ZnTiO$_3$ Nanoparticles as Novel Multifunctional Finishing of Cotton Fabric

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MULTIFUNCTIONAL textiles, a topic which is important from scientific and economic point of view will be the new direction for development of fabrics and clothing. Finishing of textiles with nanoparticles is a novel route for creation of unique functions. It is well known that ZnO and TiO$_2$ possess UV-protection, antibacterial and photocatalytic properties, but there is no enough information concerning the similar behavior of ZnTiO$_3$. This provokes the interest to synthesize that compound and to examine its UV-protection and antibacterial properties in addition to its photocatalytic activity. In this study the synthesis and use of hybrid polymers loaded with ZnTiO$_3$ nanoparticles were presented. Hybrid polymers used here are based on 3-glycidoxypropyltrimethoxysilane (GPTMS). ZnTiO$_3$ nanoparticles was used to impart cotton based fabric UV-protection, antibacterial and self-cleaning properties. The viability of the novel finishing as UV-protection will be dictated by UV-Vis spectroscopy and by assessment of the ultraviolet protection factor (UPF). The antibacterial activity of these sol-gel derived hybrid materials will be researched against Gram-negative bacterium *Escherichia coli* DSMZ 498 and Gram-positive *Micrococcus lutues* ATCC 9341. Photocatalytic degradation (decolorization) of methylene blue (MB) in both ZnTiO$_3$ nanoparticles sol-gel solution /or on the coated fabrics was evaluated. The impact of this finishing technique on other fabric properties, e.g. air permeability, whiteness, and stiffness will be investigated.

**Keywords:** Zinc titanate, Multifunctional finishing, UV protection, Antibacterial, Sol-gel coating, Textiles, Hybrid polymers.

Zinc titanates have been explored for applications in numerous fields, for example, paint shade, gas sensor and reactant sorbent lately (1-3). The ZnO–TiO$_2$ system still attracts the attention of researcher’s importance in practical application (4-6). It is well known that ZnO and TiO$_2$ possess UV protection and antibacterial properties (6), but there is no enough information concerning the similar behavior of ZnTiO$_3$. This provokes our interest to
synthesize that compound and to evaluate its antibacterial and UV protection properties. Zinc titanate ceramics draws in the consideration of specialists because of their different applications as paint colors, sorbents, microwave dielectrics and catalysts. There are several methods for preparing ZnTiO$_3$ nanoparticles, generally focused on conventional solid state reactions, mechanochemical initiation, precipitation and a few variations of the sol-gel method. Amid the late years, the sol-gel strategy has been viewed as a worthwhile one for the combination of nano powders with high virtue, ultra homogeneity, diminishment of the sintering temperature. That is the reason it was chosen keeping in mind the end goal to evade the ZnTiO$_3$ decay at high temperatures.

Researchers found that ZnTiO$_3$ has photocatalytic and antibacterial properties. Many researchers proved that ZnTiO$_3$ is stable from room temperature to 945° C, since this temperature is the temperature at which it can separate into ZnTiO$_4$ and TiO$_2$. The point of the present paper is to prepare ZnTiO$_3$ nanopowders by the sol-gel strategy. The study depends on trials utilizing Zn-acetate and Ti(OEt)$_4$ as principle precursors.

**Experimental**

**Materials**

The coating experiments were carried out using fabrics made of pure cotton (100%), mass per unit area 250 g/m$^2$ was supplied by Misr Company for Spinning and Weaving, Mehalla El Kobra, Egypt.

**Chemicals**

Zinc acetate dehydrate [Zn (CH$_3$COO)$_2$.2H$_2$O], citric acid monohydrate [C$_6$H$_8$O$_7$.H$_2$O] from Merck and titanium ethoxide[Ti (OCH$_2$CH$_3$)$_4$] from Fluka AG were used. 3-Glycidyloxypropyltrimethoxysilane (GPTMS, 98%) was obtained from ABCR. Further chemicals used were ethanol[C$_2$H$_5$OH], ethylene glycol[C$_2$H$_4$O$_2$], methylene blue (MB), and hydrochloric acidHCl from Merck.

**Preparation process**

The sol-gel method was employed to prepare TiO$_2$, ZnO and ZnTiO$_3$ at room temperature by using different chemical reagents and special equipment. Zinc acetate (ZnAc) and titanium ethoxides starting materials were used. The precursors were dissolved in ethanol at room temperature under vigorous stirring to guarantee the occurrence of hydrolysis processes. The citric acid, ethylene glycol and hydrochloric acid were added. By drying at 110 C for 5 hr, a white xerogel was obtained. Subsequently, the obtained xerogel was subject to evaporation, drying and calcination at 400, 500 and 550 C for 1 hr respectively using globar-heated electrical furnace.
Preparation of GPTMS sols

10 ml GPTMS are dissolved in 100 ml solvent before hydrolysation using 0.01M hydrochloric acid. The resulting sol is stirred for at least 3h to form the basis sol.

Preparation of the hybrid polymer

Before finishing of textiles the zinc titanate dispersion and the GPTMS sol were mixed in different ratios finally 1-methylimidazol (0.5 ml/10 ml GPTMS) was added as a catalyst for the cross-linking reaction of the epoxy group of the GPTMS.

Coating process

The hybrid polymer sol was applied to the fabrics by a pad-cure-method. The coating was carried out by a padding process with laboratory padder to a wet pick up of 100%. After padding samples were dried in a labcoater (Mathis, Switzerland) at 130 °C for 30 min before it was washed to remove residual by-products.

Tests and analysis

UV protection factor

UV– vis spectrum was recorded on Perkin Elmer Lambda 3BUV– Vis spectrometer. Ultraviolet protection factor (UPF) was measured using UV Shimadzu 3101 PC-Spectrophotometer. UVProtection and classification according to AS/NZS 4399:1996 were evaluated.

Antimicrobial testing

The antimicrobial activity of the coated fabrics was tested against the Gram-negative bacterium Escherichia coli and the Gram–positive Micrococcus luteus using Tetrazolium/formazan test (TTC).

Also, the antimicrobial activity of the prepared sol was evaluated using agar diffusion test according to AATCC Standard Test Method 147-1988.

Scanning electron microscopy SEM/EDX analysis

The particles morphology in the calcinated samples at 500 °C was investigated using Scanning Electron Microscopy. Samples for SEM/EDX were taken using FEI INSPECTS Company, Philips, Holland environmental scanning without coating. Elemental microprobe and elemental distribution mapping techniques were used for analyzing the elemental constitution of solid samples. An elemental analysis of the particles was implemented by SEM equipped with an energy dispersive spectroscope (EDX), which can provide a rapid qualitative and quantitative analysis of the elemental composition.
XRD

XRD patterns of ZnTiO$_3$ were recorded on a Philips PW 3050/10 model. The samples were recorded on a Philips X-Pert MMP diffractometer. The diffractometer was controlled and operated by a PC with the programs P Rofit and used a MoK source with wavelength 0.70930˚A, operating with Mo-tube radiation at 50 kV and 40 mA.

Fabric whiteness

Whiteness index was evaluated with a Color-Eye 3100 Spectrophotometer from SDL Inter.

Air permeability

It was tested using air permeability tester (21443, FRANK) according to DIN 53887.

Stiffness

It was tested using Shirley stiffness tester according to DIN 53362.

Result and Discussion

The sol-gel strategy has been decided for the synthesis because of the upsides of this system in particular: fine molecule size, straightforward compositional control and low handling temperature. The main precursors were titanium ethoxide with zinc acetate according to the schemes of the preparation (Fig. 1). Titanium ethoxide was picked on the grounds that it is realized that the transition metal alkoxides are highly reactive because of the existence of highly electronegative OR groups that stabilize the metal in the highest oxidation state and let the nucleophilic attack to the metal possible.$^{(9)}$

![Diagram of Synthesis of ZnTiO$_3$ by sol-gel method.](image)

**Fig. 1. Synthesis of ZnTiO$_3$ by sol-gel method.**
Such alkoxides are utilized as forerunners as a part of sol-gel handling considering that they are firmly electrophilic and in this manner less steady toward hydrolysis, buildup, and other nucleophilic responses. Besides, the gathering R from Ti(OR)₄ impacts the morphology (molecule size and surface zone) and the crystallization behavior of final gel(9).

Titanium ethoxide and zinc acetate precursors were dissolved in ethanol or ethylene glycol with addition of citric acid as indicated in the way of the scheme of the preparation (Fig.1). The hydrolysis process is fundamentally enhanced if directed at pH ≠ 7. Hence, adding acid (HCl (aq)) or base (NH₄OH) invigorates this procedure. After the hydrolysis the acidity of the sol is neutralized slowly to approx. pH=7, which stimulates the gelation process. At this stage a mechanically unstable "wet" gel is formed. Drying of wet gels prompts xerogels ("dry gels") even at ambient temperatures. So few drops HCl were added in some schemes to stimulate the hydrolysis and condensation reactions in order to obtain gel or precipitate at the end of the reactions. The as obtained gel or precipitate was transferred into a porcelain crucible and put in water bath to evaporate the excess of water then dried on a hot plate (=100 °C). After that a sequence of heating at 200 °C, 300°C, 400 °C, 500 °C and 550 °C were done so as to evaporate the organics and to start the crystallization of the powders. The phase formation and structural transformation were followed by X-ray phase analysis.

**X-ray**

The X-ray diffraction pattern of that sample is shown in Fig. 2. As it is seen at 400°C the sample preserves its amorphous condition, but at 500 °C the strongest peaks of ZnTiO₃ (JCPDS 39-0190) (the three strongest lines 2.54; 2.97; 1.49) appeared. In order to check the temperature influence on the sample an additional heat treatment at 550 °C was made. It leads to increasing the peaks intensity.

![XRD patterns of the ZnTiO₃ sample heat treated at 400, 500 and 550°C.](image)

Fig. 2. XRD patterns of the ZnTiO₃ sample heat treated at 400, 500 and 550°C.
Figure 3. shows the morphology of ZnTiO$_3$ nanoparticles since the size of the particles is between 25-50 nm.

Fig.3.TEM image of ZnTiO$_3$.

**SEM – EDX analysis of cotton fabric coated with ZnTiO$_3$**

Some regular SEM micrographs of the sol–gel treated cotton fabrics are accounted for in Fig. 4. Generally, homogeneous and conservative film is covering the fiber.

Fig. 4. SEM micrographs of ZnTiO$_3$/GPTMS treated fabric.

An essential examination of the particles was executed by SEM equipped with an energy dispersive X-ray spectrum [EDX], which can give a fast quantitative investigation of the elemental composition. Figure 5 depicts the quantitative analysis for cotton fabric treated with ZnTiO$_3$ nanoparticles which confirms that the nanostructure contains about, carbon 55.34%, oxygen 41.57%, and titanium 0.6%, zinc 0.36% and silicon 1.86%. The homogeneity of dispersion of the inorganic coatings relies on the metal utilized in the sol–gel procedure. As pointed out by the elemental maps (Fig.

_A. Farouk et al._

6) very high level of Ti distribution was observed while the distribution of Zn appears to be less homogeneous and thick when compared with Ti.

![Fig. 5. EDX spectra of ZnTiO$_3$/GPTMS treated fabric.](image)

Table: EDX Spectra of ZnTiO$_3$/GPTMS Treated Fabric

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>55.34</td>
<td>61.14</td>
</tr>
<tr>
<td>O</td>
<td>41.57</td>
<td>35.61</td>
</tr>
<tr>
<td>Si</td>
<td>1.65</td>
<td>0.91</td>
</tr>
<tr>
<td>Ca</td>
<td>0.26</td>
<td>0.09</td>
</tr>
<tr>
<td>Ti</td>
<td>0.09</td>
<td>0.17</td>
</tr>
<tr>
<td>Zn</td>
<td>0.37</td>
<td>0.08</td>
</tr>
<tr>
<td>Tota.</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 6. Element maps of ZnTiO$_3$/GPTMS treated cotton fabrics.](image)
UV protection for treated cotton fabrics

The treatments laundry test were carried out for the durability of, since all samples were washed before the UV transmission was measured. The relating information for the coated cotton fabrics are outlined in Table 1 demonstrating changes in the absorption characteristics of the treated samples which expressed as UPF value contrasted with the untreated fabrics.

From the table it can be seen that untreated cotton fabric give only moderate UV protection. Treatment with GPTMS or ZnTiO$_3$ nanoparticles results in good UV protection, but treatment with ZnTiO$_3$/GPTMS yields excellent protection.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Upf value</th>
<th>Uv protection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank cotton</td>
<td>13</td>
<td>moderate</td>
</tr>
<tr>
<td>Cotton Fabric treated With GPTMS</td>
<td>17</td>
<td>Good</td>
</tr>
<tr>
<td>Cotton Fabric treated With ZnTiO$_3$</td>
<td>22</td>
<td>Good</td>
</tr>
<tr>
<td>Cotton Fabric treated With ZnTiO$_3$/GPTMS</td>
<td>75</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

Antibacterial efficiency of treated cotton fabrics

Tetrazolium/formazan-test method TTC

The antibacterial activities of the cotton treated fabric samples were assessed against *E. coli* and *M. lutues* utilizing the TTC test technique.

This test serves as showing framework for the determination of the suitability of bacterial cell, since absorbance of formazane is straightforwardly relative to the measure of living microscopic organisms. Figure 7 demonstrates the antibacterial action (which was communicated by formazan absorbance values) for cotton fabrics treated with various ZnTiO$_3$ nanoparticle focuses (0.25%, 0.5 % and 0.75%)(w/v) in GPTMS-sol. We notice a highly reduction of the essential cells due to the existence of ZnTiO$_3$-filled sol. By increasing the amount of the ZnTiO$_3$ within the hybrid polymer, the antibacterial activity increases. Since the higher the ZnTiO$_3$ concentration, the lower the formazan absorption value (*i.e.*, more microbes are executed) which shows the higher antibacterial action.
Fig. 7. TTC test method of (a) blank, (b) GPTMS, (c) 0.25% ZnTiO$_3$/GPTMS, (d) 0.5% ZnTiO$_3$/GPTMS and (e) 0.75% ZnTiO$_3$/GPTMS against E.coli.

Disc diffusion method

Antibacterial impact of cotton treated fabrics against E.coli and M. lutues as hindrance zones, assessed by the circle dissemination examine is shown in Fig. 8. There is a reasonable zone of hindrance inside and around the examples completed with ZnTiO$_3$/GPTMS hybrid polymer compared with the untreated or only treated with GPTMS fabric.

Fig. 8. The disc diffusion test of high ZnTiO$_3$ concentration for the growth inhibition of: (a) M.lutues and (b) E.coli. (1) Untreated fabric, (2) fabric treated with GPTMS, (3) fabric treated with ZnTiO$_3$/GPTMS (0.75%)(w/v).

Photocatalytic property of ZnTiO$_3$ nanoparticles

The charge division of electrons and holes was advanced and the recombination of the hole–electron sets was diminished due to the coupling...
impact of zinc oxide and titanium dioxide in the grain-like composite nanoparticles. As an outcome, the ZnTiO₃ nanoparticles demonstrated high photocatalytic activity in the treatment of natural contaminated water.  

Fig. 9. Assumed diagram of charge separation of Zinc oxide/Titaniananomaterials. 

Photocatalytic activity of ZnTiO₃ nanoparticles toward photodegradation of methylene blue (MB) was evaluated under UV light irradiation. The results indicate that zinc titanate nanoparticles exhibit high photocatalytic action.

Fig. 10. Decolorization of MB dye after 30 min UV irradiation. Since B: Blank methylene blue, (1) methylene blue with GPTMS, (2) methylene blue with 0.5 % ZnTiO₃/GPTMS and (3) methylene blue with 0.75 % ZnTiO₃/GPTMS.
Impact of ZnTiO₃ sol on the performance properties of the fabrics

It is essential to think about the impact of this treatment on the performance properties of the fabrics contrasted with the untreated fabrics.

The impacts of the sol treatment for the level of whiteness and for the air permeability were researched and the relating information is shown in Table 2.

We can notice that there is no worsening of the air permeability but there is a slight improvement. Also, the whiteness of the fabrics is slightly decreased but in a tolerable level. The increase of the bending stiffness values was recorded by increasing the concentration of ZnTiO₃, this is because of the higher uptake of the hybrid polymer on cotton surface, as a result of the increasing of solid content for sol with higher amount of ZnTiO₃.

**TABLE 2. Effect of higher concentrations of ZnTiO₃– sol on some performance properties of cotton substrate.**

<table>
<thead>
<tr>
<th>Cotton substrate</th>
<th>Air permeability l/dm²*min.</th>
<th>Degree of Whiteness (Berger)</th>
<th>Bending Stiffness (cNcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>254.8</td>
<td>62.1</td>
<td>14.18</td>
</tr>
<tr>
<td>ZnTiO₃/ GPTMS-sol (0.25%)</td>
<td>256.2</td>
<td>59.1</td>
<td>15.36</td>
</tr>
<tr>
<td>ZnTiO₃/ GPTMS-sol (0.5%)</td>
<td>254.3</td>
<td>58.9</td>
<td>16.72</td>
</tr>
<tr>
<td>ZnTiO₃/ GPTMS-sol (0.75%)</td>
<td>252.0</td>
<td>61.2</td>
<td>17.87</td>
</tr>
</tbody>
</table>

**Conclusion**

The ZnTiO₃ nanoparticles were synthesized and utilized to prepare functional coating for inorganic-organic hybrid materials. The resulting finished fabrics achieved higher UV protection, antibacterial activity, and self-cleaning properties without affecting the mechanical properties of the fabrics.

**References**


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