NANOMATERIALS FOR LEATHER SURFACE FUNCTIONALISATION

MADALINA IGNAT[1], AURORA PETICA[1], CARMEN GAIDAU[1], LIANA ANICAI[2], STEFANIA COSOVICI[2], MADALINA POPESCU[3], ROXANA PITICESCU[3], MARCEL IONESCU[4]

[1] *INCDTP-Leather and Footwear Research Institute, 93, Ion Minulescu St, 3, Bucharest, 031215, Romania, carmen.gaidau@icpi.ro; aura_p25@yahoo.com*

[2] *Politehnica University of Bucharest, Center of Surface Science and Nanotechnology, 13, Splaiul Independenţei, 060042, Bucharest, Romania*

[3] *INCDMNR, 102, Biruintei Avn, Pantelimon, Ilfov, 077145, Romania*

[4] *SC EUROPLASTIC SRL, 98E, Timisoara Avn, 6, 061327, Bucharest, Romania*

Nanomaterials are an innovative research direction for the leather and footwear industry due to their high potential of replacing potentially toxic volatile organic materials and their ability to develop smart properties. The paper presents three directions for preparing nanomaterials with advanced properties compared to existing commercial products based on nano titanium dioxide (TiO_2) and nano zinc oxide (ZnO): electrochemical, hydrothermal and thermal synthesis. Nanomaterial performance was improved by doping and co-doping nano titanium dioxide in order to broaden the photoactivity range or increase the share of nanomaterials known for their thermal resistance properties. Characterization of these materials by specific techniques that highlight the crystalline structure (X-ray diffraction), particle size (DLS), absorption ability in UV-Vis (DRS), photodegradation ability of organic pollutant models (Vis spectroscopy) and thermal analysis (DSC) proves the performance of the new nanomaterials. By applying innovative technologies for leather finishing with composite polymers containing photocatalysts based on TiO_2/ZnO nanoparticles doped with metals/non-metals on can obtain leather products with advanced surface properties. The properties that these nanomaterials can transfer to leather surface are: self-cleaning, thermal resistance, biocide resistance, degradation of volatile substances, odorous substances etc.

Keywords: nanomaterials, photocatalysts, self-cleaning leather

INTRODUCTION

In the last years, studies indicated that great potential of nanoparticles (NPs) can be efficiently utilized for the manufacturing of high-added value products, including leather (Fujishima and Zhang, 2006). Semiconductor oxides TiO_2 and ZnO are investigated and used in photocatalytic oxidation of harmful organic compounds, including volatile organic compounds, as well as inorganic compounds due to the oxidative active species produced on their surface under UV irradiation, namely: free or attracted gaps, OH, O_2^- and O_2^{2-} radicals (Fujishima *et al.*, 2008). At present, research focuses on achieving a highly efficient photocatalytic action of these materials in visible spectrum light as well, in order to use the vast potential of solar photocatalysis (Rehman *et al.*, 2009). To achieve this, various functionalization techniques to make them absorb photons at a lower energy, including surface modification, doping and co-doping with metals/non-metals, were used (Rehman *et al.*, 2009). TiO_2/ZnO based photocatalysts can be used like photocatalytic coatings to decompose surface contamination, creating self-cleaning surfaces. Moreover, TiO_2 have antibacterial and antifungal properties, conferring a self-sterilizing effect to finished surfaces. To induce selfprotection properties of nanooxides on leather surface, composite materials based on acrylic polymers for film-forming on leather surface were used (Bitlisli and Yumurtas, 2008).

The present paper deals with some experimental results regarding synthesis, characterization and applications of the TiO_2/ZnO nanomaterials.

RESULTS AND DISCUSSION

Electrochemically Obtained TiO_2NPs

Electrochemical TiO_2NPs Synthesis from Choline Chloride Based Ionic Liquids

Electrochemical method consists in anodic dissolution of a Ti electrode in choline chloride based ionic liquids. System types are presented in Table 1.

Table 1. Ionic liquids systems used in TiO_2 electrochemical synthesis

No.	System type	Electrolyte composition	Working parameters
1	ILEG-IzOH	2:1 (volumes ratio) of ILEG(choline chloride:ethylene glycol 1:2 molar ratio): IzOH+ of tetrabutyl-ammonium bromide (Bu4N-/Br)	Temperature: 30-60°C Current density: 2-7 A/dm^2;
2	IL - EtOH	1:1 (volumes ratio) of IL (choline chloride:urea 1:2 molar ratio): EtOH + Bu4N-/Br	

Characterization of TiO_2 Nanopowder

- XRD investigations indicate anatase crystalline phase of TiO_2, a very high purity of powders and very fine particles.
- BET surface areas for TiO_2NPs have values of about 70 m^2/g, higher than commercial anatase TiO2. The adsorption/desorption isotherm is characteristic to mesoporous materials and the high surface area is mainly due to its nanometric size and then to the mesoporous structure.
- TEM micrographs of TiO_2NPs show nanometric dimensions of 10-20 nm, in accordance with XRD data.
- UV-Vis diffuse reflectance spectra indicates the shifting of the absorption toward the visible range of the solar spectrum, for TiO_2NPs obtained from ionic liquids, compared with commercial one, especially for TiO_2 from IL-EtOH system (Fig. 1). This behavior suggests a better photocatalytic activity under visible light illumination.

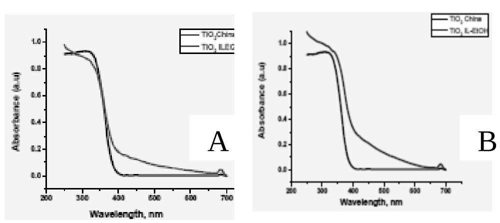

Figure 1. UV-Vis diffuse reflectance spectra of TiO_2 obtained from (A) ILEG-IZOH, (B) IL-EtOH electrolytes compared with commercial TiO_2 China

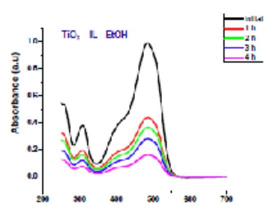

Figure 2. Absorbance spectra for a 20 ppm ORANGE II solution, in the presence of 1g/L

Photocatalytic degradation for an azo dye, namely Orange II, with 20 ppm concentration, in the presence of 0.1% TiO_2, under visible halogen lamp (150W) illumination, indicates a very good activity (Fig. 2). Also, TiO_2NPs exhibited a significant increase in OII discoloring efficiency as compared with commercial TiO_2, under UV irradiation. Moreover, ionic liquids are potentially recyclable, biodegradable and with no harm on human health and environment.

ZnO NPs Obtained from Ionic Liquids Media

ZnO NPs Synthesis Using Chemical Precipitation from Liquids Ionic

The electrochemical synthesis were performed in ionic liquid media based on choline chloride ($HOC_2H_4N(CH_3)_3Cl$), ethylene glycol and urea.

Table 2. Ionic liquids systems used in ZnO electrochemical synthesis

No.	System type	Electrolyte composition	Molar ratio Zinc acetate/NaoH	Zinc acetate concentration in reaction media
1	ZnO ILEG	ChCl:Ethylen-glycol-H_2O (3:1)	1:4	0.25M
2	ZnO IL	ChCl;urea-H_2O (3:1)	1:4	0.25M
3	ZnO standard	H_2O	1:4	0.25M

Characterization of ZnO Nanopowder

Composition and structure of the nanosized ZnO was analyzed by X-ray diffraction (XRD) and the visible light behaviour by UV-VIS absorption spectra recordings.

Table 3. Composition and crystallite sizes

System type	Composition, % (weight)	Crystallite size/ system	Network parameters a	c
ZnO-ILEG	ZnO – 45% NaCl – 35% Na_2CO_3 -15% Oxyclozanide ($C_{13}H_6Cl_5NO_3$) 1 – 5%	16.3nm Hexagonal	3.253Å	5.213Å
ZnO-IL	ZnO – 43% NaCl – 53% Oxyclozanide ($C_{13}H_6Cl_5NO_3$) 1 – 5%	16.1nm Hexagonal	3.253Å	5.213Å
ZnO standard	ZnO – 100%	31.6nm Hexagonal	3.253Å	5.213Å

All the obtained nanopowders present high crystallinity, in hexagonal system and have smaller size in ionic liquid media, of 16.1-16.3 nm, compared with 31.6 nm in the case of synthesis in aqueous media.

X-ray diffraction evidenced the presence of other chemical compounds, which were removed by washing.

UV-Vis diffuse reflectance spectra, evidenced the shifting of the absorption in visible area of spectrum greater for the ZnO obtained from ionic liquids than for ZnO from aqueous media, and higher for ZnO obtained from ChCl-urea than for the one from ChCl-Ethylenglycol electrolyte.

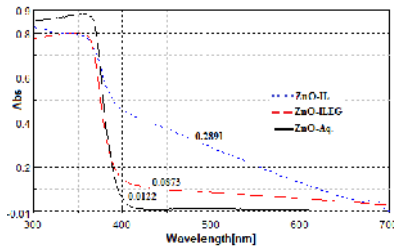

Figure 3. UV-Vis diffuse refelectance spectra for ZnO nanopowders

TiO_2 and Si Doped TiO_2 Obtained by Hydrothermal Method

Hydrothermal Synthesis of TiO_2 and Si Doped TiO_2

TiO_2Cl_2 and Na_2SiO_3 precursors were mixed, stirred and then ammoniacal solution was added to achieve the alkaline pH required for TiO_2 and Si doped TiO_2 precipitation. Suspension was transferred to an autoclave, in which, under precisely temperature and pressure working parameters, crystalline nanostructured materials were obtained. Thus, TiO_2NPs, 2% and 5%Si doped TiO_2NPs were obtained.

Characterization of TiO_2 and Si Doped TiO_2 Nanopowders

• XRD investigations indicate the main crystalline phases identified in TiO_2 and Si doped TiO_2 nanopowders and crystallite sizes (Table 3).

Table 4. Crystalline phases and crystallite sizes for TiO_2 and Si doped

System type	Crystalline phases (DRX)	Crystallite sizes (Scherrer), nm
TiO_2	91.5 % anatas; 8.5% brookit	15 nm
TiO_2-2%Si	90.6 % anatas; 7.1% brookit	16.2 nm
TiO_2-5%Si	90.1% anatas; 7.5% brookit	16.7 nm

• Differential scanning calorimetry evidenced the presence of two endothermic peaks, corresponding to the elimination of the water adsorbed on the surface (peak 1), and of the OH groups from constitution water (peak 2). In addition, an exothermic peak was observed (peak 3), which could be attributed, to the growth of grains (Table 4).

Table 5. Results obtained from thermal analysis (DSC method)

System type	Peak 1 (endotherm)		Peak 2 (endotherm)		Peak 3 (exotherm)	
	T, °C	ΔH, J/g	T, °C	ΔH, J/g	T, °C	ΔH, J/g
TiO_2-1	74.7	54.89	-	-	523.9	-8.374
TiO_2-2%Si	77.7	120.5	308.8	1.577	557.5	-1.932
TiO_2-5%Si	60.2	59.71	232.2 / 323.7	1.129/ 1.169	564.2	-0.605

These results indicate that 2% Si doped TiO_2 could induce heat and fire protection for leather treated with them.

Leather Surface with Self-Cleaning Properties Induced by NPs

The new synthesized nanoparticles were used for leather surface finishing. The procedure consisted in ultrasound mixing of solid nanoparticles in polymer finishing solutions and then spraying it on the leather surface. The surface properties of the treated leather stained with 0.05 mL of 200 ppm MB and pen ball ink lines were analyzed over time.

Photo-Degradation of a MB Spot on Leather Surface

The degradation of the MB dye on leather surface, under UV and visible light irradiation was done with Datacolor Check II Instrument based on CIELab color coordinates and recording of parameters: L* (lightness), a*(red-green color), b*(yellow-blue), C* (chroma) and h* (hue angle). Comparative representation of the L* parameter variation, which measures the lightness of a color, from completely opaque (0) to completely transparent (100) is represented in Fig. 4 and Fig. 5.

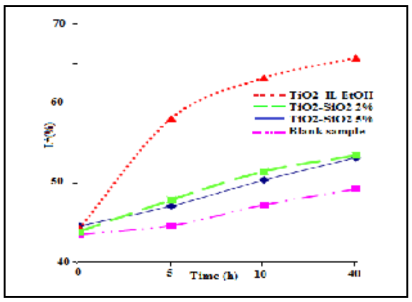

Figure 4. L* variation for treated leather in UV light

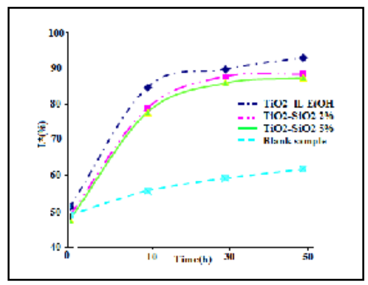

Figure 5. L* variation for treated leather in visible light

While, in UV illumination TiO_2-IL has a better photocatalytic activity than hydrothermally obtained Si-TiO_2, in visible light, all samples degrade MB dye spots.

Photographic Images of Photodegraded Leather Samples

Figures 6 and 7 present photographic images of the leather treated with polymeric composite based on TiO_2-5% SiO_2 (Fig. 6), TiO_2 obtained from IL-EtOH system (Fig. 7) and untreated leather (Fig. 8).

The experiments confirmed the photocatalytic activity increasing under Vis light exposure in the case of doped nanoparticles on leather surface.

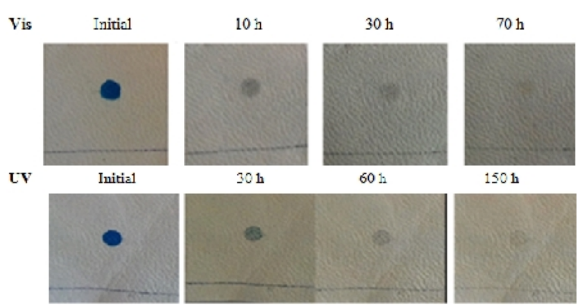

Figure 6. MB degradation onto a TiO_2-5% SiO_2 treated leather surface

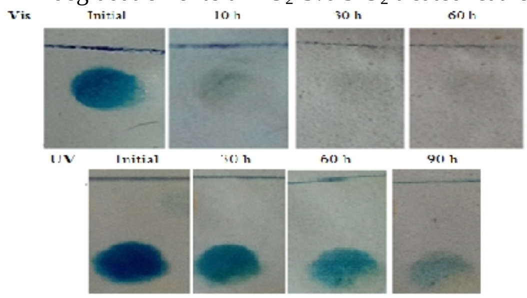

Figure 7. MB degradation onto a treated leather surface using TiO_2 from IL-EtOH

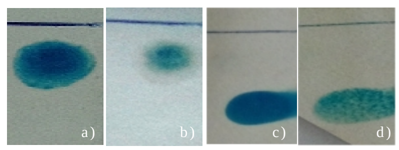

Figure 8. Dye degradation onto untreated leather: Vis light: a) initially, b) after 120h of exposure; UV light: c) initially, d) after 120h of exposure

CONCLUSIONS

The experimental results evidenced a new technique for TiO_2 and ZnO NPs synthesis from ionic liquid media with high photocatalytic activity, both in UV and visible light. TiO_2 doped with Si obtained by the hydrothermal method can provide heat and fire protection for leather treated with them. The self-cleaning properties were confirmed by colorimetric measurements for the MB spots applied to the treated leather surface exposed to UVA (λ=365nm) and visible light irradiation.

The self-cleaning leather surface using nanomaterials as photocatalysts represents a step forward in innovative upholstery material development with improved durability.

Acknowledgments

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