



FUNCTIONAL FINISHING OF FIBROUS SUBSTRATES COATED WITH AG-DEPOSITED TiO₂ NANOPARTICLES

VRINCEANU, N[arcisa]; COMAN, D[jana]; POPOVICI, E[veline]; BRINZA, F[lorin] & NICA, V[alentin]

Abstract: This research aimed at the development of nano-structural fibrous composites with optimal dispersion containing Ag deposited TiO₂ nano-particles, providing enhanced barrier properties. Firstly, the study was focused on the synthesis of Ag-deposited TiO₂ particles formed by a chemical reduction method. The morphology and micro-structure of Ag-deposited TiO₂ particles have been determined. Secondly, the characterization of the nanoscale finished surfaces has been performed using a co-assisted system: surface area measurements (adsorption/desorption isotherms, surface area measurement and pore size distribution). The structural properties of these as-prepared nanocomposites were characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD), showing that Ag-deposited TiO₂ nanoparticles were deposited on the surface of studied textile. Due to the uniformity distribution of Ag deposited TiO₂ nanoparticles onto the surface of supports, our results could be considered a preliminary step towards a safe methodology of nano-particles incorporation into selected fibrous substrates with multifunctionality, such as: self-cleaning performance, UV protection, photocatalytic, water stability etc.

Key words: fibrous substrates, nanotechnology, Ag-deposited TiO₂, nanoparticles, functionalization, finishing fibrous substrates, nanotechnology, finishing

1. INTRODUCTION

Innovative materials, including textiles for specific applications, have to satisfy consumers' growing demands (Tsuji, 2002). It is extremely important, even compulsory that a material should perform several functions, due to various applications, wearing and also economic aspects.

There are some nanoparticles of metal-oxides: titanium (TiO₂) and zinc (ZnO) belonging to a group of compounds with photo-catalytic properties, which are able to absorb UV radiation. There are researches involving metal deposition (Esumi, 1998) and much attention has been paid to doping the material with transition and noble metals such as Pd, Pt (Esumi, 1998), Rh, Au, and Ag (Innocezi, 2000). In this work, silver nanoparticles were deposited on the surface of TiO₂ particles by using a chemical reduction method (Shirai, 1999). In the formation process of silver nanoparticles by the chemical reduction method, there are several factors that influence in a great extent the preparing of nano-sized silver powder. Important parameters, such as the molar concentration ratio of R ([AgNO₃]/[reducing agent]), the dispersant concentration, and the feed rate of reactant, affect the properties of the silver nanoparticles obtained by this method (Andrzejewska, 2004; Jesionowski, 2001). The main aim of these research works was the development of nano-scaled textile composites with barrier properties.

In the first stage, the works focused on:

- a method for the synthesis of Ag - deposited TiO₂ nanoparticles by using a chemical reduction method;
- a methodology of nano-particles incorporation into selected fibrous substrates.

2. EXPERIMENTAL

Materials and methods. Nanoparticle preparation/Synthesis of Ag-deposited TiO₂ nanoparticles. In all experiments the TiO₂ nanoparticles used were synthesized. The ageing of TiO₂ suspensions lasted for 30 min in an ultrasonic bath, to which were added the required quantities of silver nitrate (AgNO₃ (99.99%), Aldrich) with SDS (sodium dodecyl sulfate (CH₃(CH₂)₁₁OSO₃Na (99%), Aldrich) such that the desired Ag/Ti atomic concentration ratio was obtained. After mixing, Ag-deposited TiO₂ suspensions were prepared by feeding in hydrazine hydrate (N₂H₄ X H₂O (98%), Aldrich) aqueous solution. In this experiment, hydrazine hydrate and sodium dodecyl sulfate played the role of reducing agent and dispersant, respectively.

2.1. Nanoscaled finishing of linen fabrics with Ag-deposited TiO₂ particles

For the experimental purpose small fine-medium weight 100% linen woven fabrics were used. Linen fabrics were washed and dried, before being used. The dimensions of samples were of 4 × 12 cm². The application of Ag-deposited TiO₂ particles on linen has been performed using pad-dry-cure method. For the successive treatment of fabrics with colloidal silver, the solution was agitated continuously. The linen samples were immersed in the solution (150 mL) containing Ag-deposited TiO₂ particles, for 5 min, then squeezed to 100% wet pick up with laboratory padder at constant pressure. A subsequently immersion for 5 min in 2 g/L of sodium lauryl sulfate has been performed to remove unbound nanoparticles. To completely take out all the soap solution, the fabric was rinsed at least 10 times. The drying took place at 70°C for 3 min, followed by curing at 150°C for 2 min.

2.2. Characterization of Ag-deposited TiO₂ nanoparticles

SEM photographs were used to observe the distribution of silver deposited on the TiO₂ surface. As shown in Fig. 1, a small amount of silver particles with a size of 5 nm was deposited on the surface of the TiO₂ particles. It can be confirmed that silver particles were deposited on the surface of the individual TiO₂ crystallites.

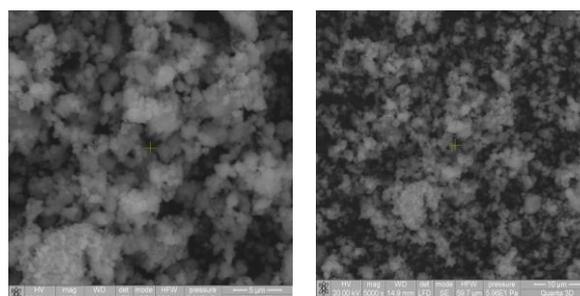


Fig.1. SEM image of Ag-deposited TiO₂ nanoparticles

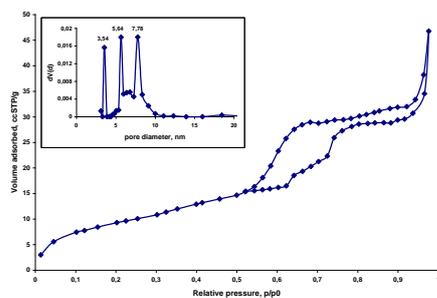


Fig. 2. Nitrogen adsorption–desorption isotherms (inset) and pore size distribution plots for linen sample treated with Ag-deposited TiO_2 particles

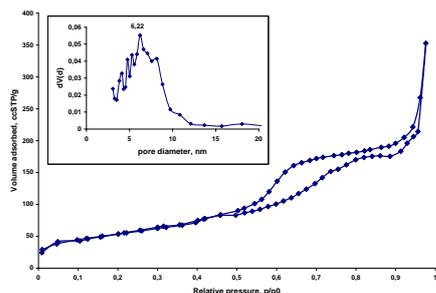


Fig. 3. Nitrogen adsorption–desorption isotherms (inset) and pore size distribution plots for Ag-deposited TiO_2 particles

The particle size and the size distribution of Ag-deposited TiO_2 nanoparticles were observed using a Nova High Speed Gas Sorption Analyser. Both reference and tested samples show a type-IV isotherm, which is representative of mesoporous solids (Fig 2 and Fig. 3). The specific surface area of the Ag/ TiO_2 composite is $176 \text{ m}^2/\text{g}$, by means of Brunauer – Emmett – Teller (BET) method. The pore diameter of the Ag/ TiO_2 is 6.22 nm (estimated using the desorption branch of the isotherm) with very narrow pore size distribution.

The TiO_2 possesses virtually identical average pore diameter (5 nm) and specific surface area ($189 \text{ m}^2/\text{g}$), considering a typical uncertainty of 5% for BET surface area measurements. The addition of Ag causes a slight decrease, from 0.261 to $0.007 \text{ cm}^3/\text{g}$, in the pore volume of TiO_2 .

Fig. 4 shows the X-ray diffraction patterns of Ag-deposited TiO_2 powders $\text{TiO}_2/\text{AgNO}_3$ for 2θ diffraction angles between 5° and 70° . The XRD pattern of TiO_2 shows five primary peaks at: 25.4° , 38.14° , 48.14° , 54.7° and 63.04° , which can be assigned to different diffraction planes of anatase TiO_2 .

As shown in Fig. 4, the most intense (101) peak was observed at $2\theta = 25.34^\circ$, meaning the interference-free reflection of the typical tetragonal anatase structure. Results reveal that the addition of silver did not significantly affect the crystal size. The XRD patterns of silver deposited TiO_2 samples almost coincide with that of pure TiO_2 showing no diffraction peaks due to silver deposition thus suggesting that the silver are merely placed on the surface of the crystals.

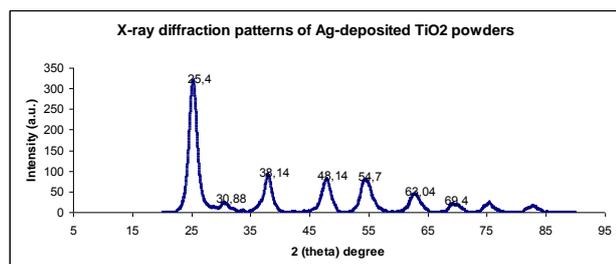


Fig. 4. X-ray diffraction patterns of Ag-deposited TiO_2 powders

Sample	S, m^2/g	Vp, cc/g	Pore diameter, nm
TiO_2	189	0.423	5
TiO_2/Ag	176.301	0.261	6.22
Linen + TiO_2/Ag	31.542	0.007	7.78

Tab. 1. Textural properties

These results show that the deposition of Ag particles does not significantly change the textural properties of TiO_2 , properly due to the small amount of Ag loaded. Thus, most of the pore channels in TiO_2 film are open, although a small portion of the channels may be filled with the Ag particles. Such open mesoporous architecture with large surface area and 3D connected pore-system is an important consideration in catalyst design because it can improve the molecular transport of reactants and products.

These results are the consequence of the presence of Ag particles and their interaction with TiO_2 particles. Summarizing, the high dispersion of silver nanoparticles is thoroughly achieved by encapsulation in the pore channels of ordered mesoporous TiO_2 film. The Ag particles are well confined in the pore channels and the particle size can be controlled to below 5 nm . Such porous architecture and dimensions are desirable features for catalytic and photocatalytic applications.

3. CONCLUSION AND PERSPECTIVES

This study revealed the silver deposited TiO_2 nanoparticles synthesis by a chemical reduction method and the nanoscaled finishing with Ag-deposited TiO_2 powders onto fabrics. The main aim of these research works was the development of appropriate nano-structural textile composites with barrier properties. The research had two phases: (1) a methodology for the synthesis of Ag - deposited TiO_2 nanoparticles by using a chemical reduction method and (2) the methodology of nanoparticles incorporation into selected fibrous substrates. The characterization of Ag-deposited TiO_2 nanoparticles suggested that such porous architecture and dimensions are desirable features for providing a high multifunctionality: photocatalytic applications, photoprotective, self-cleaning of nano-structural textile composites. Our future research will be focused towards potential barrier properties of this type of nano-scaled textile composites obtained, as well as their photocatalytic activity.

4. ACKNOWLEDGEMENTS

This work was supported by the Research Contract within POSDRU No. /89/1.5/S/49944 Project.

5. REFERENCES

- Andrzejewska, A., Krysztafkiewicz, A., Jesionowski, T. (2004), *Dyes Pigments*, 62(2), p. 121-130
- Esumi, K., Hayashi, H., Koide, Y., Suhara, T., Fukui, H. (1998). *Colloids Surf. A.*, 144, p. 201
- Esumi, K., Sakai, K., Torigoe, K., Suhara, T., Fukui, H. (1999), *Colloids Surf. A.*, 155, p. 413
- Innocezi, P., Brusatin, G., Guglielmi, M., Sognorini, R., Bozio, R., Moggini M. (2000). *J. Non-Crystalline Solids*, 265, p. 68
- Jesionowski, T., (2001). *Pigment Resin Technol.*, 30, p. 287-295
- Jesionowski T., Krysztafkiewicz A., Dec A. (2001). *Physicochemical Problems of Mineral Processing*, 35, p. 195-205
- Tsuji, H., Sagimori T., Kurita, K., Gotom, Y., Ishikawa, J. (2002). *Surf. Coat. Technol.*, 158-159, p. 208-213
- Shirai Y., Kawatsura K. and Tsubokawa N. (1999). *Progress in Organic Coatings*, 36, p. 217