STUDY THE SELF-CLEANING ABILITY OF ZNO CONTAINED COTTON FABRICS

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ABSTRACT

In this study, ZnO nanoparticles were successfully synthesized by the precipitation method, then immobilized onto cotton fabric. The metal oxide nanoparticle-contained fabric exhibits a self-cleaning effect under ultraviolet (UV) illumination. The nanostructure of the prepared samples was detected using Scanning Electron Microscopy (SEM) analysis. The chemical composition changes of the fabrics before and after the modification were detected using The Fourier transform infrared (FT-IR) and Energy Dispersive X-ray Spectroscopy (EDS). After modification with ZnO nanoparticles, the cotton fabric exerted adsorption and decomposition properties again various chemical compounds. Stains of methylene blue (MB), and methylene orange (MO) were introduced into cotton fabric, under UV light, the dyes were faded and ultimately discolored. The degradation of pigments in the solution happened faster and was expressed by the concentration of dyes decreasing over time through UV-vis measurement results. The self-cleaning ability for MB and MO stained cotton fabrics is evaluated quantitatively over time through the K/S value, which showed a good self-cleaning effect.

KEYWORDS

ZnO; Precipitation method; Photocatalysis; Compound decomposition.

INTRODUCTION

The photocatalysis process of semiconductors used in self-cleaning and environmental applications has shown great potential as a sustainable, environmentally friendly, and cost-effective technology. These semiconductor materials have also been used to functionalize various textile fabrics to give them self-cleaning properties. Functional fabrics are capable of oxidizing dyes in the form of solutions and stains. The application of ZnO as a decomposition material for environmental pollutants has also been extensively studied. ZnO is a widely used semiconductor, which not only has numerous applications for stain decomposition and selfcleaning, but is also used in many other fields such as gas sensors, photovoltaic cells, and photodiodes due to its non-toxic properties, low cost, and good optical and photochemical properties [1-3].

The band gap width of ZnO nanoparticles is determined to be 3.37 eV, so they mainly absorb light in the ultraviolet region with an absorption capacity in the range of 200 nm - 400 nm. Nano-ZnO has such an absorption band, so it is widely used as a material for absorbing ultraviolet rays in industry, cosmetics

and sunscreens, and ZnO is an important component of drugs for external use. In addition, the fluorescence of ZnO nanoparticles is also of interest in the study of their optical properties [4, 5].

The need for textile items with medical treatment, sanitation, and hygiene is growing as the ecological environment slowly deteriorates. Cotton fabric is a common material that is used extensively in all types of clothing [6]. In the field of garment, 100% cotton fabric is frequently used to create slim-fit clothes, outerwear, and other items because it is a soft natural fabric that is friendly to users' health, has good color dyeing capacity, and has a high biodegradability. However, due to its high moisture absorption and water retention capacity (up to 65% by weight), 100% cotton fabric items are prone to yellow stains and the growth of bacteria and fungi that are dangerous to human health [7-9].

Numerous cutting-edge nanotechnology solar cell applications make use of zinc oxide. Recently, fabrics that can clean themselves have been created using zinc oxide's photocatalytic properties. When a ZnO semiconductor layer is exposed to light,

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Received June 2, 2023; accepted August 21, 2023



Figure 1. Schematic diagram of the ZnO nanoparticle synthesizing process.

photons with energies equal to or higher than the band gap energy of ZnO will stimulate electrons to the conduction band. Excited electrons on the surface of the material can interact with oxygen atoms in the atmosphere to form reactive oxygen species. These oxygen species are strong oxidizers that can degrade various organic substances in an oxidation-reduction reaction. These processes transform organic substances like dirt, pollutants into things like water and carbon dioxide. ZnO just acts as a catalyst, hence there is no loss in the degradation processes. As a result, the coating layer can play the role of selfcleaning layer [10, 11]. Cotton fabric containing ZnO was reported to expand the traditional applications of textile to various new ways of uses including antibacterial and radiation barrier properties against S. aureus and E. coli [12], The ZnO also presented synergistic activities when combined with other materials such as starch, silver nanoparticles, and curcumin. The starch from corn could play the role of adhesive materials for avoiding the leaching disadvantage of nanoparticles [13]. ZnO was well known as the self-cleaning material, particularly when fabricated into hierarchical hybrid nanostructures on cotton fabric. The combination of the Ti3C2Tx MXene/Ni chain/ZnO array hybrid nanostructures endowed the cotton fabric outstanding liquid repellency and durable self-cleaning ability [14].

In this work, ZnO nanoparticles were effectively produced and applied to cotton fabric, the morphology of synthesized ZnO is usually difficult to control due to multiple factors in the reaction process. By controlling the concentrations and time of reaction between chemicals, the grow of ZnO nanoparticles was studied. The resultant materials are investigated using SEM, FT-IR, Tensile testing, and water contact angle meter. The pigment concentration reduction over time using UV-vis testing results reflects the effectiveness of color deterioration in solution. For further photocatalytic assessment, the self-cleaning capacity of ZnO against MB and MO pigments on cotton fabric was quantitatively assessed using the K/S ratio. This discoloration of stains was evaluated using Ci4200 Spectrophotometric colorimeter after exposing samples to UV light.

METHOD

Material

Zinc acetate $((CH_3COO)_2Zn)$ and Potassium hydroxide (KOH) were purchased from Shanghai Yuanye Biotechnology Co., Ltd. All the chemicals used in this study were of analytical grade, and deionized water was utilized when needed.

Methods

Synthesis of ZnO nanoparticles

Utilizing the precipitation procedure, ZnO nanoparticles were synthesized successfully. In the beginning, 100 ml of 0.2 M (CH₃COO)₂Zn solution and 120 ml of 0.4 M KOH solution were prepared. Under continuous stirring, the KOH solution was steadily added to the zinc salt solution. When the mixture's pH reached the value of 9, the process of addition ceased and the solution was continuously agitated for one hour. After settling for two hours, the precipitate was collected by centrifuging the particles with alcohol and distilled water. The solid particulates were dried at 80°C for 10 hours, then crushed and calcined at 400°C for 3 hours, with a 10°C/min heating rate. The ZnO nanoparticle synthesis was summarized in Figure 1.

The proces of creating ZnO nanoparticle-coated cotton fabrics

The cotton fabric used in this research is treated fabric, purchased in Vietnam, with the main characteristics as follows: single weave, 201.6 g/m² weight, 0.54 mm of thickness, and breathability of 220 l/m2/s. 3x3 cm cotton specimens were prepared at room temperature and pressure, and the mass of the fabric samples were ascertained at moisture saturation. In 5 mL of ethanol, one tenth mass of ZnO by the mass of the cotton sample were dissolved. Under the conditions of continuous ultrasonic vibration, the prepared cotton samples were



Figure 2. Schematic diagram of ZnO nanoparticle coated fabric.

immersed in a ZnO/ethanol solution for five minutes while maintaining ultrasonic vibration. The fabric sample was then dried at 80°C for one hour to acquire cotton fabric nanocoated with ZnO. The whole proces was summarized as illustrated in Figure 2.

Analytical methods

The morphology and elemental composition of the ZnO-incorporated cotton samples were analyzed using Scanning Electron Microscopy - Energy-Dispersive X-ray Spectroscopy (SEM-EDS) on a Hitachi TM4000 Plus instrument at Hanoi University of Science and Technology with an accelerating voltage of 15 kV. Fourier transforms infrared spectroscopy (FT-IR) spectra were collected using Nicolet iS 50 (Thermo, Waltham, MA, USA) in the range of 4000 to 400 cm-1 with accumulation over 20 scans. Ultraviolet-visible (UV-vis) spectroscopy (Agilent 8453, USA) at the RoHan Research Laboratory, School of Chemical Engineering, Hanoi University of Science and Technology was used for detecting discoloration effects.

The UV-vis measurement method is based on the Bouger - Lambert - Beer law, the optical absorbance of a color-absorbing solution is proportional to the layer's thickness and color temperature [15, 16]:

$$A = \varepsilon cd = \log\left(\frac{l_0}{l}\right) = -\log(T), \tag{1}$$

in which: A – degree of optical absorption; ε – molecular absorption coefficient; c – solution concentration (mol/l); d – light transmission thickness (cm); I_0 – initial intensity of the light source; I – intensity after passing through the solution; T – transmission.

In qualitative analysis, a common absorbance is a characteristic number for each substance; therefore, by determining the common absorbance, it is possible to determine the qualitative composition of the analytical solution. Absorption spectroscopy is used in quantitative analysis to select the wavelength for measuring optical absorbance.

Photosensitive self-cleaning fabrics are capable of self-cleaning when exposed to light; furthermore, they are resistant to antibiotics and block UV rays. A number of test methodologies can be utilized to evaluate the photoinductive performance of functionalized fabrics. The photocatalytic efficacy of functionalized fabrics is frequently determined by the decomposition of organic pollutants, such as natural colorants or synthetic pharmaceuticals, which are frequently employed as sample pollutants. The optical degradation of pigments is determined by two categories of pigment decomposition activities, including color change in solution and stain decomposition. For the solution's color change, functionalized fabrics were immersed in the dye solution and exposed to UV light. The concentrations of the dye solutions were measured using a UV-Vis spectrophotometer after periodic collection of the solutions over a specified time period [17, 18].

In this investigation, the color value (K/S) of the Ci4200 Spectrophotometric colorimeter was used to evaluate the color loss of stains exposed to UV light for a specified period of time. A decrease in the K/S ratio indicates the disappearance of stains. Self-cleaning can be determined by comparing the K/S values of exposed and unexposed sections of the same stain, as shown below [19]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R},$$
 (2)

in which: K - absorption coefficient; S - scattering coefficient; R - reflectance of the dyed cotton fabric; K/S represents the color fastness of the dye on the surface and is proportional to the amount of pigment present on the surface.







2000

Wavenumbers (cm-1)

2500

1500

1000

Figure 5. FTIR spectrum with attenuated total reflectance (ATR) of synthesized ZnO nanoparticles.

3000

3500

RESULTS AND DISCUSSION

Characterization of ZnO catalyst

20

SEM, EDS, FTIR analysis

ZnO nanoparticle catalyst was analyzed by SEM-EDS, which is shown in Figures 3 and 4. The results show that the ZnO particles are distributed on the fabric surface, Figure 3 (a). In Figure 3 (b), ZnO nanoparticles were observed to be less than 50 nm for each particle, however, without the scattering liquid environment, the ZnO nanoparticles tend to aggregate extensively. On the surface of the cotton

fiber, the white dots were ZnO nanoparticles that immobilized uniformly on the surface of the fibers.

Cotton fabrics containing ZnO with a mass ratio of 10:1, corresponding to an elemental composition ratio of 42.33 percent carbon, 47.97 percent oxygen, and 3.82 percent zinc. Figure 4 depicts the outcome of EDS analysis. According to the results, the ZnOcontaining fabric has a ZnO content comparable to theoretical calculations, and the quantity of ZnO successfully coated on cotton is lost in a negligible amount. Due to the fact that the EDS measurement is a surface measurement and the working range is on the surface and in a small area, as well as the fact



Figure 6. (a) UV-Vis DRS Absorption Spectral Range, and (b) UV-Vis Diffuse Emission Spectroscopy (UV-Vis DRS).

Table 1	. Tensile strength of cotton fabric before	ore and after trea	tment with ZnO nanopartic	les.	
		Mean tensile strength Sample size with standard deviation [N]		Mean comparison (Student's t test)	
	Warp of cotton fabric	5	647.36±8.74	Warp of cotton fabric and warp of ZnO coated cotton fabric t* (p=0.05)	
	Warp of ZnO nanoparticle coated cotton fabric	5	595.38±12.14	= 6.95 t = 2.36	
	Weft of cotton fabric	5	433.61±6.85	Weft of cotton fabric and weft of ZnO	
	Weft of ZnO nanoparticle coated cotton fabric	5	388.62±6.54	t = 2.31	

t = Student's test value; t^* = minimum t value for rejecting the null hypothesis with a 95% significance.

that the measured material surface is not perfectly flat and the ZnO coverage is not ideal, there is a discrepancy between the measurement and the theoretical calculation.

Figure 5 depicts the FTIR spectrum of ZnO nanoparticles; a broad band observed at approximately 400 cm-1 is zinc oxide's absorption band. There are additional insignificant bands in the spectrum at 1400 cm-1, 1300 cm-1, and 800 cm-1. These adsorption bands are presumably due to airborne CO2 absorption and can be disregarded [20, 21].

UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS)

UV-DRS is a technique used to investigate the optical properties of semiconductor materials. The wavelength range of the absorption spectrum shown in Figure 6 (a) is 200 nm to 800 nm. Using the graph of Tauc Figure 6 (b) and the UV-DRS spectrum, the optical transition energy of the ZnO nanoparticle samples was calculated as follows [22]:

$$(\alpha hv)^n = A(hv - E_q), \tag{3}$$

where: hv – photon energy; E_g – optical band gap; A – is constant; α – absorption coefficient, n can take the values 2 or 1/2, for direct or indirect optical transitions, respectively.

The E_g values are deduced from the graph of $(\alpha hv)^n$ relative to hv and extrapolated a line to the hv axis. Usually, ZnO is a material with a direct band gap. Accordingly, for n = 2 the highest optical transition is attributed to the difference between the valence and conduction bands, creating a functional band gap. ZnO excitation can occur through indirect optical conversion due to defect generation and/or complex phases. The energy band gap of nano ZnO is found in the range of 3.2–3.7 eV and from the graph the value was calculated to be 3.4 eV. The results show that the absorption of ZnO nanoparticles is in the UV region and therefore all irradiation experiments were performed using a UV light source [23].

Features of ZnO nanoparticles-coated cotton fabric

Tensile strength

According to national standard TCVN 1754:1986 (Woven fabrics - Method for determining tensile strength and extension at break), the experiments were conducted at the Laboratory of Textile Materials, School of Textile - Leather and Fashion, Hanoi University of Science and Technology. In particular, the dimensions of the test samples are 350x50 mm with a functional dimension of 200x50 mm. In a dried state, the external tensile force of cotton fabric was measured before and after surface treatment with



Figure 7. Mean tensile strength at break of warp of cotton fabric, warp of ZnO nanoparticle coated cotton fabric, weft of cotton fabric, and weft of ZnO nanoparticle coated cotton fabric with standard deviation.



(a)

(b)

Figure 8. Representative stress-strain diagram of cotton fabric before and after ZnO nanoparticle coating treatment a) in the longitudinal direction and b) in the horizontal direction.

ZnO in vertical and horizontal positions. The resulting mean tensile strength at break with standard deviation is depicted in Table 1 and Figure 7.

From the recorded results, it can be seen that, after immersing the cotton fabric in ethanol containing ZnO nanoparticles to create self-cleaning fabric, the breaking strength of the fabric was reduced, specifically about 8.03% in the longitudinal direction and about 10.38% horizontally, Figure 7. The explanation for the strength reduction of cotton fabric after ZnO nanocoating is due to the fact that the nanometer-sized semiconductor molecules penetrate and form bonds with the fiber structure, leading to the weakening of hydrogen bonding and intermolecular bonds within the molecular network of the fiber.

The representative graphs of contton fabrics after treatment with ZnO showed a decrease compared to the original cotton samples in terms of stress. The details are illustrated in Figure 8.

Fabric breathability

From Table 2 and Figure 9, the ZnO nanoparticlecoated fabric is less breathable than the original cotton fabric. Particularly, there is an 8.35% reduction in permeability compared to pristine fabrics. The decline in the breathability of the fabric following ZnO coating treatment can be explained by the nanometer-sized ZnO particles adhering to the surface around the fibers, thereby decreasing the pore size.

Moisture absorption

In this study, experiments were carried out with an ordinary oven with fabric samples prepared according to National Standard TCVN 1749:1986 with dimensions of 8x8 cm (weight about 8-10 g). The actual moisture content of the test sample - W in % according to the formula:

Table 2. Fabric breathability [l.m ⁻² .s ⁻¹]								
	Sample size	Fabric breathability with standard deviation [I.m ⁻² .s ⁻¹]	Mean comparison (Student's t test)					
Cotton fabric	10	221.3±2.89	t* (p=0.05) = 13.73 t = 2.09					
ZnO nanoparticles coated cotton fabric	10	202.8±3.13						

t = Student's test value; $t^* =$ minimum t value for rejecting the null hypothesis with a 95% significance.



Figure 9. Breathability of cotton fabric and ZnO coated cotton fabric.

Table 3. Results of measuring moisture absorption and liquid absorption of cotton fabric compared to ZnO nanoparticle coated cotton fabric.

	Sample size	Cotton fabric	ZnO coated cotton fabric	Mean comparison (Student's t test)
Saturation state <i>m</i> [g]	5	10.31±0.02	10.94±0.03	t* (p=0.05) = -30.69, t = 2.36
Dry state <i>m_k</i> [g]	5	8.22±0.02	8.88±0.04	t* (p=0.05) = -28.14, t = 2.45
Wet state <i>m_n</i> [g]	5	11.65±0.08	11.79±0.16	t* (p=0.05) = -1.47, t = 2.45
Water absorption capacity LAC [%]	5	41.74±0.63	32.73±1.37	t* (p=0.05) = 11.96, t = 2.45
Hygroscopicity <i>W</i> [%]	5	25.37±0.11	23.29±0.22	t* (p=0.05) = 17.17, t = 2.45

t = Student's test value; t^* = minimum t value for rejecting the null hypothesis with a 95% significance.

$$W = (m - m_k)/m_k,\tag{4}$$

where: *m* is the mass of the test piece before drying [g], m_k is the mass of the test piece after drying [g]. The resulting liquid absorptive capacity (*LAC*) of each

sample is presented in percentage:

$$LAC = \left(\frac{m_n - m_k}{m_k}\right) 100,\tag{5}$$

where: m_k [g] is the mass of the dry fiber, m_n [g] is the mass of the fiber and liquid (distilled water) absorbed at the end of the test.

From the survey results in Table 3, it can be seen that the liquid absorption capacity of cotton fabric is relatively good (more than 41.74%) and the moisture absorption is 25.36%. This result is due to the influence of hydrophilic groups in the structure of cotton fibers (the main components are cellulose molecules). In this case, there is an interaction between the water molecules and the structure of the fiber, because natural fibers (including regenerated fibers of natural origin) with hydrophilic groups interacting with OH- group containing liquid will absorb a large amount of water. During the first interaction between the fabric and water, the water will attach to the hydrophilic groups of the fabric. Then, water molecules either attach to hydrophilic groups or attach to previously attached water molecules to form a new layer. Water molecules directly bonded to hydrophilic groups are tightly bound and have limited movement. The water molecules are indirectly connected to each other, have a looser structure, and move more easily.

Liquid absorption ability (water absorption) of cotton fabric coated with ZnO nanoparticles by volume ratio of fabric: ZnO = 10:1 was experimentally recorded as 32.73% and the moisture absorption rate reached 23.28%. Values tend to decrease compared to untreated cotton samples. The reason given to reduce the hygroscopic value of the fabric is that the ZnO oxide nanoparticles tend to enter the gaps between the fabrics, capturing the localization of water molecules that can be held on the fabric. At the nanoscale, these catalytic particles are insoluble in



Figure 10. The ability (a) to absorb MB, (b) MO of ZnO nanoparticles, and (c) MB, MO colorant conversion chart of ZnO nanoparticles.



Figure 11. (a) MB and (b) MO decomposition by photodegradation effect utilized ZnO nanoparticles under UV light irradiation.

water but dispersed and suspended in water as a suspension. Therefore, the fabric coated with ZnO nanoparticles has lower hygroscopicity and water absorption capacity than ordinary cotton fabrics. In addition, the bond between the ZnO nanoparticles and the cotton fabric is mechanical bonding, with the demonstration of affinity and attraction between the molecules (Van der Waals attraction) making it possible for them to fall off the fabric.

The absorption and degradability of ZnO nanoparticles

MB, MO adsorption capacity of ZnO nanoparticles

The adsorption of pigments onto ZnO takes place due to the interaction between ZnO molecules in equilibrium state with small pigment molecules. On the surface of the ZnO molecules, the attraction happens because of various functional present groups. As a result, the pigment is adsorbed on the surface of ZnO decreasing the dye concentrations. In the practice of this experiment, the amount of ZnO used was 0.005 grams per 10 ml against 10 ppm MB and 10 ppm MO solutions. The experiment was completely done within 30 min in the dynamic state using HY4 horizontal shaker in the absence of light. According to the results from Figure 10 ZnO effectively absorbs the dye color in the first 15 min (estimated at 46.92% against MB) and slows down for the next 15 min. At the end of the adsorption process, which lasted for about 75 minutes, the MB concentration reduction over time reached 76.01%. For MO, in the first 30 minutes of the adsorption process, the amount of MO decrease reached about 42.56% and ended after about 75 minutes with the dye conversion rate in the range of 47.56%.

The ability to decompose MB, MO under UV light condition

The pigment solutions, after undergoing adsorption in the dark chamber, continue to be assessed for color reduction using the photodegradation effect using ZnO under the effect of 60W UV lamp under continuous agitation.

From Figure 11, the MB and MO dye solutions lost color quickly in the first 30 minutes (MB reached 38%, MO reached 51%), and gradually decreased in the following times. After 17 hours, the discoloration of MB ended with a result of 97%, and that of MO was 92%.

			Cotton fabric [g]				ZnO nanoparticles coated cotton fabric [g]							
Sample 1			1.19						1.29					
Sample 2					1.21					1.31				
Sar	nple 3				1.21					1.32				
Sar	Sample 4		1.19						1.31					
Sar	nple 5		1.18						1.29					
Av	erage				1.20					1.30				
otton	MB-0h	MB-2	2h N	IB-4h	MB-6h	MB-8h	MB-10h	MB-12h	MB-14h	MB-16h	MB-18h	MB-20h		
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			400		400	500	300	0		000	100			

Wavelength (nm)

(b)

Table 4. Mass of cotton and cotton fabric coated with ZnO nanoparticles.

Figure 12. (a) The color change of MB on ZnO coated cotton fabric every 2 hours and (b) The graph of color intensity change of MB on cotton fabric containing ZnO under the effect of UV light.

The self-cleaning ability of ZnO nanoparticles-coated cotton fabric

By impregnation method, the cotton-ZnO fabric samples used in the self-cleaning experiment has a mass of ZnO equal to one tenth the mass of cotton fabric. According to calculations, the amount of ZnO nanoparticles on the fabric is about 10% with the average weight value of the cotton fabric sample using the same size of 3x3cm given in the Table 4.

In this study, a catalyst-coated fabric sample containing ZnO nanoparticles was stained with 10 ml of colorant. After each period of time under UV irradiation, the color of the fabric samples was recorded on the colorimeter Ci4200 Spectrophotometer at the material testing laboratory, Hanoi University of Science and Technology.

Self-cleaning ability of cotton fabric containing nano ZnO for MB pigment

Under UV irradiation with a 60W UV lamp, the K/S values of MB tinted ZnO coated cotton samples can be displayed in Figure 12(b). After 20 h of UV

irradiation, the color of the untreated cotton sample is not changed during the test, while the color of the ZnO-coated fabric faded, the Figure 12(a) illustrates the changing color photos of MB stained ZnO-coated samples over time. The fading of the blue color of MB on the fabric can also be clearly seen with the naked eye as shown in Figure 12(a).

The color change of fabrics containing MB is wellobserved at the wavelength ranges above 630 nm. The experiment stops when the K/S value does not change or changes are small, or insignificant. Because the process of photodecomposition is a oneway reaction process.

<u>The self-cleaning ability of cotton fabric</u> <u>containing nano ZnO for MO pigment</u>

Similar to MB, the color change of MO-stained ZnO/cotton fabric can also be seen clearly and quantified through the K/S value histogram at the wavelength range of 420 - 500 nm. The color of the fabric samples changed with MO decomposed through time, and the differences were depicted in Figure 13 (a) and (b).



(b)

Figure 13. (a) The color change of MO stained ZnO coated cotton fabric every 2 hours and (b) The graph of color intensity change of MO on cotton fabric containing ZnO under the effect of UV light over time every 2 hours.

CONCLUSION

In this study, ZnO metal oxide nanoparticles were successfully synthesized and immobilized onto cotton fabrics, creating a self-cleaning fabric. The properties of ZnO nanoparticles were analyzed through SEM, FTIR, EDS, and UV-Vis characteristics. The selfcleaning ability of the ZnO coated cotton fabric was evaluated and quantified through K/S values. The results showed that under continuous UV illumination. MB and MO pigments stained cotton fabric coated with ZnO nanoparticles were faded after about 20 hours, the decoloration can be observed clearly through time. The findings of this study can be considered as a development basis for self-cleaning fabric under the effect of actual sunlight (including visible and invisible light). It is also the premise for the development of self-cleaning fashion products with high applicability.

Funding: This work was funded by the Vietnam Ministry of Education and Training under Grant No. B2022-BKA-18.

Acknowledgement: The authors would like to thank the RoHan Project funded by the German Academic Exchange Service (DAAD, number 57315854) and the Federal Ministry for Economic Cooperation and Development (BMZ) within the framework of the "Following training program". SDG bilateral university" supported a number of measurements.

REFERENCES

- Basnet P., Samanta D., Chanu T.I., et al.: Visible light facilitated degradation of alternate dye solutions by highly reusable Mn-ZnO nano-photocatalyst, Journal of Alloys and Compounds 867, 2021, 158870. <u>https://doi.org/10.1016/j.jallcom.2021.158870</u>
- Kaliraj L., Ahn J.C., Rupa E.J., et al.: Synthesis of panos extract mediated ZnO nano-flowers as photocatalyst for industrial dye degradation by UV illumination, Journal of

Photochemistry and Photobiology B: Biology 199, 2019, 111588.

- https://doi.org/10.1016/j.jphotobiol.2019.111588
- Sharma P., Kumar N., Chauhan R., Singh V., Srivastava V.C., Bhatnagar R.: Growth of hierarchical ZnO nano flower on large functionalized rGO sheet for superior photocatalytic mineralization of antibiotic, Chemical Engineering Journal 392, 2020, 123746.
 - https://doi.org/10.1016/j.cej.2019.123746
- Sarkar C., Basu J.K., Samanta A.N.: Synthesis of novel ZnO/Geopolymer nanocomposite photocatalyst for degradation of congo red dye under visible light, Environmental Nanotechnology, Monitoring & Management 16, 2021, 100521.
 - https://doi.org/10.1016/j.enmm.2021.100521
- Batra V., Kaur I., Pathania D., et al.: Efficient dye degradation strategies using green synthesized ZnO-based nanoplatforms: A review, Applied Surface Science Advances 11, 2022, 100314. https://doi.org/10.1016/j.apsadv.2022.100314
- Alagarasan D., Harikrishnan A., Surendiran M., et al.: Synthesis and characterization of CuO nanoparticles and evaluation of their bactericidal and fungicidal activities in cotton fabrics, Applied Nanoscience, 2021, pp. 1-10. https://doi.org/10.1007/s13204-021-02054-5
- Wei D.W., Wei H., Gauthier A.C., et al.: Superhydrophobic modification of cellulose and cotton textiles: Methodologies and applications, Journal of Bioresources and Bioproducts, 5(1), 2020, pp. 1-15. https://doi.org/10.1016/j.jobab.2020.03.001
- Román L.E., Gomez E.D., Solís J.L., et al.: Antibacterial cotton fabric functionalized with copper oxide nanoparticles, Molecules, 25(24), 2020, 5802. <u>https://doi.org/10.3390/molecules25245802</u>
- Qian J., Dong Q., Chun K., et al.: Highly stable, antiviral, antibacterial cotton textiles via molecular engineering, Nature Nanotechnology, 18(2), 2023, pp. 168-176. https://doi.org/10.1038/s41565-022-01278-y
- Karagoz S., Kiremitler N.B., Sarp G, et al..: Antibacterial, antiviral, and self-cleaning mats with sensing capabilities based on electrospun nanofibers decorated with ZnO nanorods and Ag nanoparticles for protective clothing applications, ACS Applied Materials & Interfaces 13(4), 2021, pp. 5678-5690.

https://doi.org/10.1021/acsami.0c15606

- Milionis A., Tripathy A., Donati M., et al.: Water-based 11. scalable methods for self-cleaning antibacterial ZnOnanostructured surfaces, Industrial & Engineering Chemistry Research, 59(32), 2020, pp. 14323-14333. https://doi.org/10.1021/acs.iecr.0c01998
- 12 Sezgin E., Esen Keçeci M., Akmaz S., et al.: Heterogeneous Cr-zeolites (USY and Beta) for the conversion of glucose and cellulose to 5-hydroxymethylfurfural (HMF), Cellulose 26, 2019. pp. 9035-9043. https://doi.org/10.1007/s10570-019-02702-8
- 13. [El-Nahhal I.M., Salem J., Anbar R., et al.: Preparation and antimicrobial activity of ZnO-NPs coated cotton/starch and functionalized ZnO-Ag/cotton their and Zn(II) curcumin/cotton materials, Scientific Reports, 10(1), 2020, 5410.
- https://doi.org/10.1038/s41598-020-61306-6 Wang S., Li D., Zhou Y., Jiang L.: Hierarchical Ti3C2T x 14. MXene/Ni chain/ZnO array hybrid nanostructures on cotton fabric for durable self-cleaning and enhanced microwave absorption, ACS nano, 14(7), 2020, pp. 8634-8645. https://doi.org/10.1021/acsnano.0c03013
- 15. Mayerhöfer T.G., Pahlow S., Popp J.: The bouguer-beer-Lambert law: Shining light on the obscure, ChemPhysChem 21(18), 2020, pp. 2029-2046. https://doi.org/10.1002/cphc.202000464
- Mäntele W., Deniz E.: UV-VIS absorption spectroscopy: 16 Lambert-Beer reloaded, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 173, 2017, pp. 965-968.
 - https://doi.org/10.1016/j.saa.2016.09.037
- 17. Dalawai S.P., Aly M.A.S., Latthe S.S., et al.: Recent advances in durability of superhydrophobic self-cleaning technology: a critical review, Progress in Organic Coatings, 138 2020 105381 https://doi.org/10.1016/j.porgcoat.2019.105381

- 18. Nguyen-Tri P., Tran H.N., Plamondon C.O., et al.: Recent progress in the preparation, properties and applications of superhydrophobic nano-based coatings and surfaces: A review, Progress in organic coatings, 132, 2019, pp. 235-256
 - https://doi.org/10.1016/j.porgcoat.2019.03.042
- Hossain I., Moniruzzaman M., Maniruzzaman M., et al.: 19. Investigation of the effect of different process variables on color and physical properties of viscose and cotton knitted fabrics, Heliyon, 7(8), 2021, e07735. https://doi.org/10.1016/j.heliyon.2021.e07735
- Estrada-Urbina J., Cruz-Alonso A., Santander-González M., 20. et al.: Nanoscale zinc oxide particles for improving the physiological and sanitary quality of a Mexican landrace of red maize, Nanomaterials, 8(4), 2018, 247. https://doi.org/10.3390/nano8040247
- 21. Zak A.K., Abrishami M.E., Majid W.A., et al.: Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified solgel combustion method, Ceramics International, 37(1), 2011, pp. 393-398.
- https://doi.org/10.1016/j.ceramint.2010.08.017
- Khan S.A., Sahani R., Tripathi R.P., et al ..: Influence of 22. gamma-irradiation on the optical and structural properties of Se85Te15-xBix nano-thin chalcogenide films, Radiation Physics and Chemistry, 188, 2021, 109659. https://doi.org/10.1016/j.radphyschem.2021.109659
- 23. Boulahlib S., Dib K., Özacar M., et al.: Optical, dielectric, and transport properties of Ag-doped ZnO prepared by Aloe Vera assisted method, Optical Materials 113, 2021, 110889. https://doi.org/10.1016/j.optmat.2021.110889