ZnO and TiO_2 Nanoparticles as Textile Protecting Agents Against UV Radiation : A review

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 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 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% infrared and 5% ultra violet radiation) [1].

UV radiation can be subdivided according to their wavelength and effect to: UV- A (320-400 nm), UV-B (280-320 nm) and UV-C (200-280 nm). 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 and more damage in (textiles, ~~–~~dyestuff, ~~–~~human skin)[2].

To block the harmful effect of UV radiation organic and ~~Inorganic~~ inorganic UV blockers are used.

Inorganic UV blockers are better than organic UV blockers because of their non-toxicity and chemical stablility when exposed to higher temperatures and UV radiation. The most common ~~Inorganic~~ 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. Ultra violet protection factor (UPF) related to reflection and absorbance of UV radiation .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 [5].

ZnO Nanoparticles in Textiles UV Protection:

~~Zno~~ 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 as shown in Figure 1 .Using zinc source such as (zinc acetate-zinc, chloride-zinc nitrate) with synthetic or natural materials.

Figure1

Chemical Synthesis

Sol Gel Method

ZnO NPs had been prepared [8] with an average size of (30-60 nm) 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).

Another group of researchers [9] prepared ZnO NPs with an average size (58 nm). The researchers also depended on Sol-Gel method and using Zinc acetate dihydrate as precursor but they used 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).

Hydrothermal Method

ZnO NPs had been prepared ~~[10]~~ by hydrothermal process using water , 1,2-ethanediol as a solvent [10]. ~~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 1-2ethanediol 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.

Taunk *et al*. [11] 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 (7 nm) and absorption in the UV region (235-407 nm).

The results of all previous researches can be summarized in Table 1. 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 (235-407 nm) .

Table 1

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.

ZnO NPs had been prepared [11] from the reaction of ~~(CMC)~~ chemically modified chitosan (CMC) ~~(~~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~~.~~, 5-3 M)~~-~~. ~~zinc~~ Zinc acetate was added to the mixture and calcined at different temperatures~~-~~. It was found that ~~Modified~~ 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 (19-54 nm).

Ramesh *et al*. [13] 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~~ uniformly distributed, had a size range from (9-10 nm) and a bsorbed UV radiation at the range (208-400 nm).

Also ZnO NPs had been produced [14] 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 (22.18 nm), showed antibacterial activity against gram positive and gram negative bacteria and absorbed UV radiation within the range (340-400 nm).

The green synthesis methods of ZnO NPs are summarized in Table 2 .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 (9-10 nm) and ~~Wider~~ wider range of UV absorption (208-400 nm).

Table 2

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 Figure 2.

Figure 2

Application of ZnO NPs without Treatment:

Single Application of ZnO NPs:

ZnO NPs had been applied [1] with (average size <35 nm) 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 improvement in antimicrobial activity against E. coli and S. aureus bacteria. On the other hand, ZnO NPs had been applied [15] 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 (2 gm) resulted in producing ZnO NPs with average size 359 nm. ZnO NPs leaded to good UPF values after 15 washes (17.6) ? and Durable antibacterial activity of cotton fabric after 20 washes.

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Another team of researchers [16] also synthesized ZnO NPs in situ to provide durable multifunctional finishing to cotton fabrics. The difference in this research 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 (<100 nm) 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 besides higher UPF values (890) after 50 washes (450).

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Previous researches in single application of ZnO NPs are summarized in Table 3.

Table 3

It is obvious that the application method of ZnO NPs made by Prasa 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 —and money), Producing producing smaller size of ZnO NPs and Providingproviding higher UPF values and more durable effect after 50 washes.

Application of ZnO NPs in Combination with Other Materials

ZnO NPs with Natural Materials

ZnO NPs could be used [17] 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~~padding and cured at different temperatures. It was found that ~~Preparation~~ preparation of ZnO/-CMCTS bionano composite at 50°C resulted in smaller size of NPs (–28 nm for ZnO NPs and 100 nm for CMCTS). Higher concentration of ZnO/CMCTS nano-composite leaded to ~~increasing~~ increase 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 [18] 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~~ showed comparatively higher UPF values (8.3) and antibacterial activity.

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 4.

Table 4

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

ZnO NPs had been combined ~~[19]~~ with sodium hypophosphite (SHP) and polycarboxylic acids to provide multifunctional finishing to cotton and cotton /polyester (56/35%) fabrics [19]. 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 30 nm. It was found that using of BTCA with 160°C as a curing temperature leaded to ~~increasing~~ increase (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~~ 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 leaded to 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.

Another work [20] used 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~~ 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 (48 nm) and increasing UV protection, hydrophilicity, thickness, wash fastness, anti-wrinkle property and improving the handle of cotton fabrics

Cons and Pros of ZnO NPs application with synthetic materials are summarized in Table 5

Table 5

Application of ZnO NPs after Plasma Treatment

A method [21] has been developed 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 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~~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 decreased dramatically after 10 washes from (58.89 to 4.58).

ZnO NPs and carboxymethyl chitosan (CMCS) have been used [22] to provide multifunctional finishing for plasma pretreated cotton fabric. Cotton fabrics were treated by O_2 plasma for 2 min at 200 W. 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 Table 6

Table 6

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 ultra violet radiation [23] due to their properties (lower cost, chemically stable, non-toxicity, photocatalytic activity and longer durability) [24].

TiO_2 NPs synthesis

There are many methods to prepare TiO_2 NPs [25] by chemical [25] or green precursors [26, 27] as shown in Figure 3.

Figure 3

Chemical Synthesis

Sol Gel Method

A group of researchers [28] 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) and higher purity, stability and dispersion ability. Higher concentrations of TiO_2 NPs leaded to higher UPF values (40) and increasing antibacterial activity ~~againt~~ against S. aureus and K.pneumoniae bacteria after 20 washes.

TiO_2 NPs had been prepared [29] 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 700^{o}C was about 67%).

Hydrothermal Method

TiO_2 NPs had been prepared ~~[27]~~ by both hydrothermal and sol gel method [27]. In hydrothermal method, sodium hydroxide was added to titanium tetrachloride and the mixture was stirred dried at 450^{o}C. 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 that TiO_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.

TiO_2 NPs had been synthesized [30] 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), higher absorbance of UV radiation and lower band–gap (3.23 eV) than commercial TiO_2 NPs .

The results of all previous researches about chemical synthesis of TiO_2 NPs are summarized in Table 7. 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 Gouda ~~and his team~~ *et al.*, [?] produced Smaller size of TiO_2 NPs, excellent and durable UV protection, simple and energy saving process.

Table 7

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 ecofriendly finishes.

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TiO_2 NPs had been prepared [31]by ecofriendly and low cost method using Aspergillus tubingensis soil fungi [31]. 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).

TiO_2 NPs had been synthesized [32] by using leaf extracts of medicinal plant Ageratina altissima and tested the photocatalytic activity of resulted NPs [32]. 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.

The results of green synthesis of TiO_2 NPs are summarized in Table 8. From the results, method made by Tarafdar and his team *et al.*, [?] 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)

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Table 8

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 with other materials to enhance UV protection and provide multifunctional finishing to fabrics Figure 4.

Figure 4

Application of TiO_2 NPs without treatment

Single Application of TiO_2 NPs

A group of researchers [33] 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.

Finishing with TiO_2 NPs and dyeing of wool fabric had been applied [34] 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 (5 h 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.

The antibacterial activity and UV protection effect of TiO_2 NPs on cotton fabric [35] had been investigated, but used urea nitrate (UN) in ~~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 (<50 nm), 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_2 NPs to provide UV protection for different types of fabrics. Cons and pros of each process are summarized in Table 9.

Table 9

Application of TiO_2 NPs in Combination with Other Materials

Sodium hypophosphite (SHP) and citric acid (CA) had been used with TiO_2 NPs to provide multifunctional finishing for cotton/polyester fabric [36]. 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 (30 gm/l) with (SHP)(18 gm/l) and TiO_2 NPs (0.5 gm/l) resulted in higher flame retardancy effect, lower pilling formation, ~~Improving~~ improving antibacterial activity against S.aureus bacteria and ~~Increasing~~ increasing hydrophilicity, photocatalytic activity, self-cleaning property and wash fastness of treated fabrics. Also, optimum conditions leaded to slight decreasing 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.

Ag NPs used in combination with TiO_2 NPs to provide multifunctional finishing to Polyester Fabrics [37]. 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.

Another team of researchers [38] 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 were in in-situ synthesized in cotton fabrics using different concentrations Ag No_3. It was found that higher concentrations of Ag and TiO_2 NPs leaded to very good and durable antibacterial activity against both E. coli and S. aureus and Increasing increasing in UPF values (from 3 to 56.39). Only slight decreasing of UPF values after 50 washes was detected.

Previous researches included application of combined TiO_2 NPs with other materials on untreated fabrics to provide durable multifunctional finishing. The advantages and disadvantages of each process are shown in Table 10.

Table 10

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 increasing affinity of treated fabric for finishing agents.

TiO_2 NPs had been applied [39] on cellulose acetate fabric (CA) after treatment with H_2O_2 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) leaded to:

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

TiO_2 NPs on polyester fabric after oxygen gas plasma treatment had been applied and its effect on fabric properties and adsorption rate of TiO_2 NPs had been investigated. It was found that treatment with Plasma before TiO_2 NPs application leaded to 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.

Polyester cotton (80:20) blended curtains pretreated with cold plasma before the application of TiO_2 and SiO_2 NPs [41]. 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_2 NPs. It was found that plasma treatment for 6 minutes before the application of NPs leaded to 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 ZnO NPs to provide enhanced finishing to the fabric [42]. 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 leaded to 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 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)

All of 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 11.

Table 11

Conclusions:

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 - CU_2O 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. 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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Tables

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) [ ]

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Table 2. Comparison between green methods of ZnO NPs synthesis.

Precursors	Optimum Size (nm)	UV Protection effect	Reference
Zinc nitrate - Modified chitosan	19-54 ~~nm~~	No tests for UV protection effect.	Thirumavalavan et al., ~~(2013)~~ [ ]
Zinc nitrate - Extract of Citrus aurantifolia leaves	9-10 ~~nm~~	absorption in UV region (208-400 nm).	Ramesh et al., ~~(2014)~~[ ]
Zinc acetate - Sodium hydroxide- extract of Aloe Vera leaves	22.18 ~~nm~~	absorption in UV region (340-400 nm).	Varghese et al., ~~(2015)~~ [ ]

Table 3. Comparison between single applications of ZnO NPs on cotton fabric.

Precursors	Size (nm)	UV Protection effect	Reference
-	The used ZnO NPs size < 35 ~~nm~~	Increasing UPF values from (27.22) to (711.44)	Abdel Ghani et 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~~ 100	UPF value 890 after 5o washes 450	Prasa et al ., ~~(2016)~~[ ]

Table 4. Cons and Pros of ZnO NPs application with natural materials.

Natural material	Advantages	Disadvantages	Reference
Carboxymethyl chitosan	-Smaller size of nano particles. - Higher antibacterial activity against both gram positive and gram negative bacteria. -Improving UV protection (7.6).	-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. - Higher UPF values (8.3). - Moderate antibacterial activity against both gram positive and gram negative bacteria.	-Comparatively larger size of chitosan/ ZnO NPs (300 nm). -No tests for finishing durability.	Abdelhady, (2012).[ ]

Table 5. 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. - Smaller size of resulted ZnO NPs. - Producing multifunctional	-Iincluding durability tests for only 2 washes. -Using BTCA leaded to increase flame retardant action but it caused	Abdelhady et al., (2013)[ ]

	finishing to cotton and CO/PET 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.	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/ ZnO NPs 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)~~[ ]

Table 6. Cons and Pros of ZnO NPs application after plasma treatment.

Plasma treatment	Advantages	Disadvantages	Reference
CF4 and H_2O plasma.	- Using lower concentrations of ZnO NPs which provide	- Decreasing in wash fastness (UPF values	Gorjanc et al., ~~(2014)~~ [ ]

	environmental and economical improvement. - Higher adsorption of ZnO NPs which resulted in higher UPF values . - Increasing hydrophilicity of cotton fabrics.	decrease from 58.89 to 4.58 only after 10 washes).	
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)~~ [ ]

Table 7. 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 and 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 and Rajendran, ~~(2012)~~[ ] .
Sol gel method	Titanium isopropoxide – Ethanol	7~~nm~~	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)~~[ ]

Table 8. 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. - Including durability tests for 25 washes. Providing durable UV protection after 25 washes. -Improving in anti wrinkle property of all treated fabrics.	- TiO_2 NPs finishing caused negative effects on physical properties of all treated fabrics (decreasing in air permeability, tensile strength and absorbency)	Adnan and Moses, (2013)[ ]
Wool fabrics	-Providing dyeing and finishing process at the same time which save money, time and effort. - Investigating the optimum concentrations of reactive dye and acetic acid. - Producing smaller size of TiO_2 NPs < 10 nm. - Improving photocatalytic activity.	- No tests for dyeing and finishing durability. - Negative effects on physical properties of wool fabric (decreasing in breaking stress, elongation rate and thermal stability).	Zhang et al., (2014)[ ].
Cotton fabrics	- In situ synthesis of TiO_2 NPs which saved (time -effort-money). - Investigating the effect of (UN) as a peptizing agent used in TiO_2 NPs synthesis.	- Also, there was negative effect on physical properties of cotton fabrics (Slight decrease in elongation rate and tensile strength).	El-Naggar et al., (2016) [ ]

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.

Table 9 comparison between green methods of TiO_2 NPs synthesis

Precursors	Optimum Size (nm)	UV Protection effect	Reference
TiO_2 salt-Extract of Aspergillus tubingensis fungi .	1.5 - 5.9 nm.	Absorbance of UV radiation at the range (300–350 nm).	Tarafdar et al., (2013)[ ].
$TiO(OH)_4$ - leaf extracts of Ageratina altissima plant .	60-100 nm	Higher absorption of UV radiation at the wavelength 332 nm.	Ganesan et al., (2016) [ ]

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Table 10. 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. - Investigating The optimum concentrations of CA , SHP and TiO_2 NPs . - Increasing flame retardancy and anti pilling effect . - Improving antibacterial activity against S.aureus bacteria . - Increasing hydrophilicity and self cleaning property . - Improving tensile strength - Including durability tests for 10 washes.	- Antibacterial tests included only one type of bacteria. - Decreasing in fabric tensile strength. - Including durability tests for only 10 washes.	Hashemikia and Montazer, ~~(2012)~~[ ].
Ag NPs - TiO_2 NPs .	- 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.	- 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)~~[ ].

	- Durable antibacterial activity after 10 washes.		
Ag NPs - TiO_2 NPs.	- Providing multifunctional finishing to cotton fabric. - 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.	-	Li et al., (2017)[ ].

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Table 11. Cons and Pros of TiO_2 NPs application on treated fabrics. 456

Treatment process	Advantages	Disadvantages	Reference
Treatment with H_2O_2 in ultrasonic bath.	- Using microwave curing after the application of TiO_2 NPs. -Including investigation of the optimum conditions (TiO_2 NPs concentration -microwave curing conditions).	- Decreasing in Roughness and tensile strength of treated fabrics. - No tests for finishing durability were	Ramadan et al., (2012)[ ].

	-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.	included.	
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	- Negative effects on physical properties of polyester/ cotton blends fabric (decreasing in elongation, tensile strength and air permeability). - No tests for UPF	Memon and Kumari, (2016)[ ] .

	polyester cotton blended fabric. - Improving UV protection, antistatic and antibacterial property of treated fabric. - Including durability tests for 50 washes.	values, antibacterial and antistatic property after 50 washes.	
(DBD) plasma treatment.	-Including comparison of Al_2O_3, ZnO and TiO_2 NPs 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. Zno NPs> TiO_2 NPs > Al_2O_3 NPs. - Providing excellent UV protection for PET fabric TiO_2 NPs> ZnO NPs> Al_2O_3 NPs.	- 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

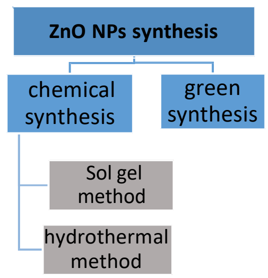

Figure 1. Synthesis of ZnO NPs.

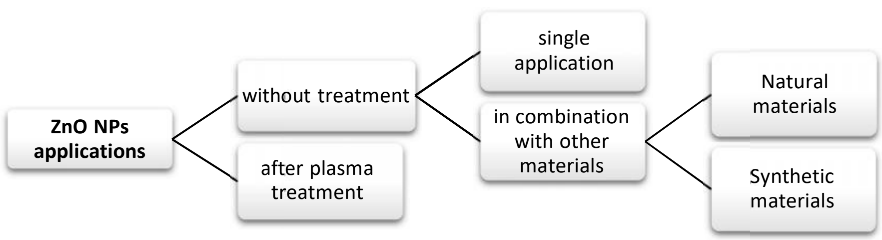

Figure 2. Applications of ZnO NPs to provide textiles UV protection

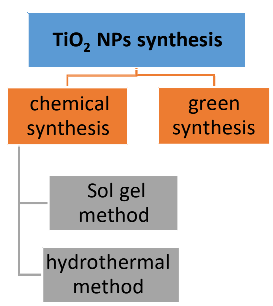

Figure 3. Synthesis of TiO_2 NPs.

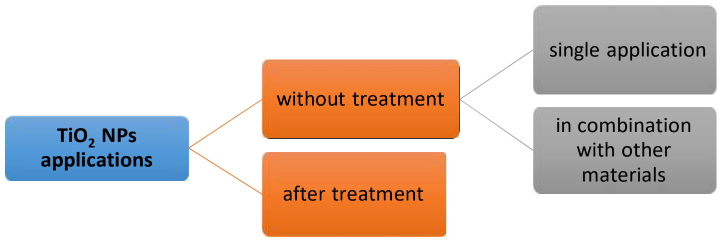

Figure 4. Application of TiO_2 NPs to provide textiles UV protection.