ZnO and TiO_2Nanoparticles as Textile Protecting Agents Against UV Radiation:A review

Abstract: This review was aimedto highlight the role of ZnO and TiO_2nanoparticles (NPs) as textile protective agents against Ultra Violet radiation. Different syntheticmethods of ZnO and TiO_2 NPs that affecting their nano size and their ability to absorb UV radiation have been reported.The formed 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 in addition tocomparison of the methods of preparation of ZnO and TiO_2 NPs werediscussedseparately in this review paper.

Keywords: ZnO NPs -TiO_2 NPs- UV protection -NPs synthesis-NPs application.

Introduction

Protection against ultra violet radiation is one of the most important concerns in textile industry.UV radiation (UV) is a form of energy which representsonly 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% infrared and 5% ultra violet radiation)[1].

UV radiation can be subdivided according to itswavelength 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 considered as dangerous UV radiation especially UV – B which has ashorter wavelength and consequently higher energy and more damage on(textiles, dyestuff, human skin)[2].

To block the harmful effect of UV radiation, organic and inorganic UV blockers are used. Inorganic UV blockers are favoredthan 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].Nanosize of ZnO and TiO_2 particles showed more durable and effective UV protection than their bulk size [4].

This reviewwasintended 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. Fabric'sUVprotection factor and properties of (ZnO and TiO_2 NPs) have been briefly explained. Different ZnO and TiO_2 NPs preparationmethods (chemical - green) and applications (individually or in combination with other materials to provide multifunctional finished fabrics) have been discussed in detail and were compared.

Ultra Violet Protection Factor:

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

Table 1

ZnO Nanoparticles in Textiles UV Protection:

ZnOProperties:

Zinc oxide (ZnO) is an inorganic semiconductor material that has a wide application in textile's UV protection due to its excellent properties (wide bandgap,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, ZnONPs are obtained by chemical or green synthesis.ZnONPs are chemically synthesized by sol gel and hydrothermal methods.Both chemical and green synthesis of ZnONPs depend on using zinc source such as (zinc acetate, zinc chloride, zinc nitrate) with synthetic or natural materials.

Chemical Synthesis

Sol Gel Method

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

Conde*et al*[9]prepared ZnONPs with an average size of (58nm). The method was based on Sol-Gel technique combined with Zinc acetate dihydrate as precursor, but they used sodium hydroxide as a reducing agent instead of lithium hydroxide. Sodium hydroxide action was investigated by using different flows and different alkaline ratios. It was found that slow addition of sodium hydroxide with maintaining alkaline ratio at 2 resulted in obtaining ZnONPs with uniform distribution and good absorption in the UV region (380 nm).

Hydrothermal Method

ZnONPs had been prepared by hydrothermal process using water and 1,2-ethanediol as a solvent [10]. Sodium hydroxide was added gradually to zinc chloride dissolved in water or 1,2-ethanediol. The resulted particles were thermally 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 ZnONPs (from 20 nm to 9 nm), more uniform distribution and higher UPF values for both UVA and UVB.UPF values of cotton fabric were (8.45) against UV-A and (10.29) against UV-B. Also,Cotton/Polyester fabric's UPF values were (11.80) against UV-A and (16.20) against UV-B.

Taunk *et al*.[11] aimed to more economical and ecological function in ZnONPs synthesis by applying hydrothermal method through using low concentration of (zinc chloride - sodium hydroxide – triethanolamine) and lower thermal treatment temperature. The resulted ZnONPs hadspherical shape, smaller size (7nm) and absorption in the UV region (235-407 nm).

It is obvious that hydrothermal process provided smaller size of ZnO NPs than sol gel method. 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).

Green Synthesis

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

Ramesh *et al*.[12] 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).

Also,ZnO NPs had been produced [13] 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 & gram-negative bacteria andabsorbed UV radiation within the range (340-400nm).

It can be concludedthat synthesis of ZnO NPs made by Ramesh [12[was better than other methodsas it usedless 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:

ZnO NPs had been applied [1] with (average size <35nm) as a coating to cotton fabrics. Treated cotton fabrics indicated complete covering by ZnO NPs and consequently increasing UPF values from (27.2) to (711.4) as well as improvement in antimicrobial activity against E. coli &S. aureus bacteria.

On the other hand, ZnO NPs had been synthesized in situ and applied to cotton fabrics to provide durable multifunctional finishing (antibacterial and UV protection).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 maintainedgood UPF values (17.6) after 15 washes and durable antibacterial activity of cotton fabric after 20 washes [14].

Prasad *et al*.[15]also synthesized ZnO NPs insitu to provide durable multifunctional finishing to cotton fabrics. The advantageof the reported methodwas dependedon 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 cause 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 besides higher UPF values (890) after 50 washes (450).

The previous finding indicated that the application method of ZnO NPs made by Prasadet al [15] is better than the other procedures because of its advantages that include using more available and less expensive reducing agent, in situ synthesis of ZnO NPs which saved (time and money), producing smaller sizeof ZnO NPs and providing higher UPF values and more durable effect after 50 washes.

Application ofZnO NPs in Combination with Other Materials

ZnO NPs with Natural Materials

ZnO NPs could be used [16] in combination with carboxy methyl chitosan to provide antibacterial and UV protection for cotton fabric. ZnO/carboxymethyl chitosan composite was preparedby stirring a mixture of (caroxymethyl chitosan and zinc sulfate) at different temperatures. Different concentrations of ZnO/ carboxymethyl chitosan composite wereapplied to cotton fabrics by padding followed by curing 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 nanocompositeimproved antibacterial activity against both S.aureus and E.coli bacteria.Increasing curing temperature to 160°C resulted in slight increasing in UPF values.

A simpler and more eco-friendly method [17]could be applied 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.

The previous methodsexpressed examples of green applicationsthat were achievedby using natural materials with ZnO NPs to provide multifunctional finished cotton fabrics.Cons and pros of each process wereshown in Table 2.

Table 2

Abdelhady *et al*'s method has the advantages of, more environmentally friendly and higher UPF values.

Application of ZnO NPs with Synthetic Materials

ZnO NPs had been combinedwith sodium hypophosphite (SHP) and polycarboxylic acids to provide multifunctional finishing to cotton and cotton /polyester (56/35%) fabrics [18]. ZnO NPs were prepared by sol-gel method using Zinc acetate as precursor and lithium hydroxide.To investigate the optimum finishing formulation, different (concentrations of ZnO NPs and sodium hypophosphite, 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 at160°C as a curing temperature was resulted inincreasing (CRA values, roughness and yellowness) than using of SA.Increasing curing temperature to 180°C was resulted in increasing (CRA values, roughness and yellowness) in fabrics treated with BTCA or SA. Using of BTCAwas improvedflame-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 yielded higher UPF values (for cotton fabric 60 for cotton/polyester fabric 57) andwas improvedflame-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.

Noorian *et al* [19]reported the use of Cu_2O NPs in combination with ZnO NPs to improve the UV protection of cotton fabrics. They added folic acid during in-situ synthesis of Cu_2O/ZnO NPs and investigated its effect. It was found that using Cu_2O/ZnO NPs resulted in more UV protection for cotton fabrics than the single application of each (87.31% protection against UV radiation). Cu_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 ofcotton fabrics. Cons and Pros of ZnO NPs application with synthetic materials are summarized in able 3.

Table 3

Application of ZnO NPs after Plasma Treatment

Amethod [20] has been developed to increase the adsorption rate of ZnONPs at lower concentrations by treating cotton fabrics with tetrafluoromethane and water plasma. The effect of plasma was investigated by treating cotton fabrics with moist CF4 plasma for 10,20 and 30 s and H_2O plasma for 10 s. ZnO NPs were applied to cotton fabrics (treated and untreated) by Pad-dry-cure method. It was found that the optimum CF4 plasma treatment time (10 s) indicated rougher surface of cotton fabrics which resulted in higher adsorption of ZnO NPs and great increasing in hydrophilic activity and UPF values of cotton fabric from 4.12 to 58.89, but UPF values was decreased dramatically after 10 washes from (58.89 to 4.58).

ZnO NPs and carboxymethyl chitosan(CMCS) have been used [21] 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.

Cons and Pros of ZnO NPs application after plasma treatment are summarized in Table4

Table4

TiO_2 Nanoparticles in textile's 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 Ultra Violet radiation [22] due to the excellentproperties (lower cost, chemically stable, non-toxicity, photocatalytic activity and longer durability) [23].

TiO_2 NPs synthesis

Many methods had been reported to prepare TiO_2 NPs by chemical[24]or green precursors[25, 26]. Solgel and hydrothermalchemical methods are the most common to synthesize TiO_2 NPs .

Chemical Synthesis

SolGel Method

Gouda *et al* [27]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 boron hydride. The resulted TiO_2 NPs were applied with different concentrations to cotton fabrics using Pad-dry-cure technique. It was found that the resulted TiO_2NPs had smaller size (5-10 nm) and higher purity, stability and dispersion ability. Higher concentrations of TiO_2NPs yieldedahigher UPF values (40) and increasing antibacterial activity against S. aureus and K.pneumoniae bacteria after 20 washes.

TiO_2NPs had been prepared [28] 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 NPshad spherical shape with uniform distribution as shown in SEM investigation (Figure 1) and average size (37 nm) which resulted ina higher absorbance of UV radiationand a higher thermal stability (the remainingafter 700^oC was about 67%).

Figure 1

Hydrothermal Method

TiO_2NPs had been prepared by both hydrothermal and sol gel method [26]. In hydrothermal method, sodium hydroxide was added to titanium tetrachloride and the mixture was stirred dried at 450^oC. In sol gel method, titanium isopropoxide (TTIP) had been used as a precursor. TTIP was dissolved in ethanol and the mixture was stirred and dried. It was found that TiO_2NPs which resulted from hydrothermal method had no spherical shape and agglomeration naturewith an average size (about 17 nm) (as shown in Figure2) which resulted in absorbance of UV radiation at the wavelength of 362 nm. The TiO_2NPs resulted from sol gel method had an average size of about 7 nm, spherical shape and more uniform distribution(Figure 3).TiO_2NPs wasresulted in greater absorbance of UV radiation at the wavelength of 351 nmand higher bandgap value about 3.5 eV.

Figure 2

Figure 3

TiO_2NPs had been synthesized [29] by hydrothermal method using ilmenite in the form of synthetic rutile as a precursor. Sodium hydroxide was mixed with synthetic rutile at 550^{o}C. The resulted TiO_2 NPs had smaller size (15.6 nm), more uniform distribution, higher absorbance of UV radiationand lower bandgap (3.23eV) than commercial TiO_2NPs.

From the results of sol gel and hydrothermal TiO_2preparation methods, it is obvious that sol gel method provided more UV protection and smaller size of TiO_2NPs. The experiment which was reportedby Gouda *et al*. [27]produced smaller size of TiO_2NPs, excellent and durable UV protection,simple and energy saving process.

Green Synthesis

Green synthesis of TiO_2NPs depends on using natural materials and it is far better than chemical synthesis of TiO_2NPs as it depends on less hazardous chemicals and produces ecofriendly finishes.

TiO_2NPs had been prepared by ecofriendly and low-cost method using Aspergillus Tubingensis soil fungi [30]. 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_2NPs ranged from (1.5 to 5.9 nm). The resulted TiO_2NPs showed an absorbance of UV radiation within the range (300–350 nm).

TiO_2NPs had been synthesized by using leaf extracts of medicinal plant Ageratina altissima and tested the photocatalytic activity of resulted NPs [31]. The resulted TiO_2NPs had an average size (60-100 nm),spherical shape,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.

As it depicted fromthe above results, Tarafdar *et al.* [30] providedbetter green synthesis of TiO_2NPs as it included smaller size of TiO_2NPs (1.5 - 5.9) nm and wider range of UV absorbance (300–350 nm).

TiO_2NPs Application to Provide Textiles UV Protection

TiO_2NPs can be applied to different types of treated or untreated fabrics individually or with other materials to enhance UV protection and provide multifunctional finishing to fabrics.

Application of TiO_2NPs without treatment

Single Application of TiO_2NPs

Adnan *et al.* [32] investigated UV protection effect of TiO_2NPs on samples of (pure lyocell, (80/20, 60/40, 50/50)% lyocell silk blends and pure silk) properties. It was found that TiO_2NPs 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 were also observed.

Finishing with TiO_2NPs and dyeing of wool fabric had been applied [33] 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_2NPs had uniform distribution and size < 10 nm. Increasing the concentration of acetic acid with 1% dye caused both exhaustion rate and color strength(K/S) values to increase. The addition of TiO_2NPs was resulted in higher photocatalytic activity (5h of exposure to UV radiation yielded 93% degradation of methylene blue) and slight decreasing in breaking stress (8.6%), elongation rate (7.8%) and thermal stability.

The antibacterial activity and UV protection effect of TiO_2NPs on cotton fabric [34] had been investigated. Urea nitrate (UN) was used in-situ preparationof TiO_2NPs as a nitric acid source and theeffect had been investigated. It was found that higher concentration of (UN) caused a smaller size of TiO_2NPs (<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.

All previous researches included single application of TiO_2NPs to provide UV protection for different types of fabrics.Cons and pros of each process weresummarized in Table 5.

Table 5

Application of TiO_2NPs in Combination with Other Materials

Sodium hypophosphite(SHP) and citric acid(CA) had been used with TiO_2NPs to provide multifunctional finishing for cotton/polyester fabric [35]. Different concentrations of CA, SHP and TiO_2NPs were used to determine optimum finishing conditions. It was found that using optimum concentrations of CA (30gm/l) with (SHP)(18gm/l) and TiO_2NPs (0.5gm/l) resulted in higher flame retardancy effect, lower pilling formation, improving antibacterial activity against S.aureus bacteria and increasing hydrophilicity, photocatalytic activity, self-cleaning property and wash fastness of treated fabrics. Also, optimum conditions resulted in slight decreasing in tensile strength,however after exposure to UV radiation there was an improvement in fabrics tensile strength due to the effect of TiO_2 NPs.

AgNPs used in combination with TiO_2NPs to provide multifunctional finishing to Polyester fabrics[36]. 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/AgNPs 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 was 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 AgNPs in first 3 washes and in artificial sweat especially alkaline sweat conditions.

Li *et al.*[37] also used AgNPs with TiO_2NPs but they produced more durable finishing to cotton fabric. TiO_2NPs were applied to cotton fabrics with two different concentrations by hydrothermal treatment. AgNPs were in-situ implimentedin cotton fabrics using different concentrations of $AgNO_3$. It was found that higher concentrations of Ag and TiO_2NPs gavevery 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.

The previous results showed the application of combined TiO_2NPs with other materials on untreated fabrics to provide durable multifunctional finishing. The advantages and disadvantages of each process are shown in Table 6.

Table 6

Application of TiO_2NPs after fabric treatment

Application of TiO_2NPs after different treatment processes on fabrics improved UV protection and other functions due to the increasing affinity of treated fabric for finishing agents.

TiO_2NPs had been applied [38]on cellulose acetate fabric (CA) after treatment with H_2O_2 in ultrasonic bath. CA samples were padded in different concentrations of TiO_2NPs, dried and cured in microwave oven at different conditions.It was found that using optimum conditions (Ultrasonic treatment -0.75 % TiO_2NPs-microwave curing at 90% for 15 seconds) was 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).

Hashemizad *et al*. [39] applied TiO_2NPs on polyester fabric pretreated with oxygen gas plasma and its effect on fabric properties and adsorption rate of TiO_2NPs had been investigated. It was found that treatment with Plasma before TiO_2NPs application resulted inamore uniform distribution of TiO_2NPs on fabric surface, higher self-cleaning property and higher UV protection (decreasing in the percentages of UV Reflectance) even after 10 washes.

Polyester cotton (80:20) blended curtains pretreated with cold plasma before the application of TiO_2 and SiO_2NPs [40]. 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 SiO_2NPs. It was concludedthat plasma treatment for 6 minutes before the application of NPs gave 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 and good adhesion of NPs in the fabric surface after 50 washes of the fabric. Also, slight decreasing in elongation, tensile strength and air permeability of treated fabric was detected.

Polyester (PET) and polypropylene (PP) fabrics pretreated with Dielectric-barrier discharge (DBD) plasma before the application of TiO_2, Al_2O_3 and ZnONPs to provide enhanced finishing to the fabric [41]. Different concentrations of Al_2O_3, ZnO and TiO_2NPs 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_2NPs(156.90). Higher concentration of ZnONPs also gaveexcellent UPF value (82.98) more than Al_2O_3NPs (36.76).
- ZnONPs showed more antibacterial activity against S. aureus and K.pneumonia bacteria.
- TiO_2NPs had no antibacterial effect against both types of bacteria, while Al_2O_3NPs had only slight effect against K.pneumonia bacteria (reduction percentage 6.5%).
- In PP fabricplasma treatment before the application of NPs leaded to:
- 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)

The aboveresearches 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 7.

Table 7

Conclusions:

This review indicatedthe great importance of ZnO and TiO_2NPs as textile protective agents against UV radiation. Different synthetic methods (chemical–green) of ZnO and TiO_2NPs werecompared to find out which is a better method. In chemical synthesis of ZnONPs it is found that hydrothermalmethod is better than sol gel method as it provides smaller size of NPs and higher absorbance of UV radiation.On the contrary, in TiO_2NPs synthesis, sol gel method included better results than hydrothermal method. Green method in both ZnO and TiO_2NPs 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 ZnONPs on treated and untreated fabrics individually or with natural materials (chitosan, carboxymethyl chitosan) or synthetic materials (UV absorber, sodium hypophosphite, CU_2O NPs, Ag NPs) werediscussed. Also, advantages and disadvantages of TiO_2NPs application on both treated and untreated textiles individually or in combination with other materials (Sodiumhypophosphite, citric acid, Ag NPs)wereincluded.Main disadvantages in ZnO and TiO_2NPs 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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Tables

Table 1. Increasing ultra violet protection with higher UPF values according to ASTM D6603 [2].

UV protection	UPF range
Excellent	**40-50, +50**
Very good	**25-39**
Good	**15-24**

Table 2. Cons and Pros of ZnO NPs application with natural materials.

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

Table3. Advantages and disadvantages of ZnO NPs application with synthetic materials

Synthetic material	Advantages	Disadvantages	Reference
Sodium hypophosphite-Polycarboxylic acids	- Polycarboxylic acids are environmental friendly materials. - Smaller size of ZnO NPs. - Producing multifunctional finishing to cotton and CO/PET	-Limiteddurability test (2 washes). -Using BTCA caused increase flame retardant action but it caused	Abdelhadyet al., [2013]

	fabric (UV protection, Wrinkle resistance and flame retardancy effect). - Discussing the effect of ZnO NPs, SHP and Curing temperatures.	increasing roughness and yellowness of treated fabric. - Increasing concentration of ZnO NPs resulted in higher UPF values but it caused increasing in yellowness and roughness of treated fabric.	
CU_2O NPs	-Synthesis of CU_2O/ZnONPs in-situ provided more durable finishing. -Adding folic acid as a bio template during in-situ synthesis of CU_2O/ZnO NPs provided greener, more effective method to improve UV protection. -Providing UV protection with improving physical properties of cotton fabric.	- Durability tests were carried out after only 5 washing cycles. - Slight increase in cotton fabric thickness.	Noorian et al., [2015]

Table4. Advantages and disadvantages of ZnO NPs application after plasma treatment

Plasma treatment	Advantages	Disadvantages	Reference
CF4 and H_2O plasma.	- Using lower concentrations of ZnONPs which provide	- Low finishing durability.	Gorjanc et al., [2014]

	environmental and economic improvement. - Providing multifunctional finishing to cotton fabric (higher UV protection and hydrophilic effect)		
O_2 plasma	-Green method using natural material (carboxymethyl chitosan). -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.	-	Wang et al., [2016]

Table5. Advantages and disadvantages of TiO_2NPs single application on different fabric types

Targeted fabric	Advantages	Disadvantages	Reference
Pure lyocell - (80/20-	- Including durability tests for 25	- TiO_2NPs finishing	Adnanand Moses,

60/40-50/50) % lyocell silk blends - Pure silk fabrics	washes. -Providing durable multifunctional finishing for treated fabrics (UV protection and anti-wrinkling effect).	caused negative effectson physical properties of all treated fabrics.	[2013]
Wool fabrics	- saving money, time and effort. - Producing smaller size of TiO_2 - Improving photocatalytic activity.	- No tests for dyeing and finishing durability. - Negative effects on physical properties of wool fabric.	Zhang et al.,[2014].
Cotton fabrics	- In situ synthesis of TiO_2 NPs which save(time -effort-money). - Investigating the effect of (UN) as a peptizing agent used in TiO_2 NPs synthesis. -Providing durable multifunctional finishing to cotton fabrics(UV protection and antibacterial activity against two types of bacteria). - Including durability tests for 20 washes.	- Also, there was negative effect on physical properties of cotton fabrics (tensile strength and elongation rate and).	El-Naggar et al., [2016]

Table 6. Advantages and disadvantages of TiO_2NPs application with other materials.

Applied material	Advantages	Disadvantages	Reference
Sodium hypophosphite -	-Providing multifunctional	-Antibacterial tests	Hashemikia and

Citric acid- TiO_2NPs.	finishing to fabric. - Investigating The optimum concentrations of CA, SHP and TiO_2NPs. - Increasing flame retardancy and anti-pillingeffect. - Improving antibacterial activity against S.aureus bacteria . - Increasing hydrophilicity and self-cleaningproperty. - Improving tensile strength - Including durability tests for 10 washes.	included only one type of bacteria. - Decreasing in fabric tensile strength. - Including durability tests for only 10 washes.	Montazer, [2012].
AgNPs - TiO_2NPs.	- Providing multifunctional finishing to Polyester fabrics - Higher antimicrobial activity aginst E.coli , S.aureus bacteria and C.albicans fungus - Increasing UV protection of treated fabrics . - Including durability tests for 10 washes. - Durable antibacterial activity after 10 washes.	- Including durability tests for only 10 washes. -Decreasing UPF values after 10 washes. -Low fastness (for washing and perspiration)due to Ag NPs release.	Milosevic et al., [2013].
Ag NPs - TiO_2 NPs.	- Providing multifunctional finishing to cotton fabric. - Investigating the effect of Ag	-	Li et al., [2017].

	and TiO_2NPs. - Including hydrothermal treatment for higher crosslinking. - In situ synthesis of AgNPs 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.		

Table 7. Advantages and disadvantages of TiO_2NPs application on treated fabrics.

Treatment process	Advantages	Disadvantages	Reference
Treatment with H_2O_2 in ultrasonic bath.	- Using microwave curing after the application of TiO_2NPs. -Including investigation of the optimum conditions (TiO_2 NPs concentration -microwave curing conditions). -Providing multifunctional finishing to CA fabric. - Improving UV protection and self-cleaning property of CA fabric.	- Decreasing in Roughness and tensile strength of treated fabrics. - No tests for finishing durability were included.	Ramadan et al., [2012].

	- 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. - Providing enhanced multifunctional finishing to PET fabric. - Including durability test. - Providing higher UV absorbance even after 10 washes. - Improving self-cleaning of treated fabric.	- Including durability tests for only 10 washes.	Hashemizad et al., [2014].
Cold plasma treatment	- Including investigation of the optimum conditions of plasma treatment. - Plasma treatment provided higher deposition of NPs on the fabric surface. - Providing improved multifunctional finishing to polyester cotton blended fabric. - Improving UV protection, antistatic and antibacterial property of treated fabric. - Including durability tests for 50	- Negative effects on physical properties of polyester/ cotton blends fabric (decreasing in elongation, tensile strength and air permeability). - No tests for UPF values, antibacterial and antistatic property after 50 washes.	Memon and Kumari, [2016] .

	washes.		
(DBD) plasma treatment.	-Including comparison of Al_2O_3 , ZnO and TiO_2NPs effect on PET and PP fabrics. -Investigating the effect of plasma treatment on PP and PET fabrics. - Providing more uniform distribution of NPs on PP fabric due to plasma treatment. - Improving UV protection of PP fabric. ZnONPs> TiO_2NPs > Al_2O_3 NPs. - Providing excellent UV protection for PET fabric TiO_2NPs> ZnONPs> Al_2O_3NPs.	- Antibacterial activity of PP fabric was not tested. - TiO_2 NPs showed no antibacterial effect on polyester fabric. - No tests for finishing durability were included.	Gawish et al., [2017].

Figures

Figure 1.SEM images of synthesized titania with different magnification [28]

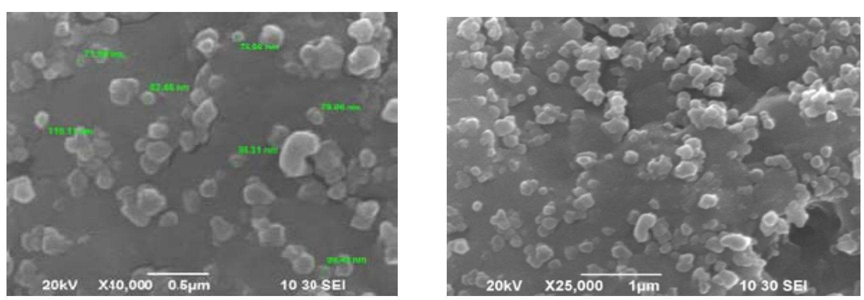

Figure 2. TEM images of TiO_2 nanoparticles synthesized and hydrothermal method [26]

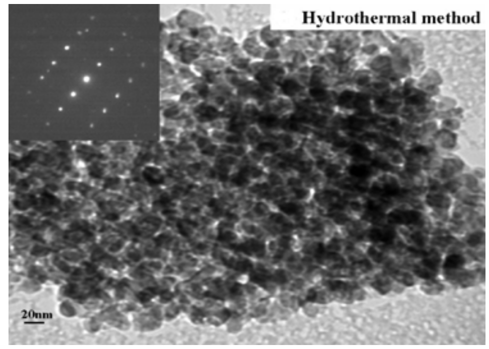

Figure 3.TEM images of TiO_2 nanoparticles synthesized via sol-gelroute [26]