HYDROTHERMAL SYNTHESIS OF DOPED ZnO AND TiO₂ NANOMATERIALS: OPPORTUNITIES FOR TEXTILE APPLICATIONS

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Hydrothermal method is a versatile method that may be used to obtain doped TiO₂ and ZnO nanostructures with desired properties to be used as stable suspensions for applications in fabrication of special textiles. XRD spectra revealed TiO₂ and ZnO nanopowders having crystallite sizes of 28 nm and 35 nm, respectively.

Powders consist from slightly agglomerated nanoparticles that can be easily de-agglomerated and dispersed for application on the textiles surfaces. The strong negative zeta potential of the powder (-40…-60 mV) shows that stable colloidal suspensions are formed. The thermal behavior of textiles embedded with these nanostructured oxides is also improved.

Keywords: hydrothermal, TiO₂ and ZnO nanopowders, textile substrate

1. Introduction

Utilization of nanomaterials in order to improve the traditional textiles by adding antiseptic, antifungal or self-cleaning functionalities is a modern trend in special textiles market niche. Anti-microbial agents are used to prevent undesirable effects in textiles. The first includes the degradation phenomena like coloring, staining and deterioration of fibers [1,2]. Because of their dye degradation potential, some fungus can be used for removing dye from textile effluent [3]. The second one produces unpleasant odor [4] and the third effect is the increase of potential health risks [5].

TiO₂ with rutile structure has the ability to block the UV radiation allowing the visible light to cross over a thin film. Alternatively TiO₂ as anatase has a very strong photo-catalytic activity and these combinations of properties are

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important in achieving optimal antibacterial, UV screen and self-cleaning and anti-stain properties of advanced textiles.

TiO$_2$ exists in three crystalline structures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [6]. TiO$_2$ nano-particles have created a new approach for remarkable applications as an attractive multi-functional material. TiO$_2$ nano-particles have unique properties such as higher stability, long lasting, safe and broad-spectrum anti-biosis [7]. TiO$_2$ nano-particles have been especially the center of attention for their photo-catalytic activities [8-10]. This makes TiO$_2$ nano-particles applicable in many fields such as self-cleaning, antibacterial agent, UV protecting agent [11], environmental purification [12], water and air purifier [13], gas sensors, and high efficient solar cell [14]. The photoactivity property is strongly related to the structure, micro-structure and the powder purification [5,14].

Nanostructured ZnO, combines interesting optical, piezoelectric and antiseptic / antifungal properties. ZnO is an n-type semi-conductor as well as TiO$_2$ [15]. Recently, ZnO has been found highly attractive because of its remarkable application potential in solar cells, sensors, displays, gas sensors, piezoelectric devices, electro-acoustic transducers, photo-diodes and UV light emitting devices, sun-screens, UV absorbers, anti-reflection coatings, photo-catalysis and catalyst [5, 15-17].

Their efficiency is strongly dependant on controlled particle sizes (< 100 nm), morphology (spherical, whiskers, fibers…..), structural features and surface characteristics ZnO has strong actions on the mono- and multi-cellular organisms. But it is not yet clarified the destructive effects over the toxins synthesized by organisms.

The photo catalytic effect is more efficient in artificial UV radiation, depending on wave length (the best results obtained at 380 nm), exposure time, oxide amount and bacteria type.

The "killer" mechanisms of ZnO is due to the controlled release of [OH] radicals and [O$^{2-}$] ions, formed in photo catalytic reactions. An important breakthrough was the obtaining of thin ZnO films doped with Ag, which may be used for avoiding room contamination.

Many techniques have been used for deposition of high quality ZnO and TiO$_2$ films such as physical vapor deposition (PVD), pulsed laser deposition (PLD), anodizing, sputtering and thermal evaporation [18-21].

The hydrothermal method is suitable for the direct preparation of nanocrystalline oxide powders, the main advantages being: one step process to produce nanopowders, no heat treatment required to obtain crystalline phases, leading to a good compatibility with organic materials during processing of textiles, low energy and materials consumption, reduced environmental impact.
due to working in close vessels without wastes or gas emissions, scalability to large production capacities.

2. Materials and methods

Obtaining of textile materials embedded with Ag-doped ZnO nanoparticles consisted in the main technological steps: one step hydrothermal synthesis of doped nanopowders, obtaining of stable colloidal suspensions based on these powders, embedding the textile substrate by dip coating and characterization of the material.

For the hydrothermal synthesis of Ag-doped ZnO nanopowders analytical grade zinc nitrate hexahidrate Zn(NO₃)₂ x 6H₂O and silver nitrate Ag(NO₃)₂ were used as raw materials while TiCl₄ was used as raw materials for obtaining TiO₂ nanopowders. Potassium Hydroxide was used as hydrolysis agent.

The starting water solutions mixed at the programmed dopant ratio were mixed with KOH solution to reach a pH > 9.0 for complete hydrolysis of metallic cations. The hydrothermal crystallization was done in Teflon autoclaves in the temperature range 200-250°C. The powder formed was filtered and washed with distilled water and ethanol to remove soluble impurities and reducing agglomeration. The powders were re-dispersed in water using ammonium salt of methyl-methacrylate as stabilizing agent and the dispersion thus obtained were used for impregnation of a the textile substrates.

Chemical analysis of the products was done by Inductive Coupled Plasma Optical Emission Spectroscopy and Atomic Adsorption Spectroscopy. The crystalline structure of powders was characterized using a Brucker D8 Advance XRD apparatus. Data analysis was performed with the software DIFFRACplus XRD Commander for CuKα radiation and the Bragg-Brentano method with Θ – Θ coupling in vertical configuration. The mean crystallite sizes were calculated from Scherrer formula

\[ d_m = \frac{k\lambda}{\delta \cos \theta} \]  

where k is a constant, θ is the Bragg angle, \( \lambda \) is the wave length of the incident XR radiation and \( \delta \) is the peak width at half height.

The particle grain sizes were measured by laser scattering method using a Malvern ZS90 apparatus. The thermal behavior of materials was characterized by DSC method with the help of a Netzsch Maya F3 system in the temperature range 20-600°C.
3. Results and discussions

The chemical reactions expected to take place in the hydrothermal solutions were estimated from the evolution of the equilibrium constant with the reaction temperature for different possible reaction pathways, with the help of HSC 6 software. According to the analysis done, the reaction for the hydrothermal synthesis of TiO₂ and doped Ag-ZnO nanopowders are respectively:

\[
\text{TiCl}_4 + 4\text{KOH(a)} = \text{TiO}_2 + 4\text{KCl(a)} + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{Zn(NO}_3\text{)}_2 + 2\text{AgNO}_3(a) + 4\text{ KOH(a)} = \text{ZnO(a)} + \text{Ag}_2\text{O} + 4\text{KNO}_3(a) + 2\text{H}_2\text{O} \quad (3)
\]

Figs. 1 and 2 show the typical XRD spectra of TiO₂ and ZnO nanopowders obtained by hydrothermal process.

Table 1 and 2 present some important characteristics of TiO₂ and ZnO nanopowders obtained by hydrothermal procedure respectively.
Hydrothermal synthesis of doped ZnO and TiO2 nanomaterials: opportunities for textile (…)

Table 1

<table>
<thead>
<tr>
<th>Phase composition</th>
<th>Lattice parameters</th>
<th>Mean size nm/ (Scherrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2/ anatase</td>
<td>Concentration 92.9%</td>
<td>a, Å 3.78944, c, Å 9.49909</td>
</tr>
<tr>
<td>TiO2/rutil</td>
<td>Concentration 7.1%</td>
<td>a, Å 9.13, c, Å 5.17</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Phase composition</th>
<th>Chemical composition, % gr.</th>
<th>Lattice parameters, Å</th>
<th>Mean size nm/ (Scherrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Zn(OH)2(CO3)2</td>
<td>Zn: 97.3 Ag: 2.3, O: 0.4</td>
<td>a 1.50, c 2.520</td>
</tr>
</tbody>
</table>

In Fig. 3 the particle size distribution of TiO2 and Ag-doped ZnO respectively are shown. It may be observed that powder consist from slightly agglomerated nanoparticles that can be easily de-agglomerated and dispersed for application on the textiles surfaces.

![Fig. 3](image1)

**Fig. 3.** Particle size distribution of TiO2 (a) and Ag-doped ZnO (b) obtained by hydrothermal procedure

Fig. 4 shows the evolution of zeta potential of Ag-doped ZnO nanoparticles during acid titration of the zinc solution with addition of ammonium
salt of methyl-methacrylate as dispersing agent. The strong negative zeta potential
of the powder shows that stable colloidal suspensions are formed.

Fig. 4. Evolution of zeta potential of stable Ag-doped ZnO colloidal suspensions

The thermal behavior of TiO_2 and Ag-doped ZnO nanostructures is
presented in the DSC diagrams from Figs. 5 and 6.

Fig. 5. DSC characterization of TiO_2 nanostructures
The first endothermic peak observed in TiO$_2$ nanostructures embedded in polyester textiles is related to the elimination of adsorbed water while the second large endothermic peak at 260°C is related to the elimination of OH groups from the TiO$_2$ lattice. In the case of textiles embedded with Ag-doped ZnO three endothermic peak are observed. The first from 260°C is related to the elimination of OH groups from the ZnO lattice while the peaks from 439°C and 496°C may be attributed to the degradation of the textile substrate.

4. Conclusions

Implementation of nanomaterials in textiles requires a strong interaction between research, industry and local agencies due to the complexity of analytical methods to be used in the preparation of technology transfer steps and funding of specific activities. Hydrothermal method is a versatile method that may be used to obtain doped TiO$_2$ and ZnO nanostructures with desired properties to be used as stable suspensions for applications in fabrication of special textiles with antifungal, antibacterial and photo-catalytic properties. The thermal behavior of textiles embedded with these nanostructured oxides is also improved.

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