HYDROTHERMAL SYNTHESIS OF DOPED ZnO AND TiO_2 NANOMATERIALS: OPPORTUNITIES FOR TEXTILE APPLICATIONS

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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. XRD spectra revealed TiO_2 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, TiO_2 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].

TiO_2 with rutile structure has the ability to block the UV radiation allowing the visible light to cross over a thin film. Alternatively TiO_2 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, anti-bacterial agent, UV protecting agent [11], environmental purification [12], water and air purifier [13], gas sensors, and high efficient solar cell [14]. The photo-activity 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 break-through 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 $Zn(NO_3)_2$ x $6H_2O$ and silver nitrate $Ag(NO_3)_2$ were used as raw materials while $TiCl_4$ was used as raw materials for obtaining TiO_2 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 DIFFRAC^{plus} XRD Commander for CuK_α radiation and the Bragg-Brentano method with $\Theta - \Theta$ coupling in vertical configuration. The mean crystallite sizes were calculated from Scherrer formula

$$\mathbf{d_m} = \frac{k\lambda}{\delta \cos\theta} \tag{1}$$

where k is a constant, θ is the Bragg angle, λ is the wave length of the incident XR radiation and δ 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 TiO_2 and doped Ag-ZnO nanopowders are respectively:

$$TiCl_4 + 4KOH(a) = TiO_2 + 4KCl(a) + 2H_2O \quad (2)$$

$$Zn(NO_3)_2 + 2AgNO_3(a) + 4\ KOH(a) = ZnO(a) + Ag_2O + 4KNO_3(a) + 2H_2O \quad (3)$$

Figs. 1 and 2 show the typical XRD spectra of TiO_2 and ZnO nanopowders nanopowders obtained by hydrothermal process.

Table 1 and 2 present some important characteristics of TiO_2 and ZnO nanopowders obtained by hydrothermal procedure respectively.

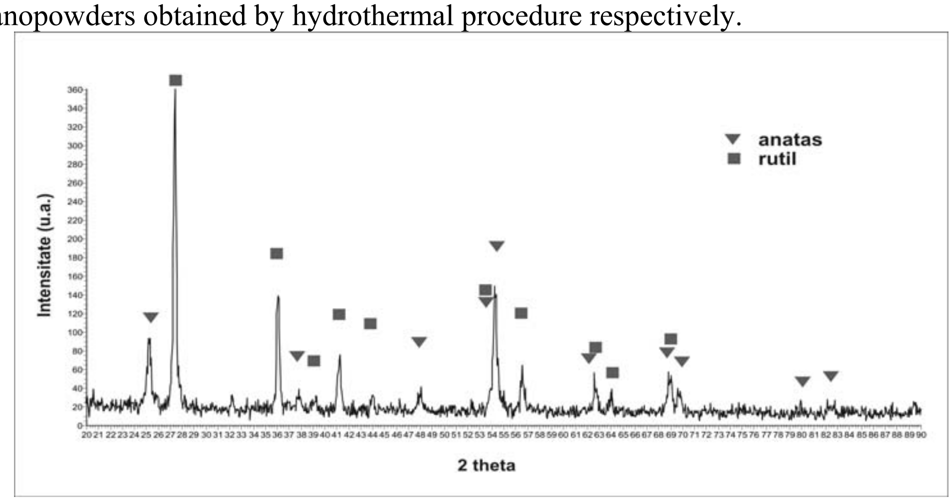

Fig. 1. XRD spectra of hydrothermally synthesized TiO_2

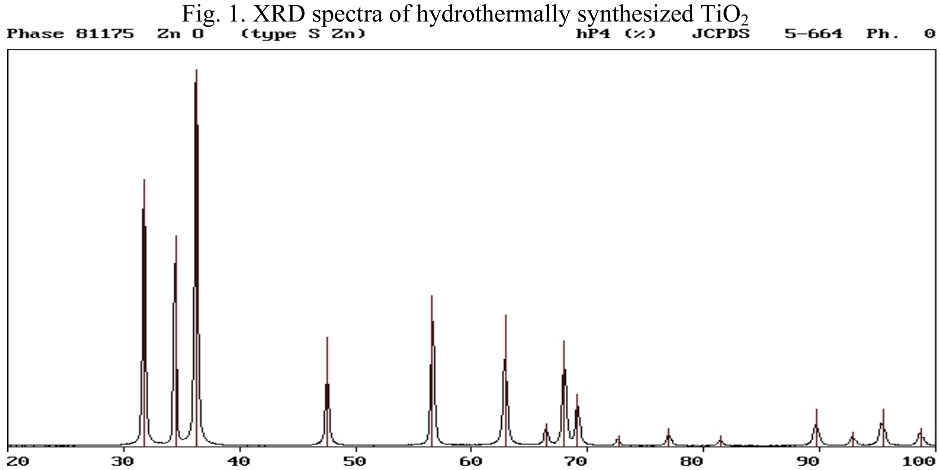

Fig. 2. XRD spectra of hydrothermally synthesized Ag-doped ZnO

Table 1

Main Characteristics of TiO_2 nanopowders

Phase composition	Lattice parameters			
	Concentration	a, Å	c, Å	Mean size nm/ (Scherrer)
TiO_2/ anatase	92.9%	3.78944	9.49909	28.3
TiO_2/rutil	7.1%	9.13	5.17	26.3

Table 2

Main Characteristics of Ag-doped ZnO nanopowders

Phase composition	Chemical composition, % gr.				*Lattice parameters, Å*		Mean size nm/ (Scherrer)
	ZnO	$Zn_5(OH)_6(CO_3)_2$	Ag_2O	*Ag*	*a*	*c*	
	97,3	2,3	0,4	1.50	3,2520	5,2097	35

In Fig. 3 the particle size distribution of TiO_2 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.

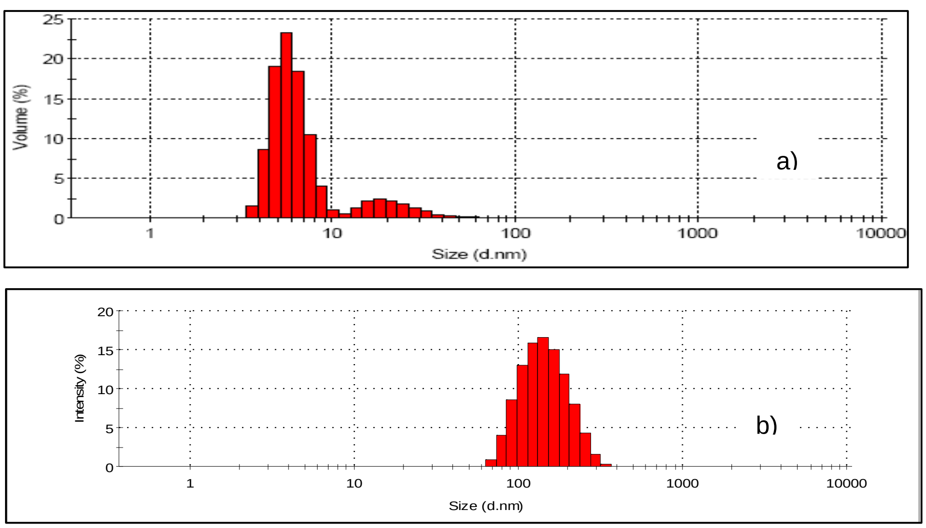

Fig. 3. Particle size distribution of TiO_2 (a) and Ag-doped ZnO (b) obtained by hydrothermal procedure

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.

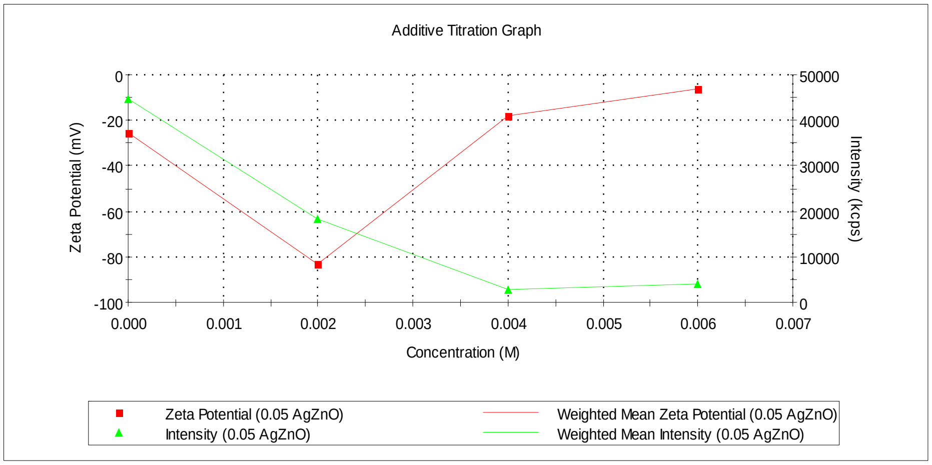

Fig. 4. Evolution of zeta potential of stable Ag-doped ZnO colloidal suspensions

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

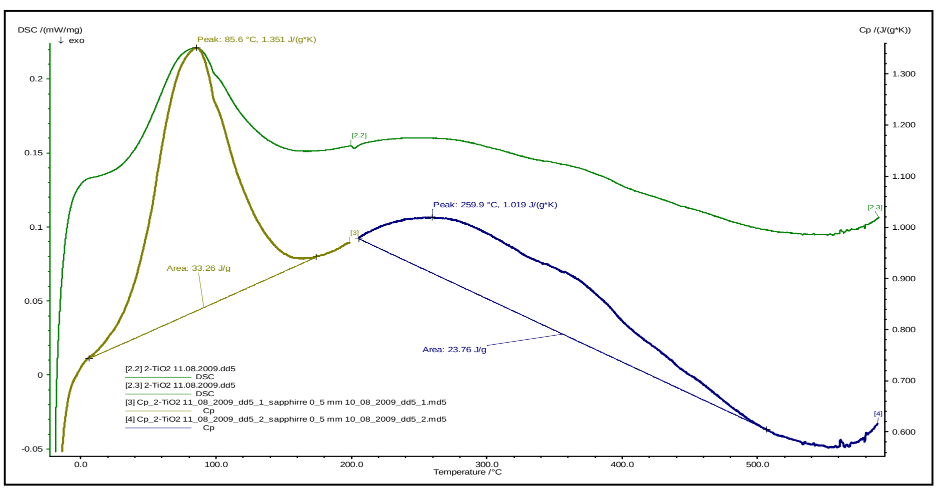

Fig. 5. DSC characterization of TiO_2 nanostructures

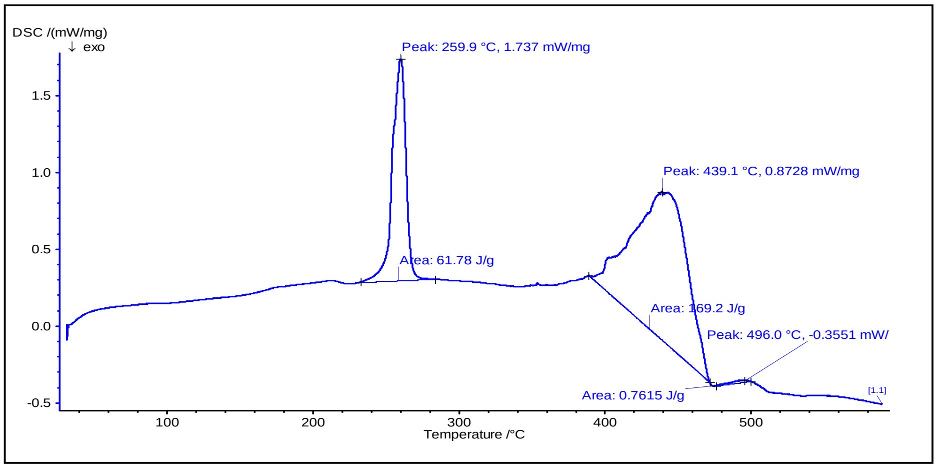

Fig. 6. DSC characterization of polyester textiles embedded with Ag-doped ZnO.

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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REFERENCES

[1] *X.H. Ren, L. Kou, H.B. Kocer, C.Y. Zhu, S.D. Worley, R.M. Broughton, T.S. Huang*, Antimicrobial coating of an N-halamine biocidal monomer on cotton fibers via admicellar polymerization, Colloids and Surfaces A: Physicochemical and Engineering Aspects 317 (2008), pp. 711–716.

[2] *R. Dastjerdi, M.R.M. Mojtahedi, A.M. Shoshtari, A. Khosroshahi*, Investigating the production and properties of Ag/TiO2/PP antibacterial nanocomposite filament yarns, Journal of the Textile Institute 101 (2010), pp. 204–213.

[3] *P. Kaushik, A. Malik*, Fungal dye decolourization: recent advances and future potential, Environment International 35 (2009), pp. 127–141.

[4] *Y. Kobayashi, T. Nakanishi, J. Komiyama*, Deodorant properties of wool fabrics dyed with acid mordant dyes and a copper salt, Textile Research Journal 72 (2) (2002), pp. 125–131.

[5] *R. Dastjerdi, M. Montazer*, Colloids and Surfaces B: Biointerfaces, 79 (2010), pp. 5-18.

[6] *L.A. Brook, P. Evans, H.A. Foster, M.E. Pemble, A. Steele, D.W. Sheel, H.M. Yates*, Highly bioactive silver and silver/titania composite films grown by chemical vapour deposition, Journal of Photochemistry and Photobiology A: Chemistry 187 (2007), pp. 53–63.

[7] *K. Cai 1, J. Bossert, K.D. Jandt*, Does the nanometre scale topography of titanium influence protein adsorption and cell proliferation? Colloids and Surfaces B: Biointerfaces 49 (2006), pp. 136–144.

[8] *P.H. Lo, S.A. Kumar, S.M. Chen*, Amperometric determination of H2O2 at nano-TiO2/DNA/thionin nanocomposite modified electrode, Colloids and Surfaces B: Biointerfaces 66 (2008), pp. 266–273.

[9] *K. Kanehira, T. Banzai, C. Ogino, N. Shimizu, Y. Kubota, S. Sonezaki*, Properties of TiO2–polyacrylic acid dispersions with potential for molecular recognition, Colloids and Surfaces B: Biointerfaces 64 (2008), pp. 10–15.

[10] *H. Wang, J. Niu, X. Long, Y. He*, Sonophotocatalytic degradation of methyl orange by nano-sized Ag/TiO2 particles in aqueous solutions, Ultrasonics Sonochemistry 15 (2008), pp. 386–392.

[11] *K. Han, M. Yu*, Study of the preparation and properties of UV-blocking fabrics of a PET/TiO2 nanocomposite prepared by in situ polycondensation, Journal of Applied Polymer Science 100 (2006), pp. 1588–1593.

[12] *S. Ikezawa, H. Homyara, T. Kubota, R. Suzuki, S. Koh, F. Mutuga, T. Yoshioka, A. Nishiwaki, Y. Ninomiya, M. Takahashi, K. Baba, K. Kida, T. Hara, T. Famakinwa*, Applications of TiO film for environmental purification deposited by controlled electron beam-excited plasma, Thin Solid Films 386 (2001), pp. 173–176.

[13] *D. Li, H. Haneda, S. Hishita, N. Ohashi*, Visible-light-driven N–F–Co doped TiO2 photocatalysts. 2. Optical characterization, photocatalysis, and potential application to air purification, Chemistry of Materials 17 (2005), pp. 2596–2602.

[14] *J. Verran, G. Sandoval, N.S. Allen, M. Edge, J. Stratton*, Variables affecting the antibacterial properties of nano and pigmentary titania particles in suspension, Dyes and Pigments 73 (2007), pp. 298–304.

[15] *N. Vigneshwaran, S. Kumar, A.A. Kathe, P.V. Varadarajan, V. Prasad*, Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites, Nanotechnology 17 (2006), pp. 5087–5095.

[16] *Z.L. Wang,* Novel nanostructures of ZnO for nanoscale photonics, optoelectronics, piezoelectricity, and sensing, Applied Physics A—Materials Science & Processing 88 (2007), pp. 7–15.

[17] *A. Becheri, M. Dürr, P.L. Nostro, P. Baglioni*, Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers, Journal of Nanoparticle Research 10 (2007), pp. 679–689.
[18] *S.-S. Lin, J.-L. Huang*, Surf. Coat. Technol. 185 (2004), pp. 222.
[19] *Ya.I. Alivov, A.V. Chernykh, M.V. Chukichev, R.Y. Korotkov*, Thin Solid Films 473 (2005), pp.241.
[20] *S. Choopun, H. Tabata, T. Kawai*, J. Cryst. Growth 274 (2005), pp.167.
[21] *O.A.Fouad, A.A. Ismail, Z.I. Zaki, R.M. Mohamed*, Applied Catalysis B: Environmental 62 (2006), pp.144-149.