magnifications. Fig. 2a, 2b, and 2c show morphologies of the Ag/TiO₂ composite. Based on the
results of characterization, there is agglomeration between the components of the composite catalyst. Through the SEM results, it is difficult to distinguish between each catalyst constituent component. Then the EDS characterization was carried out with the aim of looking at the composition of Ag which was deposited on TiO$_2$ catalysts with different loading Ag.

**Figure 2.** SEM images of (a) 1% Ag/TiO$_2$ (b) 3% Ag/TiO$_2$ (c) 5% Ag/TiO$_2$.

EDX analyses are shown in Table 1. confirm the presence of Ag-doped in TiO$_2$. Ag was well dispersion on surface TiO$_2$; it is seen that element of Ag not found on TiO$_2$ P25. The Ti, O and Ag composition as shown in Table 1. refer to the substrate composite observed with a scanning electron microscope (SEM).

**Table 1.** Comparison of the Composition of Elements of TiO$_2$ P25 and Ag/TiO$_2$ Catalysts

| Loading Ag | % mass Ag/TiO$_2$ | Total |
|------------|-----------------|-------|
|            | Ag | O     | Ti   |     |
| 1%         | 0.92 | 64.70 | 34.38 | 100 |
| 3%         | 3.08 | 55.30 | 41.62 | 100 |
| 5%         | 4.96 | 53.12 | 41.93 | 100 |

The characterization of the UV-Visible diffusion reflectance spectrum was carried out to determine the number of energy gap values that were influenced by the presence of Ag dopants on TiO$_2$. The calculated band gap energy and wavelength of TiO$_2$ P25 and Ag/TiO$_2$ are shown in Table 2. It can be seen that all samples have strong absorption in the ultraviolet region, indicating a band gap decreasing by doping with Ag, besides that it can be seen from the wavelength that Ag can increase sensitivity to visible light. Therefore, the photocatalytic reaction is active, especially in disinfecting *E. coli* and *Candida albicans* by Ag/TiO$_2$, which will then be proven by antimicrobial tests.

**Table 2.** Energy Gap Calculation Results from TiO$_2$ P25 and Ag/TiO$_2$ Catalysts

| Catalyst  | Band Gap Energy (eV) | Wavelength (nm) |
|-----------|---------------------|-----------------|
| TiO$_2$   | 3.25                | 381             |
| 1% Ag/TiO$_2$ | 3.14          | 394             |
| 3% Ag/TiO$_2$ | 3.12          | 397             |
| 5% Ag/TiO$_2$ | 3.17          | 391             |

### 3.2. Evaluation of Antimicrobial Activity

The antimicrobial activity of TiO$_2$ P25 and Ag/TiO$_2$ composites were evaluated by photocatalytic reaction against *E. coli* bacteria. Based on the growth inhibition rate shown in Fig. 3, it can be seen that
3% Ag/TiO₂ have strong antibacterial effect under UV irradiation. It is clear that the disinfection efficiency is 100% within 120 min under UV irradiation, respectively. While those of 1% and 5% Ag/TiO₂ are about 95.4% and 96.6%, respectively.

![Figure 3. Escherichia coli bacterial growth against time and disinfection percentage (%).](image1)

![Figure 4. Candida albicans and Escherichia coli microbial growth against time and disinfection percentage (%).](image2)

These results show that 3% Ag/TiO₂ have excellent results on bacteria and fungi as a photocatalysis after 2h irradiation by UV-A, which indicate that the 3% Ag/TiO₂ are effective against E. coli and Candida albicans with a 100% efficiency disinfection. TiO₂ tend to completely disinfection this kind of E. coli bacterial but the addition of Ag gives better bactericidal effect is shown in Fig.4. The Ag-doped TiO₂ have the higher disinfection efficiency than that of pure TiO₂ due to Silver species co-existed, Ag⁺ and Ag⁰ acting as photo generated electrons trapping sites prevent the electron-hole pairs recombine rapidly after photo-excitation leading to enhancement of photocatalytic activity [22]. Ionic Ag strongly interacts with thiol groups of vital enzymes and inactivates them and once treated with Ag ions the DNA loses its replication ability which results in cell death [17]. Thus, the presence of Ag in TiO₂ significantly enhanced the antibacterial property of TiO₂.
3.3. Evaluation of Self-Cleaning Activity
The self-cleaning activity was compared through monitoring the removal of sludge stain on blank cotton fabrics and cotton fabrics coated Ag/TiO\textsubscript{2}/SiO\textsubscript{2} are shown in Fig.5, the presence of silica can increase the surface activity of the photocatalyst resulting in a higher concentration of hydroxyl groups involved in photocatalytic reactions [23]. These factors played a significant part in enhancing the self-cleaning function on Ag/TiO\textsubscript{2}/SiO\textsubscript{2} treated cotton sample. The establishment of a connection between Ag, Ti, and Si results in a charge imbalance producing positive charge in photocatalyst. At this condition, a higher amount of hydroxyl groups is attracted to the surface of photocatalyst [24].

![Figure 5](image_url)

**Figure 5.** Self-Cleaning Test in Cotton Samples with Sludge Stain (a) Cotton 100% Before the Test, (b) Cotton 100% After the Test, (c) Ag/TiO\textsubscript{2}/SiO\textsubscript{2} Before the Test, (d) Ag/TiO\textsubscript{2}/SiO\textsubscript{2} After the Test

Shows that the addition of TEOS as a precursor of SiO\textsubscript{2} is able to cleanse from the most effective sludge, because the addition of TEOS hydrolysed to SiO\textsubscript{2} causes an increase in the degree of acidity of the TiO\textsubscript{2} catalyst in the fabric to the more OH radicals formed so that the thin film water layer is more, that, the dirt will be attached to a thin film layer that will be easier to clean than dirt that sticks to the cotton fabric directly.

3.4. Evaluation of Hydrophilicity Activity

| No | Material          | The initial mass of cotton (g) | Cotton after immersed in water (g) | The amount of water absorbed (g) |
|----|------------------|--------------------------------|-----------------------------------|---------------------------------|
| 1  | Cotton 100%      | 0.25                           | 0.59                              | 0.34                            |
| 2  | Cotton - Ag/TiO\textsubscript{2} | 0.26                           | 0.65                              | 0.39                            |
| 3  | Cotton - Ag/TiO\textsubscript{2}/SiO\textsubscript{2} | 0.27                           | 0.75                              | 0.48                            |

From Table. 3 it is shown that the Ag/TiO\textsubscript{2} catalyst coating has an effect on the hydrophilic nature of the cotton fabric proved by the amount of water absorption on the blank cotton the amount is not very significant whereas, with the addition of Ag/TiO\textsubscript{2}/SiO\textsubscript{2} seen more water absorption, it indicates that there has been a change of fabric characteristics becomes more hydrophilic in that the fabric in the Ag/TiO\textsubscript{2} coating with the addition of TEOS has better absorption capacity, it is in accordance with the purpose of adding TEOS as a precursor of SiO\textsubscript{2} which is to improve the hydrophilic properties and the activity of the catalyst film in which the content of SiO\textsubscript{2} compounds present in the TEOS to be forming Ti - O - Si bonds. SiO\textsubscript{2} produced by TEOS will increase the surface area so that it more easily absorbs water and produces more hydroxyl groups and then the water is easily diffused on the surface of the catalyst.
Besides having the best hydrophilic ability, it turns out that the cotton in Ag/TiO$_2$/SiO$_2$ coating has the best drying ability proven by fast drying rate are shown in Fig. 6., it also proves the formation of thin film of water will be more evaporate because thin films form on the surface so that it is easier to dry than if the water is absorbed directly into the fabric.

4. Conclusion
In this summary the antibacterial effect of nanocomposite Ag/TiO$_2$ coated cotton fabrics for footwear application found that, the optimum composition of Ag in disinfecting is 3% loading Ag it is proven by percentage of bacterial and fungal disinfection which reach 100% efficient, Ag/TiO$_2$ photocatalyst is an excellent and long-lasting antibacterial nanocomposite material and addition of SiO$_2$ coating showed a high photocatalytic activity in hydrophilic and self-cleaning ability, superior to a TiO$_2$ or Ag/TiO$_2$ coating alone due to the high dispersion and the structural effects of the silica present. of course, this study appropriate for future footwear applications.

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