Review Article

Journal of Chemistry: Education Research and Practice

ZnO and TiO_2 Nanoparticles as Textile Protecting Agents against UV Radiation: A Review

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Submitted: 15 Dec 2017; **Accepted**: 02 Jan 2018; **Published**: 17 Mar 2018

Abstract
The purpose of this review is to highlight the role of ZnO and TiO_2 NPs as textile protective agents against UV radiation. Different synthesis method of ZnO and TiO_2 NPs affecting their nano size and their ability to absorb UV radiation. Resulted ZnO or TiO_2 NPs can be applied on treated or untreated fabrics individually to provide UV protection or in combination with other materials to provide multifunctional finished fabrics. Cons and Pros of each application process besides comparison of synthesis methods of ZnO and TiO_2 NPs are included separately in this review paper.

Keywords: ZnO Nanoparticles -TiO_2 Nanoparticles – UV Protection

Introduction

Protection against ultra violet radiation is one of the most important concerns in textile industry. UV radiation is a form of energy which represented only one type of invisible radiation and it is measured on a scientific scale called the electromagnetic spectrum. Incident sunlight consists of (50% Visible light, 45% Infra-Red and 5% ultra violet radiation) [1].

UV radiation can be subdivided according to their wavelength and effect to: UV- A (320-400nm), UV-B (280-320nm) and UV-C (200-280nm). UV-C is absorbed by ozone layer and does not reach the surface of the earth, so UV-A and UV-B represent the danger of UV radiation especially UV – B as shorter wavelength resulted in higher energy (according to Plank's equation) and more damage in (textiles - dyestuff- human skin) [2].

To block the harmful effect of UV radiation, organic and Inorganic UV blockers are used. Inorganic UV blockers are better than organic UV blockers because of their non-toxicity and chemical stability when exposed to higher temperatures and UV radiation. The most common Inorganic UV blockers are semiconductor oxides such as ZnO and TiO_2 [3]. Nano-size of ZnO and TiO_2 particles showed more durable and effective UV protection than their bulk size [4].

This review is intended to focus on ZnO and TiO_2 nanoparticles and their advanced applications to block the UV radiation and enhance the protection of textiles and human skin. Fabrics ultraviolet protection factor and properties of (ZnO and TiO_2 NPs) have been briefly explained. Different ZnO and TiO_2 NPs synthesis methods (chemical - green) and applications (individually or in combination with other materials to provide multifunctional finished fabrics) have been discussed in details and compared.

Ultra violet protection factor (UPF)

When textile material is exposed to UV radiation, the action of UV included absorption, reflection, scattering and direct transmission. Transmission of UV radiation causes fiber, dye and skin damage. UPF related to reflection and absorbance of UV radiation [5]. UPF value is considered as a measure of blocking UV radiation by the fabric. The higher (UPF) value the more (UV) protection provided by the textile material [1].

ZnO Nanoparticles in textiles UV protection

ZnO properties

Zinc oxide (ZnO) is an inorganic semiconductor material that has a great interest in textiles UV protection field due to its properties (wide band gap, Chemically stable, Environmental friendly, easily grown and Longer durability) [6,7]. In UV protection finishing, ZnO materials are preferred to be used in nano size to provide higher durability and more intensive absorption and blocking in the UV region [1].

ZnO NPs Synthesis

Generally ZnO NPs are obtained by chemical or green synthesis using zinc source such as (zinc acetate-zinc chloride-zinc nitrate) with synthetic or natural materials.

Chemical Synthesis

Sol gel method

Farouk, et al., prepared ZnO NPs with an average size of (30-60nm) by simple chemical Sol-Gel method from zinc acetate as a precursor and lithium hydroxide .The resulted ZnO NPs were embedded in a hybrid polymer (GPTMS) network with different ratios and applied to cotton and cotton/ polyester fabrics by Pad-dry-cure method. The results of SEM investigations demonstrated smoother surface of treated fabrics and uniform distribution of ZnO NPs. Finished fabrics with higher concentrations of ZnO NPs indicated higher UPF values (increasing UPF value in cotton fabric from 21 to 177 and in cotton/ polyester fabric from 19 to 48) [8].

Another group of researchers led by Conde prepared ZnO NPs with an average size (58nm). They used Sol-Gel method and Zinc acetate dihydrate as precursor but they applied sodium hydroxide as a reducing agent instead of lithium hydroxide. Sodium hydroxide action was investigated by adding it with different flows and different alkaline ratios. It was found that slowly addition of sodium hydroxide with maintaining alkaline ratio at 2 resulted in obtaining ZnO NPs with uniform distribution and good absorption in the UV region (380 nm) [9].

Hydrothermal method

Kathirvelu, et al., prepared ZnO NPs by hydrothermal process using water – 1, 2-ethanediol as a solvent and investigating which is better. Sodium hydroxide was added gradually to (zinc chloride dissolved in water or 1, 2-ethanediol). The resulted particles were thermal treated at 250°C then applied to cotton and cotton / Polyester fabrics by Pad -dry-cure method. It was found that using 1,2-ethanediol instead of water resulted in smaller size of ZnO NPs (from 20 nm to 9 nm), more uniform distribution and higher UPF values for both UVA and UVB [10].

Taunk et al., aimed to more economical and ecological function in ZnO NPs synthesis by hydrothermal method through using low concentration of (zinc chloride - sodium hydroxide –M tri ethanolamine) and lower thermal treatment temperature. The resulted ZnO NPs had smaller size than previous research (7nm) and absorption in the UV region (235-407 nm) [11].

The results of all previous researches can be summarized in Table1. Hydrothermal process provided smaller size of ZnO NPs. The research made by Taunk and his team provided the smallest size of ZnO NPs, lower concentration of hazardous chemicals (for economic and ecological considerations) and wide range absorption of UV radiation (235-407nm).

Table 1: Comparison between chemical methods of ZnO NPs synthesis

Chemical methods	precursors	Optimum Size (nm)	UV Protection effect	Reference
Sol gel method	Zinc acetate - Lithium hydroxide	30-60 nm	Higher UPF value for cotton (177) Higher UPF value for CO/ PET (48)	Farouk et al.,(2010)
Sol gel method	Zinc acetate - Sodium hydroxide	58 nm	Absorption in UV region (380 nm).	Conde et al., (2011)
Hydrothermal method	Zinc chloride -1-2ethanediol Sodium hydroxide	9 nm	UPF of cotton against UVA (8,45) UPF against UVB(10,29) UPF of CO/ PET against UVA (11,80) UPF against UVB(16,20)	Kathirvelu et al .,(2009) .
Hydrothermal method	Zinc chloride - Tri ethanolamine - Sodium hydroxide	7 nm	Absorption in the UV region (235-407 nm)	Taunk et al ., (2015)

Green synthesis

Green synthesis is better than chemical synthesis of ZnO NPs as it provides the advantage of clean, non-toxic and environmental friendly finishing. Green synthesis of ZnO NPs depends on using natural materials with zinc source.

Thirumavalavan, et al., prepared ZnO NPs from the reaction of (CMC) chemically modified chitosan (by alkalization and etherification) with Zinc nitrate. Chitosan is a cheap, environmental friendly, low toxic and high stable material. This research aimed to determine optimum conditions of ZnO NPs synthesis from modified chitosan. Modified chitosan was prepared by dispersion of chitosan in (50-75%) isopropyl alcohol with gradual addition of sodium chloroacetate (1,5-2,5-3M) . zinc acetate was added to the mixture and calcined at different temperatures . It was found that Modified chitosan showed more affinity to Zinc ions than native chitosan. The optimum reaction conditions (sodium chloroacetate (1,5 M), isopropyl alcohol(75%) and 450 °C as calcination temperature resulted in more uniform distribution and smaller size of ZnO NPs (19-54nm) [12].

Ramesh, et al., prepared ZnO NPs by green method. They used the extract of Citrus aurantifolia leaves (as a reducing and stabilizing agent) and zinc nitrate. The resulted ZnO NPs Uniformly distributed, had a size range from (9-10nm) and absorbed UV radiation at the range (208-400nm) [13].

Varghese & George produced ZnO NPs by using green material (Aloe Vera) leaves as stabilizing and reducing agent. Sodium hydroxide was added gradually to mixture of (the extract of Aloe Vera leaves and zinc acetate. It was found that the resulted ZnO NPs had an average size (22.18nm), showed antibacterial activity against gram positive and gram negative bacteria and absorbed UV radiation within the range (340-400nm) [14].

It is obvious that synthesis of ZnO NPs made by Varghese is better than other methods as it included less chemical materials (only zinc source and the natural material used with no need to another reducing agent), Smaller size of ZnO NPs (9-10nm) and wider range of UV absorption (208-400 nm).

ZnO NPs application to provide textiles UV protection

ZnO NPs can be applied to fabrics after plasma treatment or without treatment individually or in combination with other materials synthetic or natural to improve protection against UV radiation and provide multifunctional finished textiles

Application of ZnO NPs without treatment

Single application of ZnO NPs

Abdel Ghani et al., applied ZnO NPs (with average size <35nm) as a coating to cotton fabrics. Treated cotton fabrics indicated complete covering by ZnO NPs, increasing UPF values from (27,22) to (711,44) and improvement in antimicrobial activity against E. Coli and S. aureus bacteria [1].

Shaheen, et al., applied ZnO NPs on cotton fabrics to provide durable multifunctional finishing (antibacterial and UV protection) to cotton fabric. ZnO NPs were synthesized in situ. Cotton samples were padded in different concentrations of zinc acetate hexahydrate and hexamethyltriethylene tetramine (HMTETA), dried and cured. It was found that optimum concentration of zinc nitrate (2gm) resulted in producing ZnO NPs with average size 359 nm. ZnO NPs gave very good UPF values after 15 washes (17.6) and durable antibacterial activity of cotton fabric after 20 washes [15].

Another team of researchers led by Prasad also synthesized Zno NPs *insitu* to provide durable multifunctional finishing to cotton fabrics. The difference in this work was represented in using sodium hydroxide (instead of HMTETA) as reducing agent which is cheaper and more available material. The precursors (zinc nitrate and sodium hydroxide) were applied to cotton samples by spraying and dipping processes. SEM images showed that dipping method was better than spraying method as it resulted in smaller size of ZnO NPs (<100nm) and 3 times more uptake of NPs that caused finishing to be effective and more durable. Dipping process included excellent and durable antibacterial activity after 50 washes against both S. aures and K. Pneumonia bacteria and higher UPF values (890) after 50 washes (450) [16]. Previous researches in single application of ZnO NPs are summarized in Table 2.

Table 2: Comparison between single applications of ZnO NPs on cotton fabric

Precursors	Size (nm)	UV Protection effect	Reference
-	The used ZnO NPs	Increasing UPF values from (27,22) to (711,44)	Abdel Ghaniet al., (2015)
Zinc nitrate + (HMTETA)	Resulted ZnO NPs size =359 nm	UPF value (22.8) after 15 washes (17.6)	Shaheen et al ., (2015)
Zinc nitrate + Sodium hydroxide	Resulted ZnO NPs size <100nm	UPF value 890 UPF after 50 washes 450	Prasa et al ., (2016)

It is obvious that the application method of ZnO NPs made by Prasad and his team is better than the other procedures because of using more available and less expensive reducing agent, in situ synthesis of ZnO NPs which saved (time – money), producing smaller size of ZnO NPs and providing higher UPF values and more durable effect after 50 washes.

Application of ZnO NPs in combination with other materials

ZnO NPs with natural materials

El-Shafei, et al., used Zno NPs in combination with carboxy methyl chitosan to provide antibacterial and UV protection for cotton fabric. ZnO/ carboxymethyl chitosan composite was made by stirring a mixture of (caroxymethyl chitosan and zinc sulfate) at different temperatures. Different concentrations of ZnO/ carboxymethyl chitosan composite was applied to cotton fabrics by padding and cured at different temperatures. It was found that preparation of ZnO/ CMCTS bionano composite at 50°C resulted in smaller size of NPs (28 nm for ZnO NPs and 100nm for CMCTS). Higher concentration of ZnO/CMCTS nano composite increased antibacterial activity against both S.aureus and E.coli types. Increasing curing temperature to 160°C resulted in higher UPF values [17].

Abdelhady applied simpler and more eco-friendly method by using only chitosan with ZnO nanoparticles to provide multifunctional finishing to cotton fabric. In order to determine optimum conditions, different concentrations of ZnO in preparation of chitosan/ ZnO NPs and different temperatures were used. The resulted chitosan/ ZnO NPs were applied to cotton fabric by Pad –dry-cure method. Treated cotton fabric samples with higher concentrations of chitosan/ ZnO nanoparticles showed comparatively higher UPF values (8.3) and antibacterial activity [18].

The previous two researches provided green application methods by using natural materials with ZnO NPs to provide multifunctional finished cotton fabrics. Cons and pros of each process are shown in Table 3.

Table 3: Cons and Pros of ZnO NPs application with natural materials

Natural material	Advantages	Disadvantages	Reference
Carboxymethyl chitosan	-Smaller size of nano particles	-More chemical content for carboxymethylation of chitosan.	El.Shafei & Abou-Okeil, (2011).
	- Higher antibacterial activity against both gram positive and gram negative bacteria.	No tests for finishing durability	
	-Improving UV protection (7.6) .		
Chitosan	Ecofriendly method only included chitosan in its simplest form	Comparatively larger size of chitosan/ ZnO NPs (300nm).	Abdelhady, (2012).
	Higher UPF values (8.3)		
	Moderate antibacterial activity against both gram positive and gram negative bacteria	No tests for finishing durability.	

Application method made by Abdelhady is better than the other method as it provided simpler, more environmental friendly method and higher UPF values.

Application of ZnO NPs with Synthetic materials

Abdelhady, et al., applied ZnO NPs with sodium hypophosphite (SHP) and polycarboxylic acids to provide multifunctional finishing to cotton and cotton /polyester (56/35%) fabrics. ZnO NPs were prepared by sol-gel method using Zinc acetate as precursor and lithium hydroxide. To investigate finishing effect different (concentrations of ZnO NPs and SHP, types of polycarboxylic acid butantetracarboxylic acid (BTCA) or succinic acid (SA), Curing temperatures) were used. Cotton and cotton/ polyester fabrics were padded in (BTCA) or (SA) and SHP, dried and cured at different temperatures then ZnO NPs were applied to fabrics by Pad-dry-cure method. The average size of resulted ZnO NPs was 30nm.It was found that using of BTCA with 160°C as a curing temperature improved (CRA values, roughness and yellowness) than using of SA. Increasing curing temperature to 180°C resulted in increasing (CRA values, roughness and yellowness) in fabrics treated with BTCA or SA. Using of BTCA increased flame retardant action for both cotton and CO/PET fabric in the presence of 6% SHP after two washes. Using of BTCA or SA with 6% SHP and 5% ZnO NPs caused higher UPF values (for cotton fabric 60 for cotton /polyester fabric 57), improving flame retardant action for both cotton and CO/PET fabrics. Adding ZnO NPs caused slight increasing in roughness and yellowness of treated fabrics especially at higher concentration [19].

Another work carried out by Noorian used $C_{u2}O$ NPs in combination with ZnO NPs to improve the UV protection of cotton fabrics. They added folic acid during in-situ synthesis of $C_{u2}O$/ ZnO NPs and investigated its effect. It was found that using $C_{u2}O$/ ZnO NPs resulted in more UV protection for cotton fabrics than the single application of each (87.31% protection against UV radiation). C_2O/ ZnO NPs caused slight increasing in thickness, decreasing CRA values and hydrophilicity of cotton fabric. Adding folic acid resulted in smaller size of CU_2O/ ZnO NPs(48nm) and increasing UV protection , hydrophilicity ,thickness , wash fastness, anti wrinkle property and improving the handle of cotton fabrics [20].

Cons and Pros of ZnO NPs application with synthetic materials are summarized in Table 4.

Table 4: Cons and Pros of ZnO NPs application with synthetic materials

Synthetic material	Advantages	Disadvantages	Reference
Sodium hypophosphite-Polycarboxylic acids	- Polycarboxylic acids are environmental friendly materials.	-Iincluding durability tests for only 2 washes.	Abdelhadyet al., (2013).
	- Smaller size of resulted ZnO NPs.	-Using BTCA leaded to increase flame retardant action but it caused increasing roughness and yellowness of treated fabric .	
	- Producing multifunctional finishing to cotton and CO/PET fabric.	Increasing concentration of ZnO NPs resulted in higher UPF values but it caused increasing in yellowness and roughness of treated fabric.	
	Discussing the effect of ZnO NPs, SHP and Curing temp .		
	Improving flame retardancy of cotton and CO/PET fabric		
	Higher UPF values for cotton and CO /PET fabric.		
	-Increasing CRA values of treated fabrics.		
CU2O NPs	-Synthesis of CU2O/ZnO NPs in-situ provided more durable finishing.	- Durability tests were carried out after only 5 washing cycles.	Noorian et al., (2015).
	-Adding folic acid as a bio template during in-situ synthesis of CU2O/ ZnO NPs provided greener , more effective method to improve UV protection.	- Slight increase in cotton fabric thickness.	
	-Providing UV protection with improving physical properties of cotton fabric.		

Application of ZnO NPs after plasma treatment

Gorjanc, et al., developed a method to increase the adsorption rate of ZnO NPs at lower concentrations by treating cotton fabrics with tetrafluoromethane and water plasma. The effect of plasma was investigated by treating cotton fabrics with moist CF_4 plasma for 10, 20 and 30s and H_2O plasma for 10s. ZnO NPs were applied to cotton fabrics (treated and untreated) by Pad-dry-cure method. It was found that the optimum CF_4 plasma treatment time (10 s) indicated rougher surface of cotton fabrics which resulted in higher adsorption of ZnO NPs and great improvement in hydrophilic activity and UPF values of cotton fabric from 4.12 to 58.89, but UPF values decreased dramatically after 10 washes from (58.89 to 4.58) [21].

Wang, et al., used ZnO NPs and carboxymethyl chitosan (CMCS) to provide multifunctional finishing for plasma pretreated cotton fabric. Cotton fabrics were treated by O_2 plasma for 2 min at 200W. Different concentrations of ZnO/CMCS composite were applied to cotton fabric by Pad-dry-cure method. It was found that plasma treatment provided rougher surface and more deposition of ZnO/CMCS NPs on cotton fabrics. Plasma treatment with higher concentration of ZnO/CMCS NPs resulted in more deposition of ZnO/CMCS NPs on the fabric, very good UPF values, durable antibacterial activity even after 30 washes and improving thermal properties of cotton fabrics [22].

Cons and Pros of ZnO NPs application after plasma treatment are summarized in Table 5.

Table 5: Cons and Pros of ZnO NPs application after plasma treatment

Plasma treatment	Advantages	Disadvantages	Reference
CF4 and H2O plasma.	- Using lower concentrations of ZnO NPs which provide environmental and economical improvement.	- Decreasing in wash fastness (UPF values decrease from 58.89 to 4.58 only after 10 washes).	Gorjanc et al., (2014).
	- Higher adsorption of ZnO NPs which resulted in higher UPF values .		
	- Increasing hydrophilicity of cotton fabrics.		
O2 plasma	-Green method using natural material (carboxymethyl chitosan).	-	Wang et al., (2016).
	-Higher adsorption of ZnO/CMCS NPs due to plasma treatment .		
	- Providing multifunctional finishing (antibacterial and UV protection finishing) to cotton fabric		
	Including durable test after 30 washes.		
	- Producing durable antibacterial and UV protection finishing after 30 washes.		
	- Improvement in thermal properties of cotton fabric.		

TiO_2 Nanoparticles in textiles UV protection

TiO_2 properties

TiO_2 is an inorganic material which belongs to transition metal oxides. TiO_2 particles in nano form are used in many fields of textile industry especially in protection against UV radiation due to their properties (lower cost, chemically stable, non-toxicity, photocatalytic activity and longer durability) [23].

TiO_2 NPs synthesis

There are many methods to prepare TiO_2 NPs by chemical or green precursors [24-26].

Chemical synthesis

Sol gel method

Gouda& Aljaafari, used sol gel method to prepare TiO_2 NPs to produce durable multifunctional finishing to cotton fabrics. Titanium Tetrachloride was used as a precursor, dissolved in water with polyvinyl pyrrolidone (as a stabilizing agent) and reduced by gradual addition of borohybride. The resulted TiO_2 NPs were applied with different concentrations to cotton fabrics using Pad-dry-cure method. It was found that resulted TiO_2 NPs had smaller size 5-10 nm, higher purity, stability and dispertion ability. Higher concentrations of TiO_2 NPs resulted in higher UPF values (40) and increasing antibacterial activity against S. aureus and K. pneumoniae bacteria after 20 washes [27].

Hema, et al., also prepared TiO_2 NPs by sol gel method. A solution of trisodium citrate was added gradually to bulk TiO_2 at room temperature with no need to calcination process. The resulted TiO_2 NPs had an average size (37 nm), higher absorbance of UV radiation and higher thermal stability (remains after 700oC was about 67%) [28].

Hydrothermal method

Vijayalakshmi & Rajendran, prepared TiO_2 NPs by both hydrothermal and sol gel method. In hydrothermal method, sodium hydroxide was added to titanium tetrachloride and the mixture was stirred dried at 450oC. In sol gel method, they used Titanium isopropoxide

(TTIP) as a precursor. TTIP was dissolved in ethanol and the mixture was stirred and dried. It was found thatTiO_2 NPs resulted from hydrothermal method had an average size (about 17 nm), higher absorbance of UV radiation at the wavelength of 362 nm. The TiO_2 NPs resulted from sol gel method had an average size (about 7 nm) and great absorbance of UV radiation at the wavelength of 351 nm and higher band gap value about 3.5 eV [26].

Mahdi, et al., synthesized TiO_2 NPs by hydrothermal method using ilmenite in the form of synthetic rutile as a precursor. Sodium hydroxide was mixed with synthetic rutile at 550oC. The resulted TiO_2 NPs had smaller size (15.6 nm), higher absorbance of UV radiation and lower band gap (3.23) than commercial TiO_2 NPs [29].

The results of all previous researches about chemical synthesis of TiO_2 NPs are summarized in Table 6. From the results it is obvious that sol gel method provided more UV protection and smaller size of TiO_2 NPs. The experiment made by M. Gouda and his team produced smaller size of TiO_2 NPs, excellent and durable UV protection, simple and energy saving process.

Table 6: Comparison between chemical methods of TiO_2 NPs

Chemical methods	Precursors	Optimum Size (nm)	UV Protection effect	Reference
Sol gel method	Titanium tetrachloride – Poly vinyl pyrrolidone-Borohybride.	5-10 nm	Higher UPF value for cotton fabric after 20 washes (40).	Gouda & Aljaafari , (2012)
Sol gel method	Bulk TiO_2 - trisodium citrate.	37 nm	Absorption in UV region at (408 nm).	Hema,et al (2013)
Hydrothermal Method	Titanium tetrachloride- Sodium hydroxide	17 nm	Absorption of UV radiation at the wavelength of 362 nm.	Vijayalakshmi & Rajendran, (2012) .
Sol gel method	Titanium isopropoxide – Ethanol	7nm	Absorption of UV radiation at the wavelength of 351 nm .	
Hydrothermal method	Synthetic rutile - Sodium hydroxide	15.6 nm	Absorption of UV radiation at the wavelength of 400 nm .	Mahdi et al., (2013)

Green synthesis

Green synthesis of TiO_2 NPs depends on using natural materials and it is far better than chemical synthesis of TiO_2 NPs as it depends on less hazardous chemicals and produces eco friendly finishes.

Tarafdar, et al., synthesized TiO_2 NPs by eco friendly and low cost method using Aspergillus tubingensis soil fungi. Salt solution of TiO_2 was added to the soil fungi to obtain nano TiO_2. It was found that the size of resulted TiO_2 NPs ranged from (1.5 to 5.9 nm). The resulted TiO_2 NPs showed an absorbance of UV radiation within the range (300–350 nm) [30].

Ganesan, et al., synthesized TiO_2 NPs by using leaf extracts of medicinal plant Ageratina altissima and tested the photocatalytic activity of resulted NPs. The resulted TiO_2 NPs had an average size (60-100 nm),higher absorbance of UV radiation at 332 nm and caused dyes degradation (86.79 %) of methylene blue, (76.32 %) of alizarin red, (77.59 %) of crystal violet, and (69.06 %) of methyl orange [31].

The method made by A Tarafdar and his team provides better green synthesis of TiO_2 NPs as it included smaller size of TiO_2 NPs (1.5 - 5.9) nm and wider range of UV absorbance (300–350 nm)

TiO_2 NPs application to provide textiles UV protection

TiO_2 NPs can be applied to different types of treated or untreated fabrics individually or in with other materials to enhance UV protection or provide multifunctional finishing to fabrics.

Application of TiO_2 NPs without treatment

Single application of TiO_2 NPs

Adnan & Moses, investigated UV protection effect of TiO_2 NPs on five samples (pure lyocell, (80/20-60/40-50/50)% lyocell silk blends and pure silk) properties. It was found that TiO_2 NPs caused durable UV protection especially for pure lyocell fabric even after 25 washes, Improving in anti wrinkle property and decreasing in air permeability, tensile strength and absorbency of treated fabrics [32].

Zhang, et al., applied finishing with TiO_2 NPs and dyeing of wool fabric at the same time by hydrothermal process. Different concentrations of reactive blue 69 and acetic acid were used to investigate the optimum concentration. Finished and dyed samples were compared to only dyed ones. It was found that resulted TiO_2 NPs had uniform distribution and size < 10 nm. Increasing the concentration of acetic acid with 1% dye caused both exhaustion rate and K/S values to increase. The addition of TiO_2 NPs resulted in higher photocatalytic activity(5h of exposure to UV radiation leaded to 93% degradation of methylene blue) and slight decreasing in breaking stress (8.6%), elongation rate (7.8%) and thermal stability [33].

El-Naggaret al., investigated the antibacterial activity and UV protection effect of TiO_2 NPs on cotton fabric, but they used urea nitrate (UN) in in situ synthesis of TiO_2 NPs as a nitric acid source and investigate its effect. It was found that higher concentration of (UN) leaded to smaller size of TiO_2 NPs (<50nm), very good UPF value (29.69) after 15 washes, excellent antibacterial activity after 20 washes against S.aureus and E.Coli bacteria besides decreasing in elongation rate and tensile strength of treated fabric [34].

All previous researches included single application of TiO_2 NPs to provide UV protection for different types of fabrics. Cons and pros of each process is summarized in Table 7.

Table 7: Cons and pros of TiO_2 NPs single application on different fabric types

Targeted fabric	Advantages	Disadvantages	Reference
Pure lyocell - (80/20-60/40-50/50)% lyocell silk blends - Pure silk fabrics	-Investigating the effect of TiO_2 NPs on both pure and blend fabrics.	- TiO_2 NPs finishing caused negative effects on physical properties of all treated fabrics (decreasing in air permeability, tensile strengh and absorbency) .	Adnan& Moses (2013).
	- Including durability tests for 25 washes. Providing durable UV-protection after 25 washes.		
	-Improving in anti wrinkle property of all treated fabrics.		
Wool fabrics	-Providing dyeing and finishing process at the same time which save money, time and effort.	- No tests for dyeing and finishing durability.	Zhang et al., (2014).
	Investigating the optimum concentrations of racive dye and acetic acid	Negative effects on physical properties of wool fabric (decreasing in breaking stress, elongation rate and thermal stability).	
	- Producing smaller size of TiO_2 NPs < 10 nm		
	Improving photocatalytic activity		
Cotton fabrics	- In situ synthesis of TiO_2 NPs which saved (time -effort-money).	- Also, there was negative effect on physical properties of cotton fabrics (Slight decrease in elongation rate and tensile strength).	El-Naggar et al., (2016).
	- Investigating the effect of (UN) as a peptizing agent used in TiO_2 NPs synthesis. Providing durable multifunctional finishing to cotton fabrics .		
	Producing Moderate size of TiO_2 NPs < 50nm.		
	Including durability tests for 20 washes.		
	Very good UPF values and antibacterial activity after 20 washes.		
	Increasing antibacterial activity against both S.Aureus and E. Coli bacteria.		

Application of TiO_2 NPs in combination with other materials

Hashemikia & Montazer, used sodium hypophosphite (SHP) and citric acid (CA) with TiO_2 NPs to provide multifunctional finishing for cotton /polyester fabric. Different concentrations of CA, SHP and TiO_2 NPs were used to determine optimum finishing conditions. It was found that using optimum concentrations of CA (30gm/l) with (SHP)(18gm/l) and TiO_2 NPs (0.5gm/l) resulted in higher flame retardancy effect, lower pilling formation, improved antibacterial activity against S. aureus bacteria and increasing hydrophilicity, photocatalytic activity, self-cleaning property and wash fastness of treated fabrics. Also, optimum conditions caused slight decrease in tensile strength but after exposure to UV radiation there was an improvement in fabrics tensile strength due to the effect of TiO_2 NPs [35].

Milosevic, et al., used Ag NPs in combination with TiO_2 NPs to provide multifunctional finishing to Polyester fabrics. TiO_2 colloidal solution was applied to polyester fabrics by Pad -dry-cure method, then the fabrics were padded in (alanine – silver nitrate - methyl alcohol) mixture, rinsed and dried. FESEM analysis showed uniform distribution of TiO_2 /Ag NPs on polyester fabrics. Treated polyester fabrics indicated:

- Excellent antimicrobial activity against both E.coli and S.aureus bacterium besides C.albicans fungus (reduction rate of the bacteria reached to 99.9% even after 10 washes).
- Higher UPF values (92.35) but after 10 washes UPF values decreased to (53.52).
- Release of Ag NPs in first 3 washes and in artificial sweat especially alkaline sweat conditions [36].

Li, et al. also used Ag NPs with TiO_2 NPs but they produced more durable finishing to cotton fabric. TiO_2 NPs were applied to cotton fabrics with two different concentrations by hydrothermal treatment. Ag NPs synthesized in situ on cotton fabrics using different concentrations of Ag NO3. It was found that higher concentrations of Ag and TiO_2 NPs yielded very good and durable antibacterial activity against both E. coli and S. aureus and increasing in UPF values (from 3 to 56.39). Only slight decreasing of UPF values after 50 washes was detected [37].

Previous researches included application of combined TiO_2 NPs with other materials on untreated fabrics to provide durable multifunctional finishing. Every process had advantages and disadvantages as summarized in Table 8.

Table 8: Cons and Pros of TiO_2 NPs application with other materials

Applied material	Advantages	Disadvantages	Reference
Sodium hypophosphite - Citric acid- TiO_2 NPs	-Providing multifunctional finishing to fabric.	-Antibacterial tests included only one type of bacteria.	Hashemikia & Montazer, (2012).
	- Investigating The optimum concentrations of CA , SHP and TiO_2 NPs .	- Decreasing in fabric tensile strength.	
	Increasing flame retardancy and anti pilling effect .	Including durability tests for only 10 washes.	
	Improving antibacterial activity against S.aureus bacteria		
	Increasing hydrophilicity and self cleaning property		
	Improving tensile strength		
	Including durability tests for 10 washes.		
Ag NPs - TiO_2 NPs .	Providing multifunctional finishing to Polyester fabrics	Including durability tests for only 10 washes.	Milosevic,et al., (2013).
	Higher antimicrobial activity aginst E.coli , S.aureus bacteria and C.albicans fungus	Decreasing UPF values after 10 washes.	
	Increasing UV protection of treated fabrics	-Low fastness (for washing and perspiration) due to Ag NPs release.	
	Including durability tests for 10 washes.		
	Durable antibacterial activity after 10 washes.		
Ag NPs - TiO_2 NPs.	Providing multifunctional finishing to cotton fabric.	-	Li et al., (2017).
	Investigating the effect of Ag and TiO_2 NPs.		
	Including hydrothermal treatment for higher crosslinking		
	In situ synthesis of Ag NPs which provided more durability.		
	Providing excellent UV protection and antibacterial		
	Including durability tests for 50 washes.		
	Durable UV protection and antibacterial activity after 50 washes.		

Application of TiO_2 NPs after fabric treatment

Application of TiO_2 NPs after different treatment processes on fabrics improved UV protection and other functions due to the increased affinity of treated fabric for finishing agents.

Ramadan, et al., applied TiO_2 NPs on cellulose acetate fabric (CA) after treatment with H2O2 in ultrasonic bath. (CA) samples were padded in different concentrations of TiO_2 NPs, dried and cured in microwave oven at different conditions. It was found that using optimum conditions (Ultrasonic treatment -0.75 % TiO_2 NPs-microwave curing at 90% for 15 seconds) resulted in:

- Increasing whiteness and slight decreasing in roughness and tensile strength of fabric.
- Higher absorbance of UV radiation and higher self-cleaning effect (87% degradation of coffee stain) [38].

Hashemizad, et al., applied TiO_2 NPs on polyester fabric afteroxygen gas plasma treatment and investigated its effect on fabric properties and adsorption rate of TiO_2 NPs. It was found that treatment with plasma before TiO_2 NPs application afforded more uniform distribution of TiO_2 NPs on fabric surface, higher self-cleaning property and higher UV protection (decreasing in the percentages of UV Reflectance) even after 10 washes [39].

Memon & Kumari, pretreated polyester cotton (80:20) blended curtains with cold plasma before the application of TiO_2 and SiO2 NPs. The effect of plasma was investigated by treatment of fabrics with cold plasma for different periods of time before the application of TiO_2 and SiO2 NPs. It was found that plasma treatment for 6 minutes before the application of NPs produced more deposition of NPs on the fabric surface, increasing UPF value from (8.51 to 40.24),improving antibacterial activity against S. aureus and E. coli bacteria, increasing antistatic property as well as good adhesion of NPs in the fabric surface after 50 washes. Also, slight decrease in elongation, tensile strength and air permeability of treated fabric were detected [40].

Gawish et al., treated polyester (PET) and polypropylene (PP) fabrics with dielectric-barrier discharge (DBD) plasma before the application of TiO_2, Al_2O_3 and ZnO NPs to provide enhanced finishing to the fabric. Different concentrations of Al_2O_3, ZnO and TiO_2 NPs were applied separately to fabrics by Pad-dry-cure method for comparing their effect on treated fabrics. It was found that in PET fabric:

- Plasma pretreatment had no significant effect on the fabric.
- The fabric indicated excellent UPF values with higher concentration of TiO_2 NPs 156.90 Higher concentration of ZnO NPs also gave excellent UPF value (82.98) more than Al_2O_3 NPs (36.76).
- ZnO NPs showed more antibacterial activity against S. aureus and K.pneumonia bacteria
- TiO_2 NPs had no antibacterial effect against both types of bacteria, while Al_2O_3 NPs had only slight effect against K. pneumonia bacteria (reduction percentage 6.5%).
- In PP fabric plasma treatment before the application of NPs resulted in: More uniform distribution of NPs on the surface of the fabric.
- Improving UV protection of treated fabric (increasing UPF values from 2.4 to 38.1 with ZnO NPs and to 17.9 with TiO_2 NPs) [41].

All the previous researches included fabric pretreatment to provide more absorbance of NPs and improve UV protection effect, but that had slight effect on fabric properties. Advantages and disadvantages are summarized in Table 9.

Table 9: Cons and Pros of TiO_2 NPs application on treated fabrics

Treatment process	Advantages	Disadvantages	Reference
Treatment with H2O2 in ultrasonic bath	Using microwave curing after the application of TiO_2 NPs.	Decreasing in Roughness and tensile strength of treated fabrics.	Ramadan et al., (2012).
	Including investigation of the optimum conditions (TiO_2 NPs concentration -microwave curing conditions).	No tests for finishing durability were included	
	Providing multifunctional finishing to CA fabric		
	Improving UV protection and self cleaning property of CA fabric		
	Increasing the whiteness of treated fabric		
	Decreasing in of CA fabric.		
Plasma and oxygen gas.	Plasma pretreatment provided more uniform distribution of TiO_2 NPs on PET fabric	Including durability tests for only 10 washes	Hashemizad et al., (2014).
	Providing enhanced multifunctional finishing to PET fabric		
	Including durability test .		
	- Providing higher UV absorbance even after 10 washes		
	Improving self cleaning of treated fabric		

Cold plasma treatment	Including investigation of the optimum conditions of plasma treatment	Negative effects on physical properties of polyester/ cotton blends fabric (decreasing in elongation, tensile strength and air permeability).	Memon & Kumari, (2016).
	Plasma treatment provided higher deposition of NPs on the fabric surface .	No tests for UPF values, antibacterial and antistatic property after 50 washes	
	Providing improved multifunctional finishing to polyester cotton blended fabric.		
	Improving UV protection , antistatic and antibacterial property of treated fabric		
	Including durability tests for 50 washes		

Conclusion

This review indicates the great importance of ZnO and TiO_2 NPs as textile protective agents against UV radiation. Different synthesis methods (chemical –green) of ZnO and TiO_2 NPs are compared to find out which is better method. In chemical synthesis of ZnO NPs it is found that hydrothermal method is better than sol gel method as it provides smaller size of NPs and higher absorbance of UV radiation. On the contrary, in TiO_2 NPs synthesis sol gel method include better results than hydrothermal method. Green method in both ZnO and TiO_2 NPs is better than chemical synthesis method as it includes natural precursor which provides more eco-friendly synthesis. Moreover, Advantages and disadvantages of the application of ZnO NPs on treated and untreated fabrics individually or with natural materials (chitosan – carboxymethyl chitosan) or synthetic materials (UV absorber - sodium hypophosphite - CU2O NPs- Ag NPs) are discussed. Also, advantages and disadvantages of TiO_2 NPs application on textiles without or with treatment to individually or with other materials are concluded [42]. Main disadvantages in ZnO and TiO_2 NPs application concern to insufficient finishing durability tests and negative effects on fabric properties which must be fixed in future researches to meet the functional demands.

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