



Sustainable usage of microwave energy to produce TiO₂ nanoparticles

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Abstract

This work's goal is to represent an innovative technique, namely microwave irradiation. It was applied as a rapid method for synthesizing titanium dioxide nanoparticles (TiO₂ NPs) within a few minutes. This takes less period and energy than that consumed when applying the conventional heating method. The effect of different microwave power levels and times on the particle size of the obtained TiO₂NPs was studied. The obtained TiO₂ NPs were characterized using scanning electron microscopy coupled with an energy dispersive spectrometer (SEM-EDX) and transmission electron microscopy (TEM). The finding demonstrated that the particle sizes of the prepared TiO₂ appear in a nano-scale size, regular and uniform particle structure, with narrow distribution, the lowest size was attained at 90% watt for 10 min. In addition, the energy dispersive spectrum (EDX) provided additional evidence that the microwave-assisted TiO₂ NPs integrated into wool fabrics were successful (signal at 0.2 KeV). The effects of TiO₂ NPs on the multifunctional properties of the wool fabrics including coloration, antibacterial and self-cleaning were evaluated. The result showed that the maximum K/S value was obtained at 40°C for 5 min when the fabric was treated before dyeing, but when the fabric was treated after dyeing, the highest value was obtained at 80°C for 20 min. Increased treatment time caused the treated colored fabrics to become lighter and more yellowish-red in color, and later the fabrics took on a more brownish-yellow hue. The overall results revealed that the oxide was successfully prepared by using microwave heating in the Nanoscale. The dyed treated fabrics by prepared TiO₂ NPs exhibited excellent color fastness, and good antibacterial, as well as self-cleaning properties. In conclusion, the procedure adopted for fabricating these multifunctional fabrics is environmentally friendly besides saving time, water, chemicals, and energy as well as the actual cost

Keywords: Titanium dioxide, microwave irradiation, multifunctional fabrics, Self-cleaning, and Antibacterial.

1. Introduction

Organic and biological molecules are transformed into minimal and less naughty substances because of TiO₂'s strong antibacterial and self-cleaning properties. In addition, TiO₂ offers a larger surface area at the nanoscale, which could improve the interaction between photocatalysts. Numerous applications, such as the creation of molecular hydrogen, self-sterilization, water purification, and air purification, may be of interest to this photo-catalytic activity. Additionally, due to TiO₂'s strong capacity for self-cleaning, chemical and biological molecules are transformed into simpler, less naughty substances. Generating TiO₂ at the nanoscale using various synthetic techniques is therefore highly helpful for maximizing the effectiveness of TiO₂ applications [1].

However, there are fewer studies regarding its synthesis to enhance the multifunctional capabilities of wool and other fabric surfaces via microwave irradiation. Many researchers have worked on synthesizing TiO₂ NPs by various procedures [2, 3]. Research on microwave irradiation is expanding quickly, and it is regarded as a cutting-edge technology that can speed up different chemical reactions. In contrast to conventional approaches, microwave activity uses less time and energy during interactions and can create nanoparticles with excellent purity and narrow molecular size distribution, which will improve a variety of molecules' physical and chemical properties [4, 5].

Using innovative technologies, the textile industry is increasingly striving to reduce the time, energy, water, and environmental damage associated with

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textile processing. Microwave irradiation is a technology that can be used in a variety of textile processes, including pretreatment, dyeing, finishing, and printing. Microwave heating can reduce heating time and energy consumption. It can also improve and accelerate many processes.

The main determinant of microwave radiation is the dielectric heating phenomenon. Some polar substances (liquids or solids) have the ability to absorb microwave radiation and transform it into heat. From this point on, the capacity of the dipoles to be oriented in the direction of the electrical field depends on the strength and direction of the electric field and is governed by either their ionic conductivity or dipolar polarization. Molecules with a persistent dipole moment can entirely or partially align themselves with the field direction by orientation. Therefore, molecular friction and dielectric loss squander energy in a variety of heat. The efficiency of the matrix directly affects the amount of heat produced by this technology [6-9].

The objective of this work is to develop a suitable, easy, affordable, and quick approach for the synthesis of TiO₂ NPs in a matter of minutes using microwave irradiation as a heating source for enhancing the dyeability and versatility of wool materials. On the production of TiO₂ NPs, the effects of time and microwave power levels have been studied. The produced TiO₂NPs are used to improve the self-cleaning, antibacterial, and coloring capabilities of wool fibers.

2. Materials and methods

2.1. Materials

2.1.1. Fabric

100% Wool fabric were kindly supplied by Misr Company for Spinning and Weaving El-Mehalla El-Kubra, Egypt. Before using, the fabrics were scoured in aqueous solution containing (3g/L) non-ionic detergent (Hostapal, Clariant, Swiss) and 2g/L of sodium carbonate at 60°C for 30 min then the fabric was thoroughly rinsed in cold water, and finally dried at ambient temperature.

2.1.2. Dyestuff

The applied dyestuff was derived from Indian-type safflower petals purchased from a commercial store (HARAZ). Dye structure showing in (Fig.1).

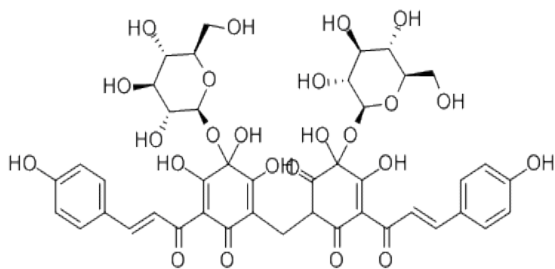


Fig 1: Structure of Safflower yellow dye

2.1.3. Chemicals

- Aldrich provided commercial titanium dioxide TiO₂ nanoparticles (100 nm).
- Fluka graciously provided titanium tetrachloride (TiCl₄, purity > 99.9%).
- Additional chemicals included laboratory-grade substances like acetic acid, citric acid, sodium carbonate, ammonia, and ethyl alcohol.

2.2. Methods

2.2.1. Synthesis of TiO₂NPs via conventional heating:

3.5 ml TiCl₄ 50 ml Deionized H₂O 0°C, Ice water bath TiCl₄ solution HN₃.H₂O White precipitate Calcination and dried at different microwave power level (60-90) and time (4-10 min.) Washing TiO₂ nano-particles 350 ml CH₃OH vigorous stirring for 30 min at room temperature. Fig. 2 presents a detailed process illustration

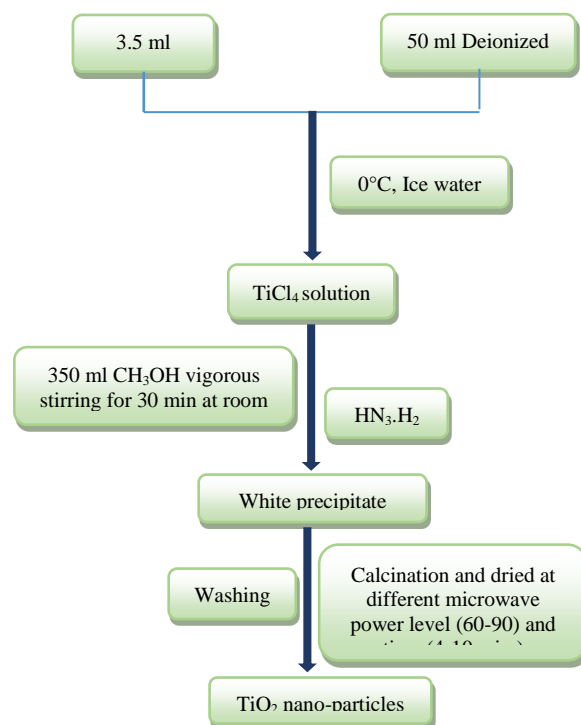


Fig.2: Synthesis of TiO₂ nano-particles via microwave heating

2.2.2. Synthesis of TiO₂ Nano particles via MW Irradiation

TiCl₄ served as the major starting material for the approach using the sol-gel method. [10, 11].

2.2.3. Dyeing processes

Wool fabrics were dyed simultaneously utilizing microwave irradiation and conventional thermal heating. For comparison, (4g dye/100 ml H₂O at 80°C for 10 min when microwave irradiation was used, and 5g dye/100 ml H₂O at 100°C for 2 hours when conventional thermal heating was used, at pH 4, L.R. 1:100.

2.2.4. Wool treatment:

2.2.4.1. Pre-treatment

By using an exhaustion procedure of 1% W.O.F., L.R. 1:100, for 20 minutes at 80°C when applying microwave irradiation while for 2 hr. at 100°C when applying traditional heating in the presence of a wetting agent, the obtained TiO₂ NPs were applied to the surface of wool fabric. Wool fabrics were similarly treated with commercial TiO₂ NPs for comparison's sake. The treated wool fabrics were dried at room temperature, then dyed as described above (2.2.1) after being cured at 140°C for 10 min, and washed at 60°C for 20 min.

2.2.4.2. Simultaneous-treatment

The above-described methods of dyeing and treating with the produced TiO₂ NPs were carried out in a single bath.

2.2.4.3. Post-treatment

In this form of treatment, dyeing methods were used initially, and then the generated TiO₂ NPs and the commercial one were used for treatment.

2.5. Analysis and Testing

2.5.1. Colorimetric Measurements

2.5.1.1. Color strength measurement

The high reflectance approach was used to assess the color strength of the dyed samples represented as K/S [12]. The printed fabrics' reflectance was measured using a PERKIN - ELMER Lambda 3B UV-V Spectrophotometer. Applying the Kubelka Munk equation, the color strength, denoted as K/S, was evaluated as follows:

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

Where K is the absorption coefficient, S is the scattering coefficient, R is the decimal fraction of the reflectance of the dyed cloth, and R^o is the decimal fraction of the reflectance of the undyed fabric.

2.5.1.2. Fastness properties

The colored samples' fastness characteristics were assessed using ISO-required techniques. Three tests, in particular, were performed: ISO 105-C06 (2010) for color fastness to washing; ISO 105-E04:2013 for color fastness to perspiration (acid and alkaline); and ISO 105-B02 (2014) for colorfastness to light [13]

2.6. Evaluation

2.6.1. Scanning Electron

Microscopy (SEM) With a Quanta FEG-250 microscope operating at a voltage of 10 KV, Surface morphologies of the samples were taken. To prevent charging, the samples were sputter-coated with gold before scanning.

2.6.2. Transmission Electron Microscopy (TEM)

A high resolution JEOL JEM-2100 Transmission Electron Microscope was used to acquire TEM images of the produced TiO₂ NPSS (Japan). The samples were placed on a micro grid covered with a thin carbon sheet

(about 200 nm) after being deposited from an aqueous dilute dispersion.

2.6.3. Antibacterial assay

Filter paper disc diffusion was used to test the antimicrobial activity. For the antibacterial assay, SMA and Mueller Hinton agar (Difco) containing 100 ppm of 2, 3, 5-triphenyltetrazolium chloride were employed. To distinguish bacterial colonies and make the inhibition zone clear, 2, 3, 5-triphenyltetrazolium chloride was added to culture media [14]. Staphylococcus aureus (G+) and Escherichia coli (G-) bacteria (0.1 ml each) were directly added to each plate from the broth. After four days of 40C incubation on all plates, the inhibition zones were measured and recorded in millimeters (mm). The scale of measurement was as follows (disc diameter included): a inhibitory zone measures 28 mm, a moderately inhibitory zone measures 16 to 10 mm, and a non-inhibitory zone measures 12 mm. 26-28. Antibiotics were used to prepare control plates [15].

2.6.4. Self-cleaning Action

By focusing visible light on the samples of wool fabric that had been treated with TiO₂, the self-cleaning ability of the wool was examined. On the wool fabric, a measured amount of 6% coffee solution was applied and allowed to spread. Each stain on the fabric had one half exposed to sunlight for 12–48 hours, while the other half was shielded from sunlight with a black piece of paper. For self-cleaning action, the exposed and covered portions of the stain were compared. SS 5100A, premier color scan Coffee stain photo degradation was measured using a spectrophotometer [16].

3. Results and Discussion

Numerous researchers used various methods to create TiO₂ NPs. [3-5, 17]; nevertheless, there are few studies that use microwave irradiation to increase the multifunctional quality of wool fabric surfaces. Nanotechnology has grown significantly during the past few decades. New physical and chemical properties will emerge after the nano particle is produced, or when the size of the substance is reduced to the nano scale. Small particle surface area is helpful for a number of characteristics, including facilitating simple interaction and absorption between both (dyes and fabrics), which depends on the material surface. However, because of its widespread availability, lack of hazardous properties, low cost, biocompatibility, and high availability, TiO₂ is one of the most widely used commercial nanomaterial's.

3.1. Scanning Electron Microscopy (SEM)

The TEM images of the produced TiO₂ NPs were shown in Figures (3a-d) and (4a-c) by employing microwave irradiation as a heating source at various power levels (60, 70, 80, and 90 watts) for 8 minutes and for various times (2, 4, 6, and 10 minutes) at power

level 90. The TEM picture revealed that the TiO₂ NPs were smaller than commercially available ones and had a regular, homogenous particle structure with a restricted size distribution (3e). The prepared TiO₂ NPs have uniformly rhombohedral morphology with average diameters of about 58.76-42.02, 57.16-10.28, 27.13-13.49, and 8.53-7.31 nm at power levels 60, 70, 80, and 90, respectively. In contrast, the prepared TiO₂ NPs at power level 90 for different time have a uniformly spherical morphology with average diameters of about 20.02-9.40, 7.51-1.61, and 1.37-1.25 nm for 4, 6, 10 min respectively. The energy dispersive spectrum (EDX) of the nanoparticles is shown in Figure 3f. This figure displayed a signal peak at ca 0.2 KeV related to the optical Plasmon resonance (OPR) which was designated to the formation of titanium oxide nanoparticles. In microwave irradiation, microwave energy is delivered through the medium as electromagnetic energy rather than a thermal heat flow. Then, as the heating rate is variable, the similarity of the heat dispersion is greatly enhanced. Molecular structure has an impact on the microwaves' capacity to interact with materials and transmit energy. The phenomenon known as "selective heating" occurs when interacting materials' own dielectric characteristics combined with the higher loss material will be done so selectively by microwaves [17- 19]. Contrarily, when conventional thermal heating is used, a lot of time and energy is expended in order to heat the interface through conduction through the substrates. However, the common interface can be internally heated while utilizing microwaves. From the all above result, we can conclude that the power level of 90 for 8 min is the preferred condition for prepared TiO₂ NPs

3.2. Treatment of wool fabric with TiO₂ NPs

3.2.1. Dyeing and incorporating TiO₂ nanoparticles immobilization into the wool fabric's matrix mechanism

The high Carthamus yellow content of the safflower aqueous extract has attracted much notice as the natural color. By forming an ionic link with the wool fabric's amino groups, the aqueous extract's high concentration of Carthamus yellow A and Carthamus yellow B rich extracts can give the surface of the wool fabric both color and multifunctional quality. Wool is made of protein fibers that include both amino groups and free carboxylic groups (-COOH) (-NH₂). When the wool fabric was dyed with saffron yellow, the dye uptake increased dramatically in the acidic medium, reaching a maximum color depth at pH 4. As a result, the electrical charges on the wool fabric depend on pH. This outcome is explained by the structural characteristics of both colorants and wool fabric. Amino groups on the surface of the wool fabric are protonated in an acidic solution. On the other hand, the

surface of the extracted yellow colorants had negative charges that were developing [20-22]. As a result, ionic bonds are created with the protonated amino groups (-NH₃⁺) on the surface of wool fiber. More (+) charges are available on wool surface textiles and more dye spots are accessible below the isoelectric point of wool keratin (at pH 4), which increases dye uptake. In an alkaline environment, wool fibers create fewer (+) charges and more (-) charges on carboxylate anions, which reduces absorption. The adsorption of safflower yellow dye on wool is suggested to be represented by a scheme (1).

3.2.2. Optimization of treatment and dyeing conditions

Wool samples were treated both before and after the dyeing procedures to ascertain the impact on K/S values of the treatment of the wool fabric by the produced TiO₂ NPs. In order to compare the treatment to the commercial one, it was performed using 2% (W.O.F) of TiO₂NPs (at power level 90 for 10 min) at various temperatures (40, 60, and 80°C) (fig.5), and for various time (5–20 min) (fig.6).

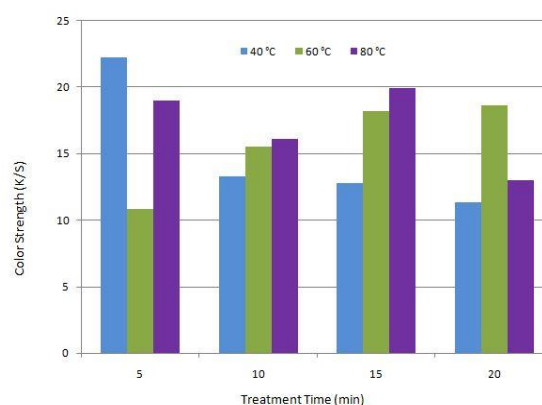


Fig 5: Effect of pre-treated fabric by prepared TiO₂ NPs on K/S of treated wool fabrics at different temperature (°C) and different time (min.)

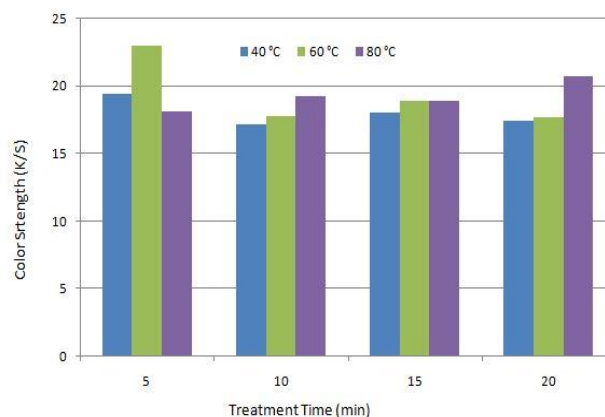


Fig 6: Effect of post-treated fabric by prepared TiO₂ NPs on K/S of treated wool fabrics at different temperature (°C) and different time (min.)

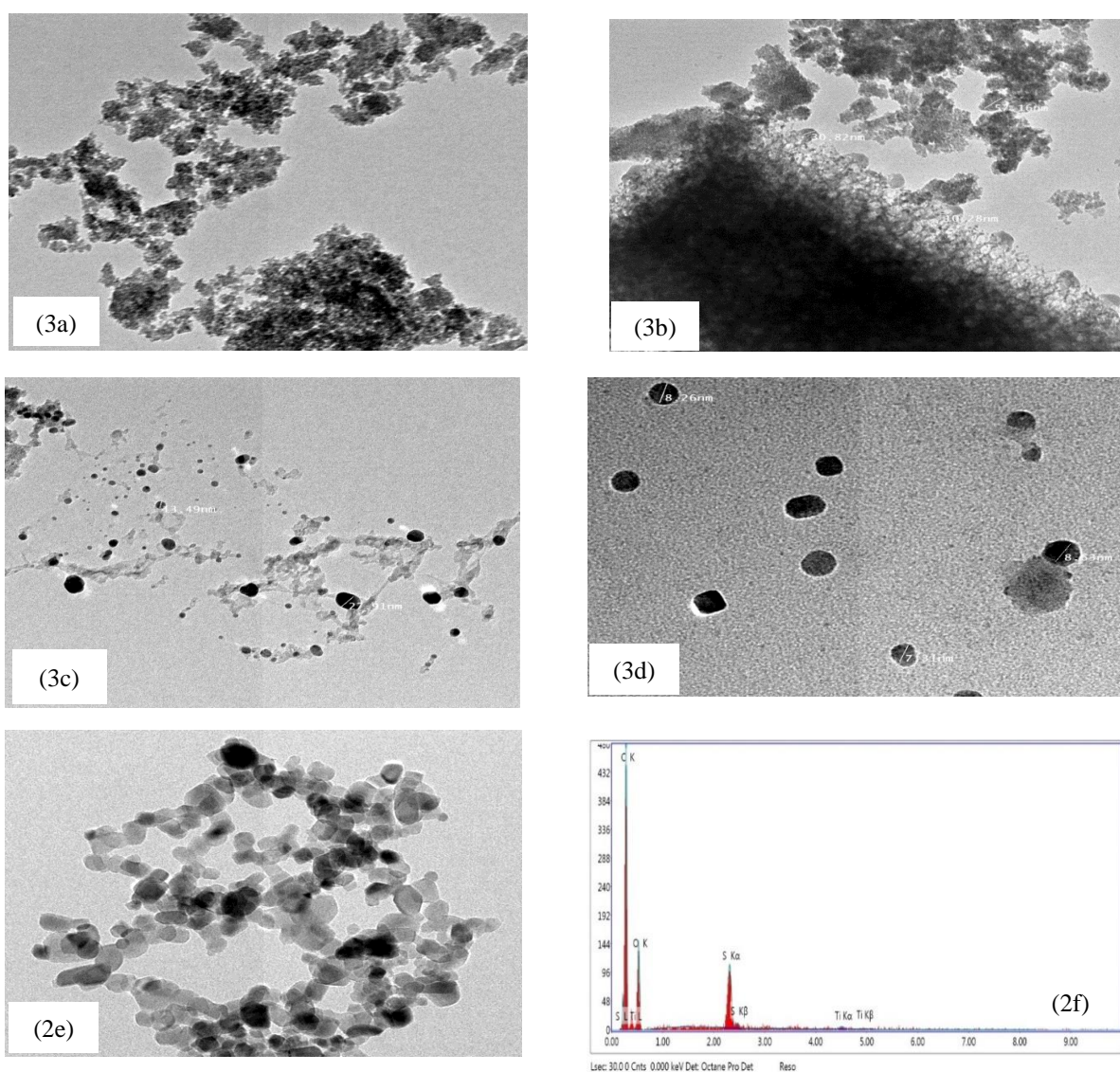
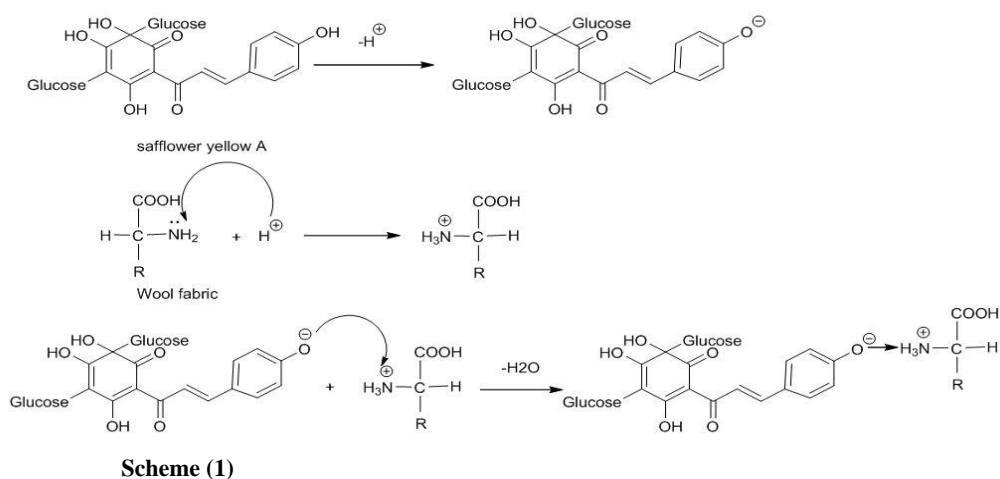


Fig 3: TEM graph of the prepared TiO₂NPs at power level (a) 60, (b) 70, (c) 80, (d) 90 for 8 min. (e) commercial TiO₂NPs and (f) EDX analysis.

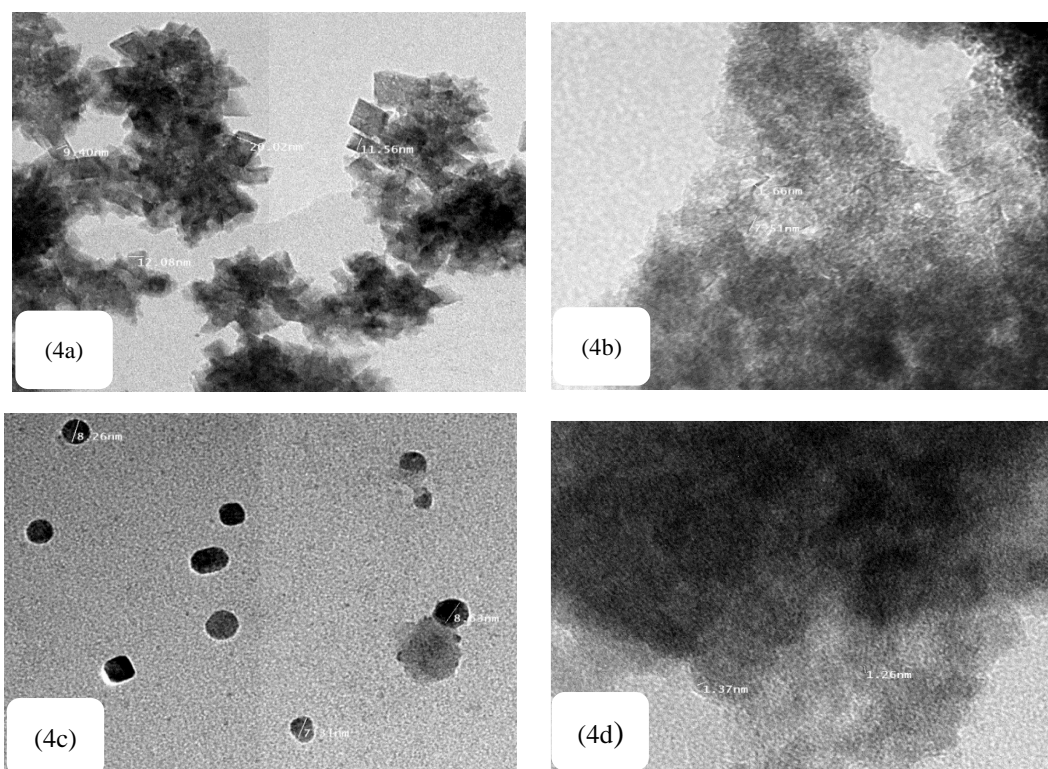


Fig 4: TEM graph of the prepared TiO_2 NPs solution at power level 90 for different time (a) 4, (b) 6, (c) 8, (d) 10 min.

Safflower yellow dyes that had been extracted were used for the dyeing procedure (MW irradiation: 4 g/100 ml, at 40°C for 10 min.), (CH method: 5g/100 ml at 100°C for 60 min at pH 4 and LR 1:50 for both approaches using the simultaneous exhaustion method K/S was measured at ($\lambda_{\text{max}}=375$). Safflower extracts were used to introduce the light/dark yellow color when dyeing wool fabrics. The color strength (K/S), and CIE (L^* , a^* , b^*) were determined in order to elucidate the impact of the various factors on the color of the treated wool (before and after dyeing), and the results are presented in Table 1 and shown in Figures 5, 6. It is clear that when temperature and time increased, the K/S at the wavelength of maximum absorption did as well. When the fabric was pretreated with the prepared TiO_2 NPs before dyeing, the adsorption increased quickly with a maximum color strength at 40°C for 5 minutes. While the maximum value was achieved after the fabric had been dyed at 60°C for 5 minutes. However, TiO_2 NPs synthesized by microwave irradiation can heat up very quickly and consequently have a higher K/S value as a result. This might be a result of both the structure of the wool fabric and the impact of microwave radiation. Opening up pores in the amorphous area of wool fabric at a higher temperature cause: a) an increase in the approachability of dye molecules; b) an easier time for

dye molecules to diffuse into the wool fabric; and c) a greater amount of dye to be adsorbed on the surface of the wool fabric. Electromagnetic waves can produce energy-rich photons concurrently. Two parameters, including wave frequency and wavelength, determine the photon energy. Near 0.125 kJ/mol, microwave radiation emits photon energy [23–25].

The CIE (L^* , a^* , and b^*) is usually employed to estimate the coloration process. The data in Table 1 illustrate the colorimetric parameters (L^* , a^* , and b^*) of wool fabrics treated before and after the dyeing process with extracted safflower yellow dye. This data reveals that increasing the treated time, as well as temperature, resulted in the increase of L^* values and thus the color of the samples got lighter. By increasing the treated bath temperature and time, a^* values dramatically decreased in the positive direction, while b^* values were increased in the same direction. The treated dyed sample fabrics turned to more yellowish red color and became lighter with increasing treated time and thereafter the fabrics are turned to a more brownish yellow color.

3.2.3. Fastness Properties of NPs-treated wool Fabrics

The fastness properties of colored treated wool fabrics before and after dyeing by the prepared TiO_2

NPs (at 90% watt for 10 min), as well as, the commercial one was further evaluated and listed in Table 2. In all treatment conditions, the commercial TiO₂ NPs incorporated wool fabrics before dyeing showed fastness results ranged from good to excellent which is due to the chemical stability of TiO₂ NPs on the wool fabrics, as well as, long-term durable interactions between TiO₂ NPs, dyes and functional

groups (-NH₂, -COOH) of wool fabrics. On the other side, the pre-treated dyed samples by TiO₂ NPs prepared by microwave may lead to the increase of dye penetration and its interaction with wool matrix fabrics. Consequently, accelerates the fixation rate of the colors. It is clear also that the light fastness is ranged from good to excellent in all cases.

Table 1: CIE Lab coordinates at different pre- and post-treated temperature and time of wool fabrics dyed with extracted safflower yellow dye.

Treatment temp °C	L*	a*	b*	ΔE				
					L*	a*	b*	ΔE
Treatment time/ min	Pre-treated				Post- treated			
40°C								
5	45.45	27.94	40.55	56.31	44.38	39.56	44.80	66.60
10	50.28	25.45	42.00	52.94	45.26	38.93	46.20	64.20
15	50.04	24.56	41.68	52.44	46.11	38.85	47.92	65.00
20	56.59	20.20	42.38	47.38	46.73	36.96	65.00	66.72
60°C								
5	46.35	21.07	41.62	48.28	44.61	38.95	39.20	64.05
10	50.59	25.66	43.18	53.47	45.82	37.91	39.66	61.99
15	50.84	36.44	42.46	49.36	46.65	36.79	44.5	63.09
20	57.30	34.36	43.87	59.38	48.61	36.11	44.93	66.03
80°C								
5	46.30	35.33	45.38	60.49	44.71	37.69	37.84	64.87
10	51.32	35.64	45.26	60.76	46.78	36.97	39.27	63.91
15	52.00	38.55	43.40	63.46	47.28	35.99	41.48	63.09
20	57.38	37.71	40.89	61.56	48.91	36.61	42.37	63.45

Table 2: Fastness properties of the untreated and TiO₂NPs-treated dyed wool fabrics

Prepared TiO ₂	Washing Fastness		Rubbing Fastness		Perspiration fastness				Light fastness
	Alt	Stain	Dry	Wet	Acidic		Alkaline		
					Alt	Stain	Alt	Stain	
Wool									
BD (p)	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	6-7
AD (p)	4-5	4	4-5	4-5	4-5	4	3-4	4	6-7
BD (C)	4	4-5	4	4	4	4	4	4	6
AD (C)	4	4	4	4	3-4	3-4	3-4	3-4	5-6

BD= Before Dyeing, AD= After Dyeing, (p) = prepared TiO₂, (c) = Commercial TiO₂

3.3. Antibacterial assay:

Organic and biological molecules are transformed into minimal and less harmful substances because of TiO₂'s strong antibacterial and self-cleaning properties. In addition, TiO₂ offers a larger surface area at the nanoscale, which could improve the interactions between photocatalysts. Numerous applications, such as the creation of molecular hydrogen, self-sterilization, water purification, and air purification, may be of interest to this photo catalytic activity. Additionally, due to TiO₂'s strong capacity for self-cleaning, chemical and biological molecules are transformed into simpler, less harmful substances. Generating TiO₂ at the nanoscale using various

synthetic techniques is therefore highly helpful for maximizing the effectiveness of TiO₂ applications. So, it was converted to evaluate the antibacterial activity of the untreated and treated wool fabric against these two bacterial strains.

Table 3 shows that there is no difference between treated and untreated wool materials in terms of resistance to bacterial adhesion. On the other hand, the antibacterial effect of the treated fabric with the produced TiO₂NPs in wool fabric matrix has been noticeably significantly increased. This finding showed that the microwave-assisted synthesis of TiO₂NPs endows the wool fabric with potent

antibacterial properties, reinforcing the fabric's antimicrobial properties.

The precise mechanism of toxicity is still only partially known, despite the fact that numerous mechanisms for the antibacterial activity of nanoparticles have been identified [28–30]. The primary mechanism put forth is that Ti-containing materials can release Ti ions, which can then interact with proteins' ASH groups to inactivate those proteins.

Additionally, TiO₂ NPs have the ability to enter bacterial cell walls, which may modify the structure of the cell membrane, weakening or even killing the bacterium. Although there is a minor increase in bacterial resistance, this could be because titanium may also interact with the protein found in woolen fibers, which could result in a reduction in bacterial resistance.

Table 3: Antibacterial activity of TiO₂ NPs-treated wool fabrics

Treatment Method	Escherichia coli (G -) /cm	Staphylococcus aureus (G+) /cm
Blank	0	0
Prepared TiO ₂	17	15
Prepared TiO ₂ +Dye (pre-treatment)	20	17
Prepared TiO ₂ +Dye (Post-treatment)	15	12
Commercial TiO ₂	10.5	8
TiO ₂ + Dye (Pre-treatment)	9.5	4
Commercial TiO ₂ +Dye (Post-treatment)	6.5	2

Dyeing condition: 4 g/50 ml H₂O, pH: 4, L.R.1:50, at 60° for 10 min

3.4. Self-Cleaning of wool fabrics treated with the prepared TiO₂ NPs

Due to their chemical stability, nontoxicity, and high reactivity, several kinds of TiO₂ are regarded as potent photocatalysts for various important processes. The primary locations of titanium dioxide photocatalytic activity are depicted in Fig. 7. The photocatalysts technology has some benefits over conventional advanced oxidation procedures (ease of setup and operation at room temperature, no need for post processes, low energy consumption, and therefore low cost).

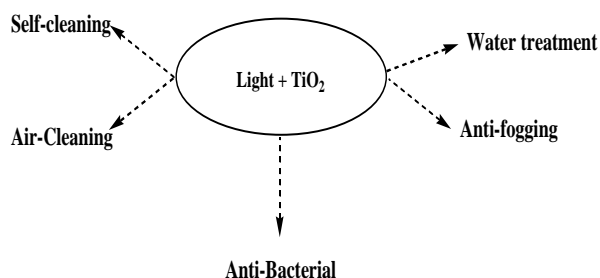


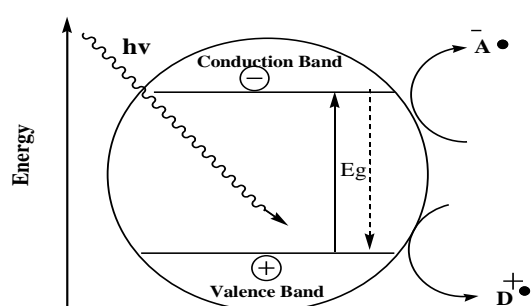
Fig 7: Essential areas of activity in titanium dioxide photocatalysis

On the other hand, exposing the catalyst to light-initiated states can initiate subsequent in contrast, exposing the catalyst to light-produced states that could start future processes including redox reactions

and/or molecular changes. Semiconductors such as metal oxides or sulfides like TiO₂, Fe₂O₃, ZnO, and ZnS can operate as sensitizers for light-induced redox reactions cost because of their electronic structure, which is characterized by a saturated valence band and a non-saturated conduction band. However, when a photon with a high valence energy surpasses the band gap energy (The energy difference between the lowest energy level of the conductive band and the highest energy level of the valence band is responsible for making the material electrically conductive). A whole (e+) is left behind when one electron (e-) is promoted from the saturated level (valence band) to the unsaturated level (conduction band). Negatively charged electrically conducting materials (-) recombined right away [31, 32]. In semiconductors, electron-hole pairs that have been photo excited are trapped at the surface and participate in chemical reactions with the adsorbed donor (D) or acceptor (A) molecules. While the conduction band electrons can decrease the appropriate electron acceptor molecules, the holes can oxidize donor molecules (Fig. 8)

Table 4: Self-cleaning % of wool fabrics treated with different prepared TiO₂ NPs

Treatment Method	Cleaning %
Prepared TiO ₂	75%
Prepared TiO ₂ +Dye (pre-treatment)	85%
Prepared TiO ₂ +Dye (Post-treatment)	70%
Commercial TiO ₂	60%
Commercial TiO ₂ + Dye (Pre-treatment)	75%
Commercial TiO ₂ +Dye (Post-treatment)	65%

**Fig 8:** Processing of photochemical excited TiO₂ molecules

Conclusion

In this study, a novel method involving microwave irradiation was used to speed up the production of titanium dioxide nanoparticles (TiO₂NPs) within a short period. When compared to the thermal heating method, this uses less time and energy. When the synthesis of TiO₂NPs was explored utilizing microwave irradiation at various Watts (60, 70, 80, 90) for various times (4, 6, 10 minutes), the following conclusions could be drawn from the results:

- The particle sizes of the prepared TiO₂ appear in a nano-scale size, regular and uniform particle structure, with narrow distribution if compared with the particles of the commercial one,
- The lowest size was attained at 90 watt for 10 min,
- The prepared TiO₂NPs had uniformly rhombohedra particle size with an average diameter about 57.16-10.28, 27.13- 13.49, and 8.53-7.31nm at 70, 80, and 90 Watt, respectively,
- While the particle sizes of the prepared TiO₂NPs at 90 Watt for different times ranged from 20.02-9.40, 7.51-1.61, and 1.37-1.25 nm for 4, 6, and 10 min respectively.

- The energy dispersive spectrum (EDX) provided additional evidence that the microwave-assisted TiO₂ NPs integrated into wool fabrics successful. The EDX Conduction Band Valence Band Eg Energy hv A D spectrum's signal at 0.2 KeV for elemental Ti showed that the TiO₂NPs were immobilized on the wool fabrics.

- Wool samples are pretreated before and after dyeing procedures, with 2% WOF of produced TiO₂NPs (at 90 watts for 10 minutes), and compared with the commercial one at various temperatures (40, 60, and 80°C), as well as for various times (5-20 min). When the fabric was treated with prepared TiO₂NPs before dyeing, the maximum K/S value was obtained at 40°C for 5 min, but when the fabric was treated after dyeing, the highest value was obtained at 80°C for 20 min. Increased treatment time caused the treated colored sample fabrics to become lighter and more yellowish-red in color, and later the fabrics took on a more brownish-yellow hue.

- The pretreated wool fabrics before dyeing had excellent fastness properties than those of post treated wool fabrics.

- Commercial TiO₂ as well as prepared TiO₂NPs are exhibit potent antibacterial properties against both Gram-positive (ve+) and Gram-negative (e-) bacteria. Treated wool with prepared TiO₂NPs show an antibacterial quality. The resistance to bacterial adhesion is unaffected by the blank fabric. The treated fabric has a remarkable antibacterial effect when the prepared TiO₂NPs are incorporated into a wool fabric matrix. This finding indicated that strong antibacterial properties endowed wool fabrics with microwave-assisted TiO₂NP synthesis, enhancing the fabric's antimicrobial properties.

- When exposed to UV light for 24 hours, the effect of the prepared TiO₂NPs on untreated and treated wool fabric revealed that the color of the TiO₂NPs-striated wool fabric was partially altered. This is because the treatment of wool caused a thin layer of TiO₂NPs to emerge, increasing its hydrophilic properties and causing a high decay effect to appear on the treated wool fabrics.

Conflicts of interest

There are no conflicts to declare.

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References

- [1] 1. Kongsuebchart W., Praserttham P., Panpranot J., Sirisuk A., Supphasirongjaroen P. and Satayaprasert C., "Effect of crystallite size on the surface defect of nano-TiO₂ prepared via solvothermal synthesis." *J. Cryst. Growth*, 297, 234-238 (2006).

<https://doi.org/10.1016/j.jcrysgro.2006.09.018>

- [2] M. Cargnello, T. R. Gordon and C. B. Murray, *Chem. Rev.*, 114, 9319-9345 (2014).
<https://doi.org/10.1021/cr500170p>
- [3] T. Peng, D. Zhao, K. Dai, W. Shi and K. Hirao, *JPC B*, 109, 4947-4952 (2005).
<https://doi.org/10.1021/jp044771r>
- [4] M. Sundrarajan and S. Gowri, *Chalcogenide Lett*, 8, 447-451 (2011).
- [5] H. D. Jang and S.-K. Kim, *Mater. Res. Bull.*, 36, 627-637 (2001).
[https://doi.org/10.1016/S0025-5408\(01\)00552-9](https://doi.org/10.1016/S0025-5408(01)00552-9)
- [6] N. S. Ahmed and R. M. El-Shishtawy, *J. Mater. Sci.*, 45, 1143-1153 (2010).
<https://doi.org/10.1007/s10853-009-4111-6>
- [7] N. Elshemy and K. Haggag, *Journal of Textiles, Coloration and Polymer Science*, 16, 33- 48 (2019).
[10.21608/JTCPS.2019.9928.1019](https://doi.org/10.21608/JTCPS.2019.9928.1019)
- [8] N. Elshemy, M. Elshakankery, S. Shahien, K. Haggag and H. El-Sayed, *Egypt. J. Chem.*, 60, 79-88 (2017).
[10.21608/EJCHEM.2017.1604.1131](https://doi.org/10.21608/EJCHEM.2017.1604.1131)
- [9] M. Rehan, S. Mowafi, S. A. Aly, N. S. Elshemy and K. Haggag, *Eur. Polym. J.*, 86, 68-84 (2017).
<https://doi.org/10.1016/j.eurpolymj.2016.11.022>
- [10] M. Sundrarajan, and S. Gowri, *Chalcogenide Lett*, 8(8), 447-451 (2011).
- [11] G. A. Rajakumar, B. Abdul Rahuman, V. Priyamvada, D. Gopiesh Khanna, Kishore Kumar, and P. J. Sujin. *Materials Letters* 68, 115-117(2012).
doi:10.1016/j.matlet.2011.10.038
- [12] N. ELSHEMY and K. HAGGAG, *Al-Azhar Bull. Sci.*, 21, 35-52 (2010).
- [13] A. Hebeish, A. Abdelrahman, S. Nassar, H. Elsayad and N. Elshemy, *Egypt. J. Chem.*, 63, 7-8 (2020).
[10.21608/EJCHEM.2019.5236.1466](https://doi.org/10.21608/EJCHEM.2019.5236.1466)
- [14] H. El-Hennawi, N. Elshemy, K. Haggage, A. Zaher and A. Shahin. *Biointerface Res. Appl. Chem.*, 10, 5174 - 5181 (2020).
<https://doi.org/10.33263/BRIAC102.174181>
- [15] H. Helmy, M. Kamel, K. Hagag, N. El-Hawary and N. El-Shemy, *Egypt. J. Chem.*, 60, 103-116 (2017).
[10.21608/EJCHEM.2017.1601.1129](https://doi.org/10.21608/EJCHEM.2017.1601.1129)
- [16] H. Gaminian and M. Montazer, *J. Photochem. Photobiol. A* , 332, 158-166 (2017),
<https://doi.org/10.1016/j.jphotochem.2016.08.022>
- [17] S. MALAKPOUR and Z. RAFIEI, Application of microwave-assisted reactions in stepgrowth polymerization: *Iran. Polym. J.* 17 (12), 907-935 (2008).
- [18] M. A. Herrero, J. M. Kremsner and C. O. Kappe, *J. Org. Chem.* , 2008, 73, 36-47.
<https://doi.org/10.1021/jo7022697>
- [19] C. Zhang, L. Liao and S. S. Gong, *Green Chem.*, 9, 303-314 (2007).
DOI: [10.1039/B608891K](https://doi.org/10.1039/B608891K)
- [20] N. Elshemy, S. Mahmoud, H. Mashaly and K. Haggag, *Int. J. Pharm. Sci. Rev. Res.*, 41, 41-47 (2016).
- [21] N. Elshemy, M. Megaly, K. Haggag and A. Hashem, *Egypt. J. Chem.*, 62, 231-245 (2019).
DOI: [10.21608/ejchem.2018.5119.1453](https://doi.org/10.21608/ejchem.2018.5119.1453)
- [22] V. K. Gupta, *Chemistry and technology of natural and synthetic dyes and pigments*, (2019).
- [23] B. L. Hayes, *Microwave synthesis: chemistry at the speed of light*, *Cem. Publ. USA* (2002).
- [24] C. O. Kappe, *Angew. Chem. Int. Ed.*, 43, 6250-6284 (2004).
<https://doi.org/10.1002/anie.200400655>
- [25] J. P. Tierney and P. Lidström, *Microwave assisted organic synthesis*, Wiley Online Library (2005).
- [26] M. Rehan, S. Mowafi, S. A. Aly, N. S. Elshemy, and K. Haggag, *Microwave-heating for insitu Ag NPs preparation into viscose fibers*. *Eur. Polym. J.*, 86, 68-84 (2017),
<https://doi.org/10.1016/j.eurpolymj.2016.11.022>
- [27] J. Prakash, S. Sun, H. C. Swart and R. K. Gupta, *Appl. Mater. Today*, 11, 82-135 (2018).
<https://doi.org/10.1016/j.apmt.2018.02.002>
- [28] M. J. Hajipour, K. M. Fromm, A. A. Ashkarran, D. J. de Aberasturi, I. R. de Larramendi, T. Rojo, V. Serpooshan, W. J. Parak and M. Mahmoudi, *Trends in biotechnology*, 30, 499- 511 (2012).
<https://doi.org/10.1016/j.tibtech.2012.06.004>
- [29] A. Baranwal, A. Srivastava, P. Kumar, V. K. Bajpai, P. K. Maurya and P. Chandra, *Front. microbiol*, 9, 422 (2018).
<https://doi.org/10.3389/fmicb.2018.00422>
- [30] W. Jiang, H. Mashayekhi and B. Xing, *Environ. Pollut.*, 157, 1619-1625 (2009).
<https://doi.org/10.1016/j.envpol.2008.12.025>
- [31] O. Allam, N. Elshemy, O. Hakeim and K. Haggag, *Int. J. Sci. Res.*, 4, 1697-1705 (2015).
- [32]. R. Benedix, F. Dehn, J. Quaas and M. Orgass, *Lacer*, 5, 157-168 (2000).