



Article The Comparison of Metal Doped TiO₂ Photocatalytic Active Fabrics under Sunlight for Waste Water Treatment Applications

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Abstract: The release of toxic effluents and microfibers during the frequent washings of textiles poses a major threat to the environment. On the one hand, the detrimental effluents from detergents pose a threat to marine biota in peril, and on the other, microplastics have even been found in breastmilk. According to this study, functionalized metal-doped TiO₂ nanoparticles can be immobilized to create fabrics that are hygienic and antibacterial. There is a need to reduce the amount of different detergents, surfactants and chemicals used to remove stains. The manufacture of pristine and Cu-, Ag- and Zn-doped TiO₂ nanoparticles having trace molar ratios of dopant chosen with a simple sol–gel approach using pad–dry–cure silane coupling agents, firstly with the functionalization and then the immobilization of nanoparticles, was successfully performed on cotton fabric. The asobtained fabrics were evaluated for their crystallinity, chemical functionalized materials were assessed in ambient sunshine against five commercial colors. Within three hours of sunshine exposure, according to color strength analysis and antibactericidal activities, 95–98% of the dye was degraded from the functionalized fabric surface. Additionally, the treated content kept its mechanical and comfort qualities.

Keywords: photocatalytic active fabrics; dye degradation; self-cleaning fabrics; metal-doped; photocatalysts

1. Introduction

Every living thing on Earth needs water in order to survive. For life to continue on Earth, fresh water must be available. More specifically, clean water is required for human activities, including drinking, cooking, cleaning and agriculture. Environmental pollution, particularly industrial pollutants, has negatively impacted life on Earth. Industries release a number of hazardous chemical substances into water, including industrial effluents that contain a number of organic compounds [1,2]. Among these pollutants, dyes are one of the chemicals used most frequently in a variety of sectors, including textiles, paper, foundation, leather, plastic and printing [3–5]. Methylene blue (MB), a traditional water-soluble dye that



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). belongs to the phenothiazine family and that is widely used in industry, causes significant aquatic contamination [6]. As a result, it is critical to create more practical, eco-friendly and green techniques to solve the issues associated with dye waste discharge.

A promising method to dramatically reduce the rapid use of fossil fuels and combat climate change is solar-driven photocatalytic CO_2 conversion to beneficial compounds [7]. Global warming is primarily caused by CO_2 emissions, which has detrimental effects on human health. Semiconductor photocatalysts are used to convert solar energy into chemical energy for a reduction in CO_2 . These catalysts rely on charge generation, transfer and separation facilities. Semiconductor photocatalysts are used to convert solar energy into chemical energy for a reduction in CO_2 , and these catalysts depend on charge generation, transfer and separation facilities [8]. The standard semiconductor photocatalyst that has undergone extensive research for the photoreduction of CO_2 is titanium dioxide (TiO₂) [9]. Due to its narrow light absorption range, electron–hole recombination and slow surface reaction kinetics, TiO₂ still has limited commercial uses [10]. In terms of light absorption and significant electron–hole recommendations, other well-known wide-band-gap semiconductor photocatalysts like ZnO, BiOCl, SiC and SrTiO₃ have also demonstrated comparable limitations [11].

Due to its potential benefits in environmental conservation, such as water purification, photocatalysis has recently attracted significant attention [12]. Photocatalysis uses photodegradation and is a complicated oxidation method that may eliminate harmful organic substances from the environment [13,14]. Different semiconductor photocatalysts are employed in the photocatalysis process, but most of them can only use 4–5% of sunlight [15,16]. Due to its broad bandgap (Eg), photogeneration from solar energy is less [17]. As a result, it is important to put together photocatalysts that can operate effectively in the visible spectrum and have increased photocatalytic activity. TiO₂ possesses wider bandgap, exhibiting itself in three crystalline phases: anatase, brookite and rutile. For photocatalysts and photovoltaics, the most useful form is anatase [18].

The bandgaps for these mentioned crystal phases are rutile-3.0 eV, brookite-3.3 eV, and anatase-3.2 eV, only for UV light, as they do not perform in visible light [19]. Because of the anatase phase's large bandgap (3.2 eV), it can only absorb a limited portion of the solar spectrum (5% or less). For enhancing the photocatalytic efficacy of TiO_2 using visible light for photocatalysis, it is crucial to lower its bandgap. There is a need to lessen the charge transfer restrictions, since the TiO₂ surface is where photocatalytic degradation happens most frequently. In addition, the photocatalytic breakdown rates are reduced due to TiO₂'s limited affinity for organic pollutants, particularly hydrophobic pollutants [20]. Additionally, during photocatalytic degradation, the scattering instability of TiO₂ nanoparticles may create clustering, lowering light incidence on active centers, which has a significant impact on the catalytic activity [21,22]. However, compared with large particles, small particles have a higher surface area and better absorption, which can lower their photocatalytic activity [23]. Considering the benefits and limitations of these materials, several researchers have attempted to increase the photocatalytic activity of these materials by the use of various techniques. Enhancing the photocatalytic properties of various materials has been accomplished through the surface and interface modification by altering the morphology and particle size, composites or couplings, doping with metals and nonmetals and codoping transition metals and nonmetals. Other methods have included the deposition of noble metals and surface sensitization with organic dyes and metal complexes.

To overcome all the limitations of TiO₂-based photocatalysis, some countermeasures have been developed in previous studies, for example, modification of a TiO₂ catalyst to achieve the utilization of visible light [23,24]; optimization of catalyst synthesis to obtain catalysts with a defined crystal structure, small particle size and high affinity to various organic pollutants [15,16]; and design and growth of the second generation of TiO₂ catalyst with high separation ability, which can be recovered and regenerated effectively [17,18]. Another popular approach to overcome the restrictions is to optimize catalyst production to produce catalysts with a defined crystal structure, small particle size and strong affinity

to different organic contaminants [25,26]. Yet another approach is to create and improve the second generation of TiO₂ catalysts to obtain excellent charge separation as well as effective regeneration [27,28]. To overcome the limitation of the wide bandgap of TiO₂, surface-tuning strategies and modification of oxides on the nanometer scale have been exploited through doping or surface modification [29,30]. Indeed, TiO₂ doping with metal nanoparticles Silver (Ag), Copper (Cu) and Zinc (Zn) has extended its activity towards the visible region [31]. Photocatalytic active fabrics have been developed to reduce the use of surfactants, because these fabrics utilize the potential of light for cleaning without the use of surfactants.

Recent studies used the coprecipitation approach to create progressions of Mn/g-C₃N₄/ZnO (Mn/GZ) and Ni/g-C₃N₄/ZnO (Ni/GZ) nanocomposites (NCs) with various concentrations (wt%) of g-C₃N₄. The photocatalytic efficiency of the composite materials was tested using the target pollutants methyl orange (MO) and eryochrome black T (EBT) dyes. The generated Mn/GZ and Ni/GZ NCs demonstrated greater photocatalytic activity than g-C₃N₄/ZnO and g-C₃N₄. The increased photocatalytic performance of Ni/GZ and Mn/GZ NCs may be due to synergistic interactions at the g-C₃N₄ and ZnO interface, which create a more efficient separation and conduction [32]. In this study, cobalt-doped tin oxide (Co-SnO₂) nanoparticles (NPs) and Co-SnO₂/SGCN (sulfur-doped graphitic carbon nitride) nanocomposites (NCs) were used in the photocatalytic degradation of methylene blue (MB) for wastewater treatment. The photocatalysts were created using the coprecipitation approach. Compared with other Co-SnO₂ NP concentrations (1, 3, 5 and 9 wt%), the 7% Co-SnO₂ NPs showed the greatest photocatalytic degradation of methylene blue (MB) [33].

The efficiency of charge transfer and separation, which affects the photocatalytic outcomes, depends on the interfacial interactions between the metal and semiconductor components in metal-doped photocatalysts [34]. In the mobile phase (powder form), nanoparticles have the capability to trap higher light and interact intensely with dyes, because the high surface area is exposed. Therefore, photocatalysts in the mobile phase are highly active compared with the passivated phase, because the catalytic reaction is highly concerned with diffusion. In the mobile phase, recovery is not 100%, which causes secondary pollution by nanocatalysts. In addition, complex separation procedures are required for separation of nanoparticles from treated water, such as filtration and centrifugation, which are not scalable in continuous procedures. On the other hand, the photocatalyst process in a passivated state on porous substrates is closer to that in practical applications because recovery is easy. Similarly, the repeated cyclic execution of photocatalysts in a passivated state is also better because there is insignificant leaching off of active materials. In photocatalysts based on metal-doped nanostructures, improved light absorption and charge separation are responsible for better performance [35]. Due to the wide range of electronic facet engineering in the metal/semiconductor interfaces, several parameters are taken into account for tuning the Schottky barrier, modifying the band arrangement and smoothing the transfer of charges between surfaces.

In this work, pristine TiO_2 and Cu-, Ag- and Zn-doped TiO_2 nanoparticles were synthesized by sol–gel methods with trace ratios at the same requirements. These photo catalysts were applied on cotton fabric surfaces to detect the capability of functionalization and to make photocatalytic activity. We propose a surface functionalization technique for strong adhesion of nanocatalysts on the fabric surface so that secondary pollution by the nanocatalysts can be avoided. The restriction of functionalized nanoparticles was attained by soaking the fabric in a 3-glycidoxypropyl trimethoxy silane (GPTS) functionalized nanoparticle solution. Morphological and crystallographic characterizations were detected by scanning electron microscope and X-ray diffraction analysis. Functional groups were identified by Fourier transform infrared spectroscopy. There were five dyes: Drimaren ultimate yellow, methylene blue, Drimaren ultimate red, methyl orange and Drimaren ultimate blue discovered as waste product. For detection of the photocatalytic activity of the undoped and Zn-, Cu- and Ag-doped TiO₂ nanoparticles, GPTS functionalized Zn, Agand Cu-doped TiO₂ nanoparticles and Zn-, Ag- and Cu-doped TiO₂ nanoparticles were tested. Kinetic experiments were also used to determine the rate of color deterioration. Finally, the comfort properties were also measured at different washing rates.

2. Results and Discussion

2.1. Morphological and Crystallographic Characterization

Figure 1 displays SEM images of functionalized cotton fabric with NPs, Zn-doped TiO₂ nanoparticles and functionalized cotton fabric after ten washings. These results show uniformly distributed, circular-dimensional Zn-doped TiO₂ nanoparticles. The nanoparticles are homogenous and cover the whole surface with dense morphologies. When these nanoparticles were functionalizing the cotton surface, microscale fibers appeared on the surface of functionalized cotton fabrics with parallel ridges. When the fabrics were functionalized by using metal-doped TiO₂ nanoparticles, the surface roughness is enhanced, also showing in SEM morphologies [13]. After functionalizing the cotton fabric, we found that the uneven morphology created at the micro- and nanoscale was beneficial enhancing adsorption surface particular area. The functionalized cellulose surfaces also had the ability to exhibit required concentration when checked after 10 washes. It means the functionalized nanoparticles have been strongly bonded with cotton surface by using GPTS, a silane coupling agent. This is mainly due to redox reaction, thereby enhancing the surface parameters and washing rates of modified textile surfaces compared with bare textile surfaces.



Figure 1. SEM morphology: (a) pristine Zn-doped TiO_2 nanoparticles, (b) Zn-doped TiO_2 functionalized cotton fabric and (c) functionalized cotton fabric.

Figure 2 displays the X-ray diffraction (XRD) patterns of Zn-doped TiO₂-0.5% (optimized), Ag-doped TiO₂-10% (optimized) and Cu-doped TiO₂-2.5% (optimized) NPs. The high crystallinity of the manufactured NPs is represented by the strong and precise diffraction peak. In spectra, diffraction peaks are placed at 2 Theta = 25.2° , 37.9° , 48.0° , 53.8° , 55.0° , 62.8° and 70° , highly corresponding to the crystal planes of (101), (004), (105), (211), (204), (126) and (220). These planes all represent the anatase phase of pure TiO₂ revealed the anatase phase. After metal doping, there are not any minority peaks showing, and

there is not any impurity or formation of any ionic site after doping. The identification of materials was further supported by XRD Joint Committee on Powder Diffraction Standards (JCPDS) card number (21-1272). The absence of additional peaks in Zn-, Ag- and Cu-doped TiO₂ NPs suggests that the crystal structure of tetragonal TiO₂ has not actually changed from doping. This can be reason for the similarity in ionic sizes of the Ti⁴⁺ [36], Zn²⁺ [37], Ag²⁺ [38] and Cu²⁺ [39]. However, due to the production of ionic species with increased Zn loading, there was a slight drop in anatase phase peak intensities after Zn doping [40]. Consequently, there was an increase in anatase to rutile phase change facilitated by Zn doping, which favored the production of ZnTiO₃. Using the Scherrer formula as described in the characterizations section, the crystallite sizes of NPs were determined to be 10.4 nm and further as 8.8 nm, 6.8 nm and finally 5.6 nm, respectively, for TiO₂, Zn-doped TiO₂-0.5, Zn-doped TiO₂-1 and Zn-doped TiO₂-2, respectively. It was observed that after metal doping, the crystallite size is reduced accordingly.



Figure 2. XRD Spectra for TiO₂, Zn-TiO₂, Ag-TiO₂ and Cu-TiO₂.

High-resolution transmission electron microscopy was characterized for optimized doped TiO_2 photocatalysts, as shown in Figure 3. TEM images were used to demonstrate the morphology, particle size and particle size distribution of the TiO_2 nanoparticles, as shown in Figure 3a. The TEM images were in agreement with the morphology observed via SEM. In the right-side images of Figure 3b, fringes are aligned in different directions, showing a polycrystalline structure. In addition, the metal dopant reduces crystallinity, as defect sites are created via doping.



Figure 3. TEM images: (a) doped TiO₂ at 0.2 um and (b) doped TiO₂ at 2 nm.

The electron and hole recombination of TiO_2 and doped TiO_2 was compared using photoluminescence (PL) spectra as shown in Figure 4. The high peak intensity of TiO_2 shows higher direct recombination of electron–hole pairs, whereas optimized doping of Zn decreases the recombination of charges, thus resulting in better charge separation and associated photocatalytic activity. As charges have longer dwell times, charges can participate in photocatalytic reactions for longer times. This better charge separation was related to doped metal centers, serving as an electron sink due to their ability to accommodate excessive electrons. The least amount of dopant promotes the charge separation dynamics, whereas excessive doping causes recombination of electrons as both electrons and holes can diffuse to metal centers; therefore, doping concentration was optimized here.



Figure 4. PL spectra for TiO₂ and doped TiO₂.

The bandgap for undoped TiO_2 and doped TiO_2 was calculated by indirect bandgap in Equation (1) from UV–Vis absorbance, as shown in Figure 5, where the X-intercept of the Tauc plot was used to determine the bandgap.

$$(\alpha hv)1/n = A[(hv - Eg)] \tag{1}$$



Figure 5. Bandgap for TiO₂, Cu-, Zn- and Ag-doped TiO₂.

Titania possesses a bandgap around 3.12 eV, as shown in Figure 5; however, after metal doping with Cu, Ag and Zn, the bandgap is reduced to 3.10, 3.08 and 3.04 eV, respectively. This is due to intermediate states formed after metal doping in titania lattice, also previous reported, thereby supporting conduction of electrons [41]. The reduction in the bandgap is also proved from Burstein–Moss effect; it is due to reduction in fermi levels after intermediate states. Now, electrons have shorter paths to jump from valence band to conduction band, thereby reducing band gaps. These fermi levels and intermediate states also support the conduction of photoelectrons with minimum possible energies. The photoabsorption range is also enhanced due to higher photoconduction of electrons. This tuning of bandgap supports the photocatalytic activity of metal-doped titania, and the bandgap is significantly reduced from 3.38 to 3.18 eV, which allows the electron transitions to an excited state with lower energies [42,43]. The intermediate states also enhance the electrons density in photocatalysis. When there are intermediate states, the chances of recombination are also reduced. Recombination is only based on longer dwell time, where the photon energy is reduced and recombination occurs. But, when the bandgap is reduced, the electrons easily jump from valence band to conduction band, which is potentially useful for photocatalysis. After being excited into conduction bands, the electrons can also jump back into valence bands and combine with holes, releasing energy. Recombination is the reverse process of excitation and leads to the elimination of charge carriers.

2.2. Chemical Characterization

FTIR spectroscopy was used to analyze the chemical composition of Zn-doped TiO₂coated fabrics, functionalized cotton fabrics, undoped cotton fabrics and GPTS-coated fabrics. Figure 6a shows the FTIR spectra for nanoparticles. In the spectra, there is a broader peak between 3200 cm⁻¹ and 3500 cm⁻¹, representing the hydroxyl (O–H) content stretching in TiO₂ and Zn-doped TiO₂ NPs. The hydroxyl content is necessary for photocatalytic reduction, thereby enhancing its rate. The second peak is between 1575 cm⁻¹ and 1635 cm⁻¹, which is due to the coordination of water molecules along with OH groups; it is due to the bending vibrations present in Ti–OH. The peak positioned at 775 cm⁻¹ is due to Titania lattice vibrations, which are shifted to 785 cm⁻¹ after Zn doping in TiO₂ NPs. The right-side of Figure 6b depicts a characteristic broad peak representing hydroxyl content in functionalized fabric. In these spectra, there is also OH-stretching vibration by hydrogen bonding in cellulose with titania. Peaks in the -CH symmetric stretching and bending vibration bands are also noted in spectra positioned at 2893 cm⁻¹ and 1308 cm⁻¹, respectively, responsible for redox reaction. Furthermore, the absorption band of the cotton fiber's cellulose at around 1157 cm⁻¹ is related (1–4) to the glycosidic connections of stretching of C–O–C photoactive material with a cotton cellulose base structure [44,45].



Figure 6. (a) FTIR spectra for TiO_2 , Zn- TiO_2 , Ag $-TiO_2$ and Cu $-TiO_2$ (b). FTIR spectra for fabrics, (c) FTIR T% for controlled and GPTS fabrics and (d) transmission rate for coated samples.

When GPTS is coated on cotton fabric, it exhibits various peaks corresponding to the cellulose unique properties. It enhances lattice vibrations and increases the photocatalysis reaction rate. It is important to note that the epoxy peak is positioned at 910 cm⁻¹, showing that additional reaction is occurred between epoxy and the hydroxyl group of cellulose, but its intensity is not significant, as seen in the bottom left inset of Figure 6b. Zn-doped TiO₂ NPs are attached on cellulose surface using GPTS as a binder to increase the resection rate, uniformity and stability for cellulose. The functionalized fabrics' FTIR spectra (position at bottom right Figure 6b) show a distinctive band at 600–630 cm⁻¹, which is indication of NPs on the cotton fabrics after binding agent. M–O stretching vibration is exhibited by Zn-doped TiO₂ NPs but is absent in untreated cellulose and GPT-coated fabric; this vibration is responsible for stabilizing the structure, thereby supporting the photocatalysis reaction under sunlight.

2.3. Photocatalytic Degradation Experiment

Photocatalytic degradation by metal-doped NPs is mainly affected by these factors, including solution concentration, pH, reaction time and rate and dopant concentration in wastewater treatment. The dye degradation should be carefully investigated to detect the effect of metal dopant NPs on textile surfaces. Determining the correct dopant concen-

tration in a photocatalyst is essential. Doping induces the formation of a heterostructure at a sublevel in a pure photocatalyst (in this case, TiO₂). The heterostructure keeps crucial radicals and recombination to increase photocatalytic rate. Along with preventing recombination, a dopant's inclusion decreases the bandgap simultaneously for electron excitation. Metals like Zn, Cu and Ag act as a recombination center for electrons, but it reduces the efficiency of degradation when the dopant concentration surpasses a particular limit [31]. Ag-doped TiO₂ with 0.1 mol percent dopant was optimized photocatalyst for the degradation of dyes both anionic and cationic and anionic. It was selected for further investigation. Cu- and Zn-doped TiO₂, with Cu and Zn doping of 2.5 and 0.5 mol, was the most effective photocatalyst for dye degradation in wastewater treatment. The pH conditions of an acidic, basic and neutral solution were examined on each of the dyes: MB, MO, Y, R and NB. In pH, 3–11 was optimized for the degradation of the MB and MO dyes, whereas the Y, R and NB dyes show maximum degradation at acidic (pH = 4) and basic (pH = 9) pH levels. All of the concentrations were taken (10 ppm) treated with the photocatalysts Zn-doped TiO₂-0.5, Ag-doped TiO₂-01 and Cu-doped TiO₂-2.5 (dye solution 50 mg/100 mL).

The MB dye degradation is increased from 82% to 99% by increasing the pH from 3 to 8 in sunlight. The association between a change in photocatalyst degradation efficiency and a change in solution pH may be further explained by taking TiO₂ behavior in a changeable pH solution into account. In aquatic conditions, TiO₂ is hydrated, resulting in Ti–OH groups on the surface, according to Equation (2). TiO₂ takes up H+ ions and acquires a positive charge when the pH is acidic. The positively charged TiO₂ NPs are desirable adsorption sites to accommodate (anionic dye; negative site). TiO₂ has a negative charge, according to Equation, it releases protons to HO-ions. MB attaches to negatively charged surfaces more easily, since it is a cationic dye. For photocatalysis to be effective, dye molecules must be well adsorbed. MB dye adsorption at TiO₂ functionalized surfaces is restricted in acidic conditions due to electrostatic repulsion. Because both photocatalysts MB dye molecules are positively charged, which results in lowering the efficiency interacted with acidic conditions [46].

For acidic (media)

$$Ti - OH + H^+ \rightleftharpoons TiOH_2^+$$
 (2)

For basic (media)

$$Ti - OH + HO^{-} \rightleftharpoons TiO^{-} + H_2O$$
 (3)

The MO dye is reduced from 95% to 40% by increasing the pH of the solution from 3 to 9. TiO₂ NPs does not encourage anionic dye adsorption in basic solutions. Figures 7–9 show functionalized GPTS TiO₂ and Zn, Ag and Cu-doped TiO₂ NPs being used to photocatalytically degrade MB and MO dye. The role of GPTS was investigated before and after washes to observe the photocatalytic activity of NPs coated textiles. It was observed that the performance of functionalized fabrics almost remains the same before and after washes. TiO₂ NPs show a little increase in response variable following GPTS functionalization. The doped NPs operate nearly identically when functionalized with GPTS or without.

Using undoped and Zn-doped electrodes, we calculated the photodegradation of dyes after reaching saturation of adsorption. The sample was then subjected to visible light for photocatalytic dye degradation, as shown in Figure 7a–d. We discovered that the doped Titania electrode destroyed more than 80% of the original concentration, while the undoped TiO₂ electrode only degraded 20% of the original concentration when comparing the photocatalysis of all the electrodes. The best dye degradation is achieved by 0.5% Zn-doped TiO₂ out of all the samples. It is the optimized doping rate at which the metal-doped titania possesses the highest catalysis and reducing the recombination. Due to their conductivity, metallic centers in semiconductors also act as an electron sink. Better charge separation and a longer dwell time are produced by this effect. The mobile phase photocatalysts are more active (in powder form) as compared with passivated state; when

these are in a passivated state, the catalytic reaction slows down and the performance is drastically lowered due to a diffusion-controlled process.

After saturation of adsorption was reached, we estimated the photodegradation of dyes using undoped and Ag-doped electrodes, and the sample was exposed to visible light for photocatalytic dye degradation, as illustrated in Figure 8a–d. When comparing the photocatalysis of all electrodes, we found that the doped titania electrode destroyed more than 80% of the original concentration, while the undoped TiO_2 electrode only degraded 20% of the original concentration. TiO₂ with 1% Ag provided the best dye degradation of all the tests. This is the optimized doping rate at which the dopant is surrounded with enhanced photocatalytic reaction. The microdefects and vacancies also support the photocatalysis on the cellulose surface. This effect is retained under multiple washes, also explained in further results. This has to do with the active material's smaller surface area, organic pollutants and diffusion-controlled reaction kinetics. Our proposed electrode's photocatalytic degradation significantly improved, demonstrating how closely doping and photocatalytic activity are coupled. However, too much doping (4%) causes the development of conductive centers, which act as an exciton recombination site [47]. Excessive doping also creates macrolevel defects which distort the structure, and stability is also reduced. Only optimized doping is favorable for enhanced photocatalytic reaction. However, the suggested treatment system is closer to being employed in practice due to the faster recovery of active materials and the low secondary pollution created by active materials themselves [48,49].



Figure 7. Photocatalytic dye degradation for (**a**) TiO₂, (**b**–**d**) Zn-doped TiO₂.



Figure 8. Photocatalytic dye degradation for (**a**) TiO₂ and (**b**–**d**) Ag-doped TiO₂.

Following adsorption saturation, the photodegradation of dyes using pure TiO_2 and Cu-doped TiO_2 electrodes was determined. The sample was then exposed to light for photocatalytic dye degradation, as shown in Figure 9a–d. When comparing the photocatalysis of all the electrodes, we found that the doped titania electrode degraded more than 80% of the original concentration, while the undoped TiO_2 electrode only degraded 20% of the original concentration. For all samples, 2.5% Cu-doped TiO_2 provided optimal dye degradation. As the dye molecule links there, defects and oxygen vacancies serve as active sites where photoactive charge can breakdown the dye molecules. In the optimized sample, the dye molecule has the best combination with defects and oxygen vacancies, thereby enhancing the degradation rate in visible light. Defects and vacancies act as a place for photogenerated electrons to capture during photocatalytic activity, successfully preventing charge recombination. Additionally, severe flaws hinder mobility, and they can speed up the recombination of charges. Therefore, in the optimized sample, there were linear defects not opposing photocatalysis reaction and hindering recombination. This effect is varied according to the doping rate and photocatalytic substrate.

Photographic images of fabric at different developmental stages are shown in Figure 10, where cotton fabric is shown without coating (Figure 10a), where only the cellulose structure is visible in the image, after coating with nanoparticles (Figure 10b), where nanoparticles are attached on the cellulose surface with binder GPTS and by dip–dry coating, and after dye degradation (Figure 10c), where photoactive fabrics are degraded to check their effectiveness with respect to metal-doped titania.



Figure 9. Photocatalytic dye degradation for (**a**) TiO₂ and (**b**–**d**) Cu-doped TiO₂.



Before Coating

After Coating

After Dye Degradation

Figure 10. Photoactive fabrics (a) before coating, (b) after coating and (c) after dye degradation.

Comparison of previously reported photocatalysts with our photocatalysts is shown in Table 1.

| Nature of Dopant | Doped TiO ₂ Synthesis Route | Doped TiO ₂ Loading (g/L) | Optimum Calcination Range (°C) | Organic Pollutant | Initial Pollutant Conc (mg/L) | Light Source | Deg Efficiency (%) | Ref. |
|-----------------------------|--|--|---|----------------------|--|--------------|--------------------------|----------|
| Fe Mobile phase | Solgel | 5.0 | 400 | Methyl orange | 20 | UV-vis | 99.7 | [50] |
| Pt Mobile phase | Photochemical reduction | 2.0 | 110 | Methyl orange | 20 | UV | 87.7 | [51] |
| I, F Mobile phase | Solgel- impregnation | 1.0 | 500 | Methylene blue | 10 | Sunlight | 98 | [51] |
| Sm, N Mobile phase | Coprecipitation | 1.0 | 400 | Nitrate | 50 | UV-vis | 67 | [52] |
| Fe Mobile phase | Solgel | 0.02 | 450 | Phenol | 70 | Ultrasonic | 83 | [53] |
| Cu, S Mobile phase | Hydrolysis | 1.0 | 400 | Methyl orange | 350 | Sunlight | 65 | [54] |
| Pt, Cu Mobile phase | Solgel | 1.0 | 400 | Methylene blue | 10 | UV | 93 | [54] |
| Cu, Ag and Zn Passivated | Sol-gel | 1, 2 and 4 mol% | 400 | Multiple | 10 | Sunlight | 80–90% | Our work |

Table 1. Comparison of photocatalysts activity.

2.4. Color Strength (K/S)

The color strength of untreated and functionalized fabrics was assessed to check its color fastness after multiple washes. For this purpose, the cotton fabric was dipped into the dye solution (that was taken 50 ppm for all colors as standard concentration and value). Firstly, it was cut into two halves in dip solution for accessing the functional self-cleaning activity. The half side interacted with the dark side, while the other was in ambient sunlight. Then, the fabrics were sent to K/S analysis following a three-hour exposure, as illustrated in Figure 11. The K/S analysis results are shown in the results, which demonstrate that Zn- and Ag-loaded NPs on fabric (o.w.f.) significantly reduced K/S values compared with Culoaded NPs on fabric. In the inset of each bar graph, there are actual photographs of the fabric (C) for each color, Zn-doped TiO₂ (4) is positioned in the dark (D) and in direct sunshine (S). The results show that dyed materials have far better photocatalytically assisted self-cleaning activity when exposed to sunlight, indicating that functionalized fabrics with Zn-doped TiO₂ and Ag-doped TiO₂ possess highest self-cleaning ability when it is daylight. Drimaren blue, yellow and red, which are widely used and resistant to effective degradation of textile dyes; these all have the same effect for degradation with Ag-doped TiO₂. The self-cleaning activity of fabrics with Cu doping of TiO₂ is reduced [55].

The following formula is used for K/S % reduction:

$$\% decrease in \frac{K}{S} = \left(\frac{\left(\frac{K}{S}\right)unexposed - \left(\frac{K}{S}\right)exposed}{\left(\frac{K}{S}\right)unexposed - \left(\frac{K}{S}\right)unstained}\right) \times 100$$
(4)

Table 2 displays the percentages of dye removal on fabrics that have undergone photocatalytic treatment when exposed to sunshine.



Figure 11. (K/S) comparative result uncoated and functionalized fabrics for (**a**) methylene blue, (**b**) Methyl orange, (**c**) Drimaren ultimate blue, (**d**) Drimaren ultimate red, and (**e**) Drimaren ultimate yellow.

| Fabric | Dye | % Red | Fabric | Dye | % Reduction |
|-----------------------|-----|-------|-----------------------|-----|-------------|
| | MB | 96 | | MB | 94 |
| | MO | 88 | | MO | 76 |
| C-Zn@TiO2 | R | 85 | C-Ag@TiO ₂ | R | 83 |
| | Y | 83 | Ū. | Y | 76 |
| | NB | 89 | | NB | 91 |
| | MB | 90 | | MB | 47 |
| | MO | 63 | | MO | 45 |
| C-Cu@TiO ₂ | R | 90 | C-TiO ₂ | R | 31 |
| | Y | 75 | | Y | 34 |
| | NB | 93 | | NB | 54 |
| | MB | 51 | | | |
| | MO | 46 | | | |
| Control | R | 28 | | | |
| | Y | 36 | | | |
| | NB | 49 | | | |

Table 2. K/S analysis for all photocatalysts.

2.5. Antibacterial Activity Analysis and Washing Durability Test

Qualitative antibacterial assessment of cotton fabric against Gram-positive and negative bacteria was carried out to detect the self-cleaning abilities of functionalized and unblemished cotton materials. To achieve this, clean cotton fabric and C-Zn-doped TiO₂, C-Ag-doped TiO₂ and C-Cu-doped TiO₂ were selected. Based on their top 20 reductions in K/S values, functionalized fabrics were chosen. Figure 12 displays the results of a qualitative antimicrobial analysis that was conducted. The bacterial counts were performed immediately after introducing bacteria to the fabric (t = 0) and 24 h later (t = 24 h). No decrease in cell counts was seen, which proved that the pure cotton cloth was not impervious to bacterial attack. As a result, the bacterial action caused the cloth to degrade. With a 98.54% decrease in bacterial counts, the functionalized cotton fabrics (C-Zn-doped TiO₂, without washing) demonstrated outstanding antibacterial action. Similar to this, a 97.99% decrease in bacterial growth was seen in the fabric after 10 washings (10 W). The C-Ag-doped TiO₂ functionalized cotton fabrics demonstrated outstanding antibacterial activity with a 99.99% decrease in bacterial counts. Similar to this, the fabric showed a 99.00% decrease in bacterial growth after 10 washings (10 W). With a 99.31% decrease in bacterial counts, the functionalized cotton fabrics (C-Cu-doped TiO2, without washing) demonstrated outstanding antibacterial action. Similar to this, a 98.86% decrease in bacterial growth was seen in the fabric after 10 washings (10 W). Due to the efficient control of dope NPs employing GPTS as a coupling agent, there was only a slight difference between the outcomes of bacterial cell decrease by unwashed and washed fabrics. The catalyst surface's production of reactive oxygen species, which are essential in bacterial cell wall breakdown, may be the cause of the functionalized cotton fabric's effective antibacterial action. After several cycles of laundry washing, the nanoparticle adherence may have decreased, which could account for the slight decline in antibacterial activity of the 10 washed samples. The presented results, however, suggest that the cotton fabrics with added functionality had better antibacterial properties. We evaluated 10 W textiles for photocatalytic activity against MB dye under the same reaction conditions as earlier described in order to determine the wash ability of the functionalized material. When the K/S values were computed, the 10 W fabrics did not exhibit a noticeably stronger color. This indicates that after numerous washings, the fabric demonstrated efficient self-cleaning photocatalytic activity [56].



Figure 12. Antibacterial activity for photocatalysts.

2.6. Comfort Properties

The air passing vertically through a certain region of a fabric specimen over a specific time under a specific pressure difference is referred to as the fabric's air permeability. The 'breathability' of various textiles is typically assessed in terms of clothing by measuring air permeability [40]. Clothing comfort always relates to the maintenance of body temperature and air permeability. Many characteristics of fabrics are directly associated with comfort, namely water absorbency rate, air permeability, wicking, fabric porosity, thermal resistance, its packing factor, density and many more. Many physical factors affect air permeability, which includes the balancing of heat and moisture, better transferring of air throughout the fabric and also related structural parameters. Comfort is both in physiological and psychological conditions. It is pure fibrous property or just human perception to feel it—to feel smoothness, well parallelized and not more affected by external factors. Woven fabrics have higher strength than knitted or any other, and this is the most important prerequisite in outerwear fabrics. The comfort of outerwear fabric effect wearer's activities positively. Thus, we needed to determine whether cotton cloth that had been cleaned and

functionalized was permeable to air and water. The results are shown in Figure 13a–j. The spotless material had high air permeability. The cloth cover factor (sometimes referred to as cloth openness) and the fabric's construction have the biggest effect on a textile's ability to breathe [41,42]. Uncoated fabric's high air permeability revealed a significant number of exposed holes that help air permeate through garments. The functionalized textiles (C-Zn-, Ag and Cu-doped TiO₂-4), on the other hand, showed a small reduction in air permeability. The decrease in air permeability values till 33 mm/s from 42 mm/s not a significant in terms of fabric comfort. The thermal equilibrium of the body depends on the ability of textiles to control moisture [44,45]. Cotton has excellent wettability assets [41]. The results for the water absorbency indicated no appreciable decrease in values, indicating its comfortability. Similar to this, it is intriguing to see how exposure to sunlight (for 72 h) affects tensile strength. The tensile strength did not significantly decrease after exposure to sunshine. This showed that even after repeated exposure to sunshine, the cloth was resilient.



Figure 13. (a–j) Air permeability for photocatalysts.



We also conducted tests on vertical wicking and water vapor permeability to assess the fabrics ability to withstand environmental stresses. Cu–doped TiO₂ possessed the highest wicking measurement among all the samples. Water vapor permeability was reduced with the dopant and it was optimized with Ag–doped TiO₂ as shown in Figure 14.

Figure 14. (a) Vertical wicking test and (b) water vapor permeability for photocatalytic active fabrics.

3. Materials and Methods

3.1. Chemicals

All of the compounds were of a critical grade and were not further purified before usage in this study. Polyethylene glycol (1000 Biochemical, Northampton, UK) was obtained from AppliChem (London, UK), 3-Glycidoxypropyl tri-methoxy silane (GPTS), silver nitrate and copper sulphate were obtained form Scientific chemicals, dopant salts zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O purity >98.0%) was obtained from Sigma Aldrich (St. Louis, MO, USA), Titanium tetra isopropoxide (TTIP) 97% was also purchased from Sigma Aldrich (St. Louis, MO, USA), solvent 2-Propanol was received from nature chemicals purity (99%) and ethanol (Lab Scale) from ACI Labscan (Islamabad, Pakistan) was used. The entire investigation was conducted with deionized water. The contaminants that were targeted for extraction from Archroma (Pratteln, Switzerland) were five commercial colors.

3.2. Synthesis of TiO_2 and Doped TiO_2 NPs

The sol-gel method was used to prepare two solutions and create pure TiO2 nanoparticles (NPs). Solution 1: Under ultrasonic sonication, 20 mL of 50 mmol of encompassing titanium isopropoxide was added to a solution of 160 mL of ethanol and 20 mL of isopropanol, respectively, having an 8:1 v/v ratio. Then, Solution 2 was taken with 100 mL deionized water and mixed with 2 g of cetyltrimethyl ammonium bromide (CTAB). After that, solution 1 was gradually incorporated into solution 2 while it was continuously stirred for 4 h at 80 °C. After that, the solution's solvent was recovered using a rotary evaporator, and the powdered particles were then calcined for four hours at 500 $^{\circ}$ C in a muffle furnace. The above-described process was used to create Zn@TiO₂ NPs, without doping of any salt in solution 2, Zn-doped TiO₂-having a trace ratio 0.5, Zn-doped TiO₂-1 and Zn-doped TiO_2 -2 (0.5, 1 and 2 mol%) with Zn. In a muffle furnace, the synthesized NPs were calcined at 500 °C for four hours. Due to their capacity to accept too many electrons, doped metal centers have been linked to improved charge separation. Since both electrons and holes can diffuse to metal centers, a higher concentration of dopant encourages charge separation dynamics, whereas a higher concentration of dopant produces electronic recombination. For this reason, the concentration of the dopant was optimized. The sol–gel technique was used to create Ag-doped TiO₂ NPs. First, 5 mL of glacial acetic acid and 80 mL of deionized water were used to dissolve silver nitrate. A combination of 70 mL of 100% ethanol and the same stoichiometric amount of titanium tetra isopropoxide were mixed together. Next, the two solutions were combined by stirring them for two hours. Ag-doped TiO₂-1, Ag-doped TiO₂-2 and Ag-doped TiO₂-4 with three distinct mol ratios (1, 2, and 4 mol%) of Ag doping were chosen. A 48 h aging period at room temperature was then applied to the generated sol–gel. Dry sol–gel was aged for 12 h at 110 °C before being calcined for 4 h at 500 °C. Cu-TiO₂ was created using sol–gel synthesis as follows: Solution A was created by mixing 100 mL of isopropanol and 20 mL of TTIP for 15 min. The necessary amount of copper sulphate was combined with 100 mL of deionized water, and the mixture was stirred for 15 min (solution B). An equal amount of each solvent was employed. Solution B was then added to Solution A in slow, steady drips while stirring continuously. At room temperature, the mixture was then allowed to gel for an additional two hours. Cu-doped TiO₂-1, Cu-doped TiO₂-5 and Cu-doped TiO₂-10 with the three distinct mol ratios of Cu doping (1, 5 and 10 mol%) were chosen. The gel was then dried by baking it at 100 °C for 12 h. The powder was then calcined at 500 °C for 4 h.

3.3. Functionalization of Pristine TiO₂ and Zn-, Ag- and Cu-Doped TiO₂ NPs Using GPTS

Trace ratios of dopant with TiO₂ NPs (4, 6 and 8) according to the weight of fabric (o.w.f.) were dissolved in solution of 100 mL isopropanol and ultrasonically processed for one hour for functionalization of the NPs. There were also different GPTS concentrations (75 and 125% on the weight of NPs, o.w.n.) used in the solutions. The pH was adjusted to 4.5 according to the solution using 0.01 M HCl. Then, it was allowed to refluxed for 4 h with temperature set to 60 °C. According to the weight percentage of NPs that were o.w.f., the GPTS (75% o.w.n.) functionalized nanoparticles were labeled Zn-doped TiO₂ (4), Zn-doped TiO₂(6) and Zn-doped TiO₂(8).

3.4. Immobilization of TiO₂ Nanoparticles on Cotton Fabric

The fabric was treated with GPTS functionalized NPs solution using a padder machine to immobilize the NPs. The textiles were then dried at 100 °C and cured in a Stenter Frame (pin TC-M-28) for three minutes at 150 °C. The samples with immobilized nanoparticles (NPs) on cotton fabric were labeled C-Zn doped TiO₂(4), C-Zn doped TiO₂(6), and C-Zn doped TiO₂(8). The same labeling was used for Ag-doped TiO₂ and Cu-doped TiO₂.

The following stages are description of Zn-, Ag- and Cu-doped TiO₂ NPs on the cellulose-based substrate: In the first stage, hydrolysis of silane agents and GPTs was removed by solvent isopropanol. It was achieved by reduction reaction, when it was interacted with the –OH groups on Zn-, Ag- and Cu-doped TiO₂ NPs. Reducing agents were hydrolyzed methoxy groups of GPTS. The NPs were functionalized with GPTS (silane group) while epoxy is interacted with cellulosic part. Finally, GPTS serves as a link between cellulose and functionalized NPs resulting in highly durable functionalized fabrics. The as-prepared distribution reacts with the OH groups of the cotton fiber when it is applied to the fabric, thereby anchoring the doped TiO₂ NPs to the fabric surface [57]. The detailed reaction mechanism is described in Figure 15.



Figure 15. Mechanism of functionalization of cotton fabrics by photocatalysts.

3.5. Testing and Characterization

The morphology of nanoparticles and functionalized fabrics were detected by using scanning electron microscope (SEM) having model (JSM 6490, JEOL, Tokyo, Japan) with accelerating voltage 20 V. For crystallographic characterization, XRD was performed by using Cu k as the radiation source (=0.154 nm) to examine the structural phases of the nanoparticles. The Debye–Scherrer formula calculated the average crystallite size of the synthesized nanoparticles from the XRD profile (Equation (5)).

$$D = k\lambda / (\beta cos\theta) \tag{5}$$

In this equation, D represents the average crystallite size, X-ray wavelength (0.154 nm), λ is Bragg's angle and k is the Scherrer constant. The charge recombination kinetics of the photocatalysts was studied using the PL spectrophotometer DW-F97 (Drawell, Shanghai, China). The materials were tested using a 0.5% aqueous solution and an excitation wavelength of 360 nm for the PL test. Then, the absorption spectra of undoped, metal-doped and functionalized cotton fabrics were evaluated for testing the photocatalytic activity of metal-doped TiO₂ NPs as well as the GPTS functionalized metal@TiO₂ NPs immobilized on the cotton fabric surfaces. There were five dyes used as pollutants, also mentioned in the Materials Section. Firstly, ppm solutions were taken with different pH levels e.g., basic, acidic and neutral, and then 30 mg nanoparticles were dipped with nanoparticles (1 mL) and functionalized cellulose (22 cm) into the dye solution (100 mL) already prepared. LUX meter was used for calculating the reaction time under ambient light. The absorption spectra with respect to degradation rate having varying intensities were measured by UVvisible spectroscopy having model number (CECIL CE 7200). The absorption maximum as 664 nm, 446 nm, 415 nm, 542 nm and 600 nm, respectively, for all dyes calculated. After being air-dried in the dark and under direct sunlight, the K/S values of the treated functionalized and reference fabrics were evaluated. The K/S (color strength) was measured for each fabric having a unique code for identification and easy processing; it was measured by spectrophotometer Gretag Macbeth 700 (X-Rite, Grand Rapids, MI, USA) in the dark and in ambient light. The dyed sample's K/S max (color strength) was measured by Kubelkae Munk Equation, written as (6).

$$KK/SS = (1 - R_{\infty})^2 / 2R_{\infty}R$$
 (6)

Here, K stands for the absorption coefficient, S represents scattering and *R* represents reflectance (color sample). The ISO 20743:2013 transfer method was used to test the antibacterial activity of the cotton fabrics that were both untreated and coated. Each sample of fabric was placed in a nutrient agar plate having 1 mL bacterial culture, while the plates were then filled with 200 g of weight for 60 s to press the samples for 60 s. Utilizing the ISO 105 CO3 technique, functional characteristics of functionalized materials were evaluated after they were washed. The comfort analysis of the cloth was determined based on its tensile strength and air and water permeability.

4. Conclusions

TiO₂ nanoparticles with metal doping functionalized on cellulose surface were suggested as an efficient photocatalysts for dye degradation in wastewater treatment. The NPs were synthesized by sol–gel route and coated on cellulose by dip–dry with GPTS as a coupling agent during the refluxing process. Using the dip–dry–cure technique, the functionalized NPs were immobilized on cotton fabric. We investigated the self-cleaning activity of the Cu-, Ag- and Zn-doped TiO₂ NPs-coated fabrics. We extensively characterized these fabrics using several analytical techniques. Due to the Cu, Zn and Ag heterojunction, the Zn-doped functionalized fabric's efficient photocatalytic activity was concluded as optimized charge transfer photocatalyst. Within three hours of reaction time (sunlight), the optimized fabric demonstrated a reduction in dye concentration of 90–98% (for five commercial dyes). The materials demonstrated exceptional durability after 10 washes, and there was no appreciable drop in photocatalytic activity. According to the SEM analysis of 10 washed sample fabrics, this was caused by the doped NPs being effectively immobilized on the cloth. As a result, the proposed photocatalytically active self-cleaning materials are a strong contender for environmental cleanup.

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