DOI: 10.6060/ivkkt.20246701.6962

СИНТЕЗ И ИССЛЕДОВАНИЕ НАНОЧАСТИЦ Ag-TiO_2 ДЛЯ ПРИМЕНЕНИЯ В САМООЧИЩАЮЩИХСЯ ТКАНЯХ

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В данной работе нанокомпозит Ag-TiO_2 был синтезирован золь гель методом и охарактеризован с помощью полевой эмиссионной сканирующей электронной микроскопии (FE-SEM), рентгеновской дифракции (XRD) и УФ-видимой спектроскопии. Соотношение Ag^+/Ti^{4+} существенно влияет на фазовый переход TiO_2 из анатаза в рутил в нанокомпозите: содержание анатаза снижается с 94,9% до 52,6% при увеличении этого соотношения с 1,0 до 4,0%. Для дальнейших исследований выбрано исходное соотношение Ag^+/Ti^{4+} 1,0% в связи с наибольшим содержанием TiO_2 в фазе анатаза. Наночастицы достаточно монодисперсны и имеют сферическую форму со средним размером около 18-24 нм. Самоочищающаяся ткань из полиэстера (ПЭТ) была успешно модифицирована наночастицами Ag-TiO_2 погружным методом. Нанокомпозит Ag-TiO_2 был покрыт полиэтиленгликолем (ПЭГ) с размером 100-200 нм и нанесен на поверхность ткани ПЭТ. Была демонстрирована самоочищающаяся поверхность ткани благодаря гидрофобной поверхности по эффекту лотоса и фотокаталитической деградации родамина Б под действием солнечного света. Ткань ПЭТ, покрытая композитом Ag-TiO_2, демонстрирует более сильную антибактериальную активность (зона ингибирования 1,3 см) по сравнению с тканью, покрытой только TiO_2 (зона ингибирования 0,8 см). Результаты исследования показали, что после 6 ч облучения фотокаталитическая активность образца ткани Ag-TiO_2/ПЭТ была значительно лучше, чем у образца ткани TiO_2/ПЭТ. Способность превращаться из гидрофобного в гидрофильный особенно многообещающа для интереса к самоочищающимся поверхностям, текстильной промышленности и очистке окружающей среды.

Ключевые слова: антимикробная активность, тканевая поверхность, фотокатализатор, наночастицы, самоочищающийся

SYNTHESIS AND STUDY OF Ag-TiO$_2$ NANOPARTICLES FOR APPLICATION IN SELF-CLEANING FABRICS

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In this work, the Ag-TiO$_2$ nanocomposite was prepared by sol-gel method and characterized using the Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and UV-Vis spectroscopy. The Ag$^+$/Ti^{4+} ratio significantly influences the phase transition of TiO$_2$ from anatase to rutile in the nanocomposite: the anatase content decreases from 94.9% to 52.6% as this ratio increases from 1.0 to 4.0 %. The initial Ag$^+$/Ti^{4+} ratio of 1.0 % was chosen for further research due the highest content of TiO$_2$ in the anatase phase. The nanoparticles are fairly monodisperse and have a spherical shape with an average size of about 18-24 nm. Self-cleaning fabric polyester (PET) was modified successfully with Ag-TiO$_2$ nanoparticles by an immersed method. The nanocomposite of Ag and anatase TiO$_2$ was coated by binder in 100-200 nm in size which coating onto the surface of fabric demonstrated self-cleaning surface with different mechanisms: hydrophobic surface as "lotus leaf" effect, photocatalytic degradation Rhodamine B under solar irradiation. The PET fabric coated with the Ag-TiO$_2$ composite demonstrates stronger antibacterial activity (inhibition zone of 1.3 cm) compared to the fabric coated with TiO$_2$ alone (inhibition zone of 0.8 cm). The results showed that after 6 h of irradiation, the photocatalytic activity of the Ag-TiO$_2$/PET fabric sample is significantly better than that of the TiO$_2$/PET fabric sample.

The ability to change from hydrophobic to hydrophilic is especially promising to the interest in self-cleaning surfaces, the textile industry, and environmental cleanup.

Key words: antimicrobial activity, fabric surface, photocatalyst, nanoparticles, self-cleaning

Для цитирования:

Тхи Лан Фам, Тхи Нгоан Нгуен, Ван Куонг Буй, Ань Сон Нгуен, Чонг Хиен Дао, Тхи Тхюй Нгуен, Тхи Ми Хань Ле, Минь Нгок Нгуен, Фуонг Лан Ву, Дай Лам Тран Синтез и исследование наночастиц Ag-TiO$_2$ для применения в самоочищающихся тканях. *Изв. вузов. Химия и хим. технология*. 2024. Т. 67. Вып. 1. С. 128–135. DOI: 10.6060/ivkkt.20246701.6962.

For citation:

Thi Lan Pham, Thi Ngoan Nguyen, Van Cuong Bui, Anh Son Nguyen, Trong Hien Dao, Thi Thuy Nguyen, Thi My Hanh Le, Minh Ngoc Nguyen, Phuong Lan Vu, Dai Lam Tran Synthesis and study of Ag-TiO$_2$ nanoparticles for application in self-cleaning fabrics. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*.]. 2024. V. 67. N 1. P. 128–135. DOI: 10.6060/ivkkt.20246701.6962.

INTRODUCTION

In the fabric industry, nanotechnology has been used to provide multifunctional properties to the fabric as self-cleaning, antibacterial, antistain, and other properties [1-3]. These multifunctional properties can be maintained permanently after washing, laundering, and wearing. On the other hand, nanotechnology and nanomaterials also enhance the durability of fabrics due to their large area to volume ratio and high surface energy [4].

Nano-engineered fabrics refer to the modification of cotton's cylindrical structure in fabric. At the micro scale, the microstructure of cotton fiber looks like tree trunks. Using nanotechnology and nanomaterials, the cushion of air (through a fuzz of minute whiskers) could be created around the cotton fiber, leading fabric in the super-non wet table or super-hydrophobic stages [5]. These whiskers also can create points of contact for dirt when fabrics are contaminated. The self-cleaning effect of fabrics refers to the hydrophobic water-repellent double structure of the surface, which reduce significantly the adhesion force between fabric surface and water droplet. Thus, when water contacts the contaminated/inclined superhydrophobic fabric, the water droplet should roll off rather than slide off.

Regarding the nanomaterials used in fabrics, various nanoparticles have been reported for their effective photocatalytic and antibacterial activities, such as ZnO, Ag, Cu, Au, and TiO_2 nanoparticles [6-11]. Among these nanoparticles, TiO_2 has been considered as the promising nanophotocatalyst with highly reactive oxygen species for both antibacterial and decomposition of organic pollutants. Under UV light exposure, pairs of free electrons and holes are formed on the surface of TiO_2. Thereafter, they can react with oxygen and absorb the hydroxyl group to produce superoxide and hydroxyl radicals. In the case of polyester (PET) fabrics, nano-TiO_2 can be applied in two roles, as an efficient photocatalyst and as a hydrophobic agent. In this direction, the possible recovery from hydrophilic to hydrophobic states could provide the flexible and self-cleaning abilities for PET fabrics.

However, the bandgap energy of TiO_2 nanoparticles is high ($E_g = 3.2$ eV); moreover, TiO_2 only exhibits photocatalytic effects when stimulated by ultraviolet radiation ($\lambda < 388$ nm). Therefore, this limits its antibacterial activity and self-cleaning ability when using sunlight or visible light as an external stimulus [12]. Silver nanoparticles (AgNPs) have long been known for their broad-spectrum antibacterial capabilities without requiring UV irradiation and have been applied in various fields such as textiles and food [13, 14]. The nanosilver coated fabric can be used in a wide range of applications such as wound dressings, hygienic clothing and medical applications where the presence of bacteria is hazardous [15]. For example, it can be used for the fabrication of face masks, surgical gloves and military uniforms where the infection of the wound can have severe effects. The high flexibility of fabric textiles allows them to be employed in the health, leisure and sports industries [15]. These silver nanoparticles are either incorporated into the fibers of the fabric, or coated afterwards. If they are impregnated into the material then the useful effect lasts longer than if they are coated on the surface [16].

However, AgNPs are susceptible to transforming into Ag_2O (silver oxide), and additionally, silver metal is an expensive material. A low concentration of Ag nanoparticles in many cases may not be effective for various practical applications, while using AgNPs at higher concentrations leads to higher costs. To harness the beneficial effects of both titanium dioxide and silver nanoparticles while minimizing their respective drawbacks, Ag/TiO_2 composite materials have been fabricated using various methods to enhance antibacterial properties and photocatalytic efficiency [17, 18]. Some studies have shown that the deposition of silver nanoparticles can enhance the photocatalytic performance of titanium dioxide. This might be attributed to the ability to attract electrons at the Schottky barrier of the silver nanoparticles at all contact regions of the Ag/TiO_2 composite, reducing the recombination of electron-hole pairs on the surface of titanium dioxide. As a result, this creates charge separation and leads to more electron transfers, resulting in a longer lifetime of electron-hole pairs [19].

In this work, a facile and effective method was described for the production of the $Ag\text{-}TiO_2$ coated PET fabrics at ambient temperatures from an aqueous $Ag\text{-}TiO_2$ nano-sol, which was obtained via hydrolysis and condensation of tetrabutyl titanate in water. Then, the self-cleaning (in photocatalytic degradation of dyes) and hydrophobic abilities of these $Ag\text{-}TiO_2$ coated PET fabrics have been evaluated.

MATERIALS AND METHODS

Materials

$AgNO_3$ and tetrabutyl titanate 99% were provided by Sigma-Aldrich, whereas polyester fabric (PET) – WW-3009 was obtained from KM, Ltd. (Korea). Rhodamine B dye was purchased from Duc Giang Scientific Co., Vietnam. Nitric acid, ethanol, and ethyl acetate were provided by Merck and used without any further purification. The residual water in ethanol was determined densimetrically to be 1.95 wt. %.

Synthesis of Ag-TiO_2 composite

A typical synthesis of the TiO_2 and Ag-TiO_2 composite by the sol-gel method can be described as follows: 10 mL of tetrabutyl titanate was dissolved in 260 mL of ethanol (solution A). The $AgNO_3$ 0.0185 M solution was added into a beaker, containing 15 mL of water and 30 mL of ethanol with the added amount of HNO_3 until the pH reached 3 (solution B). The initial ratio of Ag^+/Ti^{4+} was 1.0, 1.5, 2.0, 3.0 and 4.0%. The solution B was slowly added to the solution A. Then, the mixture was stirred vigorously at room temperature for 24 h to obtain a gel solution. The gel was dried at 60 ºC for 24 h and calcined at 450 °C for 3 h to obtain nanoparticles.

Pretreatment of PET fabrics

To remove contaminants from PET fabrics, they were firstly immerged in the nonionic detergent solution (at 80 ºC for 30 min), then washed with deionized water. Thereafter, the fabrics were sonicated in ethanol solution for 10 min to remove all organic components then multiply cleaned with deionized water and dried at 50 ºC.

Coating preparation

The as-synthesized TiO_2 or Ag-TiO_2 powders were dispersed in ethyl acetate with binder (PEG from Merck, molecular weight = 6.000 g/mol), the suspension was stirred in 20 min and sonicated further for 5 min to achieve the good suspension of Ag-TiO_2 in ethyl acetate.

The treated PET was immersed in suspension of nanoparticles in ethyl acetate for 1 h, then dry at room temperature for 30 min. Following that, the process was repeated once more time for 30 min then dry. Finally, the fabrics were immersed in deionized water at 70 ºC for 3 h to remove residual nanoparticles from PET fabrics.

Characterization

The microstructures of TiO_2, Ag-TiO_2 nanoparticles and fabrics were characterized by the Field emission scanning electron microscopy (FESEM, FEI SIRION 200, FEI, USA) and Transmission Electron Micro- scope (TEM, JEM-100CX, JEOL, Japan). Crystal structures of Ag-TiO_2 nanoparticles were determined by XRD Patterns (XRD, D/max-2200/PC, Rigaku Corporation, Japan) with Cu Kα radiation, operating at 40 kV and 30 mA, where λ=0.15418 nm for the Cu Kα line. UV-Vis spectra in powder form of TiO_2 and Ag-TiO_2 Jasco-V670.

Antimicrobial activity

The antibacterial activity of TiO_2 and Ag-TiO_2 coated fabrics was tested against *Escherichia coli* (ATCC 8739) as a selected Gram-negative bacterium by the disk diffusion method. Mueller–Hinton agar was used as the growth medium. Briefly, the square PET pieces with the size 5 mm x 5 mm were placed on an *E. coli* cultured agar plate. After being incubated for 24 h at 37 ºC, the diameter of the inhibition zone was determined. The diameter of inhibition zone (DIZ) was considered as a measure of the antibacterial activity.

Photocatalytic degradation of Rhodamine B dye

The photocatalytic degradation of Rhodamine B dye on the surface of TiO_2 or Ag-TiO_2 coated fabrics was tested under a solar simulator irradiation. Both solid and liquid of 20 mL Rhodamine B solution (20 mg. L^{-1}) were put on the surface of coated fabric (5 mm × 5 mm) under the solar irradiation for 3 h.

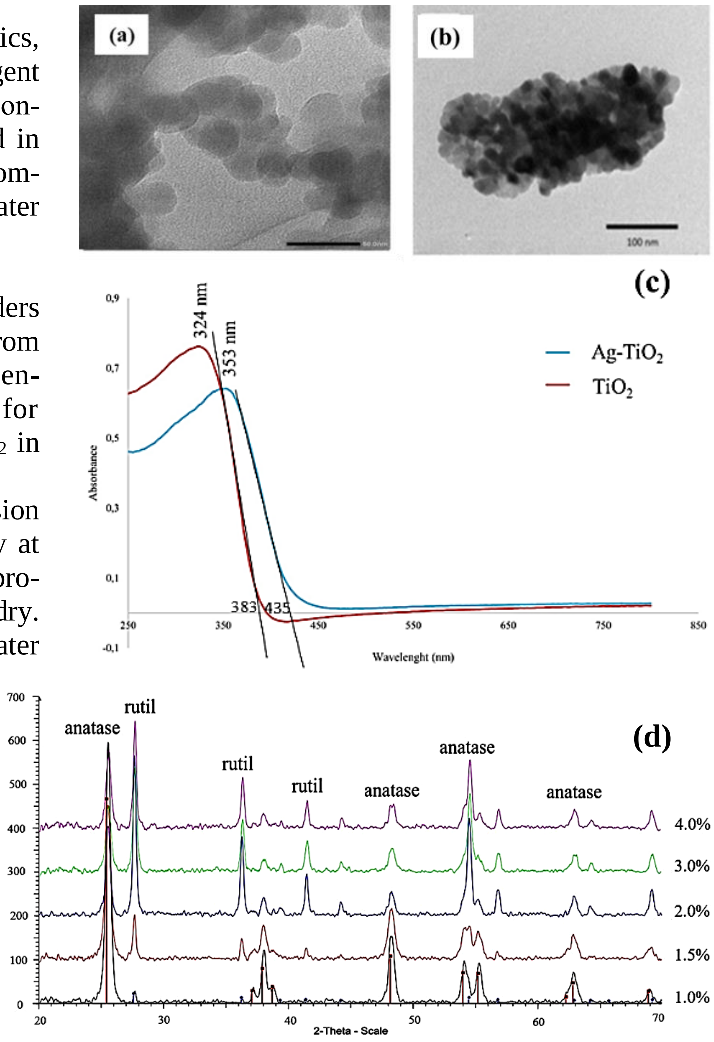

Fig. 1. Characterization of TiO_2 and Ag-TiO_2 nanoparticles: TEM images of TiO_2 (a), and Ag-TiO_2 (b) nanoparticles; UV-Vis spectra of Ag-TiO_2 and TiO_2 nanoparticles (c) and XRD spectra of Ag-TiO_2 nanocomposite in different ratios Ag^+/Ti^{4+} (d).
Рис. 1. Характеристика наночастиц TiO_2 и Ag-TiO_2: изображения TiO_2 FE-SEM (a), изображения FE-SEM (b) и TEM (c) наночастиц Ag-TiO_2; УФ спектры наночастиц TiO_2 и Ag-TiO_2 (d) и рентгеновские спектры нанокомпозита Ag-TiO_2 в различных соотношениях Ag^+/Ti^{4+} (d).

RESULTS AND DISCUSSION

Characterization of Ag-TiO_2 nanoparticles

From Figure 1e, it can be observed that the Ag^+/Ti^{4+} ratio significantly influences the phase transition of TiO_2 from anatase to rutile in the nanocomposite. The rutile content increases from 5.1% to 47.4% as this ratio increases from 1.0 to 4.0 % (Table 1). At the same time, the average size of Ag-TiO_2 nanoparticles is less than that of TiO_2 in all studied Ag^+/Ti^{4+} ratios, however, increases with the Ag^+/Ti^{4+} ratios. (Table 1). These results can be explained as follows: the atomic radius of Ag^+ ions is much larger than that of Ti^{4+} ions. Consequently, during the sol-gel transformation, Ag^+ ions do not participate in the crystalline network of the anatase phase of TiO_2.

It can be showed that, the size of anatase grains of TiO_2 decreases with the Ag in nanocomposite, and therefore, the total boundary energy for TiO_2 powder increases. The driving force for rutile grain growth then increases and the anatase to rutile phase transformation is promoted [20].

Table 1

TiO_2 content in anatase and rutile phases in Ag-TiO_2 samples and the average size of Ag-TiO_2 particles corresponding to different Ag^+/Ti^{4+} ratios in the various reactions.

***Таблица 1.* Содержание TiO_2 в фазах анатаза и рутила в образцах Ag-TiO_2 и средний размер частиц Ag-TiO_2, соответствующих разным соотношениям Ag^+/Ti^{4+} в различных реакциях.**

Ratio of Ag^+/Ti^{4+} in reaction, %	Anatase (%)	Rutil (%)	Average size (nm)
0.0			25.0
1.0	94.9	5.1	18.0
1.5	75.0	25.0	18.7
2.0	58.4	41.6	19.4
3.0	56.1	43.9	22.3
4.0	52.6	47.4	24.1

For photocatalytic materials, the particle size has a significant impact on the catalytic efficiency. Smaller particle sizes result in a larger surface area, leading to higher electron absorption from light. Moreover, the results in Table 1 also demonstrate that, for the photocatalytic effect of Ag-TiO_2 to be most effective, TiO_2 should predominantly exist in the anatase phase. Besides that, the increases of the ratio between Ag^+ and Ti^{4+} decrease the band gap energy of the samples [21]. Therefore, the Ag^+/Ti^{4+} ratio of 1.0 % is chosen for further research.

Fig. 1a-b show the TEM images of the TiO_2 and Ag-TiO_2 nanoparticles. The TEM images indicate that both TiO_2 and Ag-TiO_2 samples have spherical shapes. From Table 1, it can be seen that, the particle size of TiO_2 nanoparticles falls in the range of 25 nm, while the Ag-TiO_2 nanoparticles are in the range of 18-24 nm, depending on the Ag^+/Ti^{4+} ratio, with a relatively uniform distribution. The calculated size of the Ag-TiO_2 composite particles using the Scherrer equation aligns well with the measurement results from TEM.

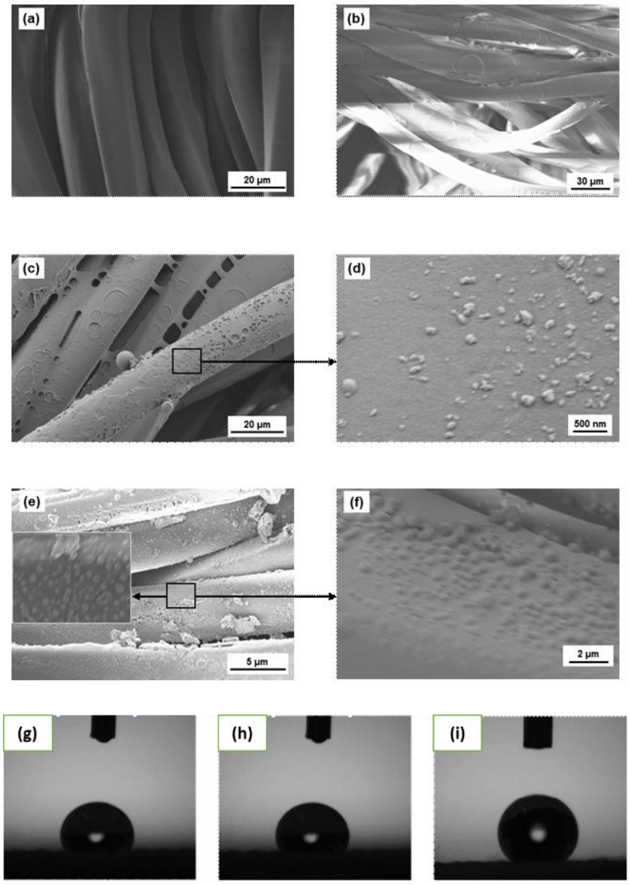

Fig. 2. SEM surface images of untreated PET fabric (a), treated PET fabric with binder (b), PET fabrics coated by TiO_2 nanoparticles with binder (c, d) and PET fabrics coated by Ag-TiO_2 nanoparticles with binder (e, f) and static water contact angle on the surface of fabric by binder (g) coated with TiO_2 (h) and Ag-TiO_2 nanoparticles (i).

Рис. 2. СЭМ-изображения поверхности необработанной ПЭТ-ткани (a), обработанной ПЭТ-ткани со связующим (b), ПЭТ-ткани, покрытой наночастицами TiO_2 со связующим (c, d) и ПЭТ-ткани, покрытой наночастицами Ag-TiO_2 со связующим (e, f) и статический угол контакта воды с поверхностью ткани связующим (g), покрытым TiO_2 (h) и наночастицами Ag-TiO_2 (i).

The UV-VIS spectra of the nano-TiO_2 and Ag-TiO_2 particles are shown in Fig. 1c. The results indicate that the samples have absorption band edges that shift to longer wavelengths (red shift) compared to the regular TiO_2 sample (from 324 nm to the range of 353 nm). This suggests that the Ag-TiO_2 samples hold the potential for photocatalytic activity when stimulated by visible light with longer wavelengths than ultraviolet light. This red shift was also observed in other works on Ag-TiO_2 hybrid nanoparticles for antibacterial application in polyethylene [22, 23].

Characterization of fabric surface

The morphological properties of the PET fabrics before and after treatment with TiO_2 or Ag-TiO_2 nanocomposite were explored using scanning electron microscopy (SEM) (Fig. 2a-f). As shown in Fig. 2, after dispersing in the solution of binder, the average size of TiO_2 and Ag-TiO_2 nanoparticles is in the range of 100 - 200 nm.

Following the microscope, Fig. 2 shows the changes on the surface of PET, before and after being treated with TiO_2 and Ag-TiO_2 nanoparticles and binder. The surface of initial states is quite smooth (Fig. 2a), then becomes roughly after coating with binder (Fig. 2b) and then TiO_2 (Fig. 2c, d) and Ag-TiO_2 nanoparticles (Fig. 2e, f).

From the WCA measurements, it can be considered to show hydrophobic properties as the contact angle (Fig. 2g-i). Static water contact angle on surface of fabric treated by binder (Fig. 2g), TiO_2 (Fig. 2h) and Ag-TiO_2 nanocomposite (Fig. 2i) with contact angle (CA) values of 113º, 134º and 140º, respectively. Thus, the Ag-TiO_2 nanocomposite increases hydrophobic property of PET surface through “lotus effect”. Ag-TiO_2 already created “lotus leaf” effects on the surface of the fabric to increase the hydrophobic properties of the fabric. When water is exposed to the treated fabric, the dirt will be carried away more easily.

Antibacterial effect of PET fabrics coated by nano TiO_2 and nanocomposite Ag-TiO_2

The antibacterial properties of Ag and TiO_2 have been demonstrated and widely used as additives in antibacterial materials. Since nano Ag and nano TiO_2 both have individual antibacterial capabilities, combining them is expected to provide synergistic antibacterial effects.

The results of the antibacterial test on the fabric against *E. coli* show that the antibacterial effects are evident in PET fabric coated with TiO_2 and Ag-TiO_2 composite, while pure PET fabric (blank) does not exhibit antibacterial effects against *E. coli* (Fig. 3). The PET fabric coated with the Ag-TiO_2 composite demonstrates stronger antibacterial activity (inhibition zone of 1.3 cm) compared to the fabric coated with TiO_2 alone (inhibition zone of 0.8 cm). This synergistic effect was also observed in a study with a similar approach by Abualnaja et al. [24] where the Ag-TiO_2 nano-composite exhibited stronger inhibition of *E. coli* compared to TiO_2 alone. The results were measured based on the optical density (OD) of the bacterial solution. In another study conducted by da Silva et al. [25], fabric coated with Ag-TiO_2 nanocomposite even demonstrated a 50% inactivation of the SARS-CoV-2 virus when it came into contact with the fabric. Other authors have also reported similar results [22, 23]. Additionally, in this study, the inhibitory effects were also observed on both Gram-negative bacteria (*E. coli*) and Gram-positive bacteria (*S. aureus*). This indicates that the Ag-TiO_2 nanocomposite exhibits a broad spectrum of antimicrobial activity, including against both viruses and bacteria. It can be concluded that the combination of Ag and TiO_2 nanoparticles on the fabric surface enhances the antibacterial activity, making it a promising approach for developing antibacterial materials.

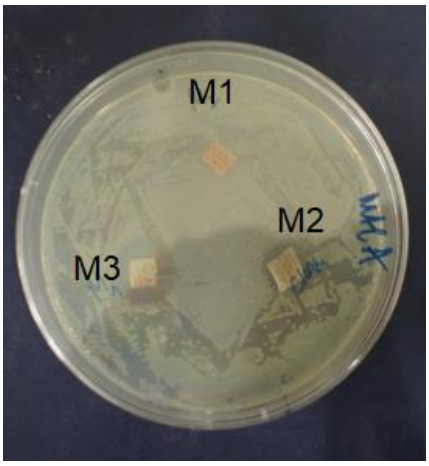

Fig. 3. Antibacterial effect of PET blank (M1), PET coated by TiO_2 (M2) and PET coated by Ag-TiO_2 (M3).
Рис. 3. Антибактериальный эффект ПЭТ-заготовки (M1), ПЭТ с покрытием TiO_2 (M2) и ПЭТ с покрытием Ag-TiO_2 (M3).

Photocatalyst degradation of Rhodamine B

The decrease of Rhodamine B concentration over the Ag-TiO_2 coated PET fabric under simulated solar irradiation was shown in Fig. 4. According to Figure 4, 20 mL of 20 mg. L^{-1} Rhodamine B were degraded absolutely under solar irradiation with a 0.25 cm^2 piece of treated fabric by TiO_2 (Fig. 4 a,b,c) or Ag-TiO_2 (Fig. 4 d,e,f).

It is evident that after 6 h of irradiation, the photocatalytic activity of the Ag-TiO_2/PET fabric sample (Fig. 4e) is significantly better than that of the TiO_2/PET fabric sample (Fig. 4b). Table 2 presents the contact angles with water of the fabrics taken at different time points. The hydrophobic properties of the fabric samples can be restored after being kept in the dark for about 2 h (Fig. 4c, f): the contact angle with water of the fabric samples is recovered to its initial value (Table 2).

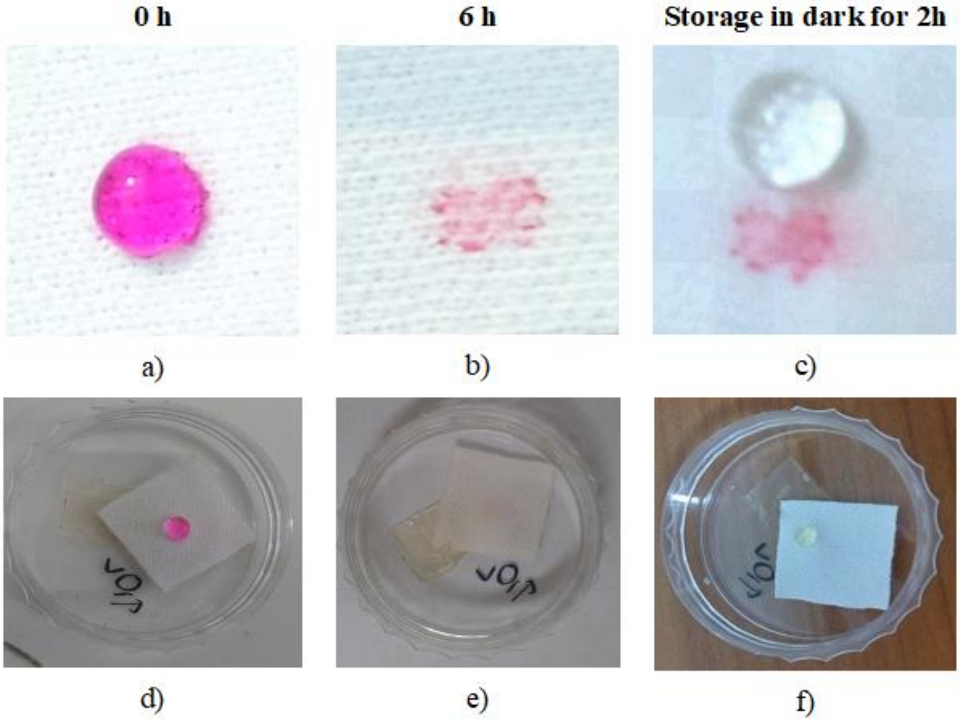

Fig. 4. Photodegradation of Rhodamine B in TiO_2/PET (a, b, c); Ag-TiO_2/PET (d, e, f) under visible light in solid state after 6 h
Рис. 4. Фотодеградация родамина Б в составе TiO_2/ПЭТ (a, b, c) Ag-TiO_2/ПЭТ (d, e, f) под действием видимого света в твердом состоянии через 6 ч

Table 2

Values of the water contact angle (CA) on the fabric surface. Water contact angles were recovered after storage in dark

Таблица 2. **Значения угла контакта воды (CA) с поверхностью ткани. Углы смачивания воды были восстановлены после хранения в темноте**

Ag-TiO_2/PET	**Contact angle [deg]**			
	Initial	Irradiation 30 min	Irradiation 3h	Storage in dark 2h
CA	122	10	0	122

CONCLUSIONS

The TiO_2 nanoparticle and Ag-TiO_2 nanocomposite have been synthesized by sol-gel method, then coated on the surface of PET fabrics by dipping the fabrics in the nanoparticles suspension. XRD, FE-SEM and TEM studies indicated that the TiO_2 nanoparticles in the composite were crystallized in the anatase phase. Both TiO_2 and Ag-TiO_2 samples have spherical shapes. The particle size of TiO_2 nanoparticles falls in the range of 25-30 nm, while the Ag-TiO_2 nanoparticles are in the range of 18-24 nm. Data from the test of photocatalytic degradation of dye confirmed the self-cleaning ability of Ag-TiO_2 coated PET fabrics against Rhodamine B. The PET fabric coated with the Ag-TiO_2 composite demonstrates stronger antibacterial activity compared to the fabric coated with TiO_2 alone. Their photocatalytic degradation is achieved through their hydrophobic surface and photocatalytic activity. From these findings, the self-cleaning performance of Ag-TiO_2 coated PET fabrics is very promising in the textile industry and environmental remediation due to the catalytic decomposition of the organic substances on the surface under solar irradiation without human intervention.

ACKNOWLEDGEMENTS

This work was supported by The Vietnam Academy of Science and Technology (VAST) under the grant numbers TĐVLTT.01/21-23 and NCVCC13.02/22-23.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Работа выполнена при поддержке Вьетнамской академии наук и технологий (VAST) в рамках грантов TDVLTT.01/21-23 и and NCVCC13.02/22-23.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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Поступила в редакцию (Received) 28.08.2023
Принята к опубликованию (Accepted) 14.09.2023