Hybrid materials based on ZnO and SiO_2 nanoparticles as hydrophobic coatings for textiles

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ABSTRACT – REZUMAT

Hybrid materials based on ZnO and SiO_2 nanoparticles as hydrophobic coatings for textiles

This study presents a strategy to obtain textile materials with hydrophobic/oleophobic effect by applying hybrid coatings based on a mixture of flower-like ZnO nanoparticles and organically modified SiO_2 nanoparticles (ORMOSIL). The obtained dispersions based on both types of nanoparticles are stable, with unimodal distribution of smaller quasi spherical shape and average size of 158 nm for SiO_2 nanoparticles and respectively, with bimodal distribution with a broad distribution of particle size and average size of 144 nm and 435 nm for ZnO flower-like nanoparticles. The ZnO/SiO_2 NPs based dispersions were then applied on 100% cotton fabrics on a laboratory scale by padding method in two successive phases. The functionalized cotton fabrics were evaluated in terms of surface morphology changes, whiteness degree and water and oils repellent properties. The developed textile materials exhibited a low wetting capacity, with high values of water absorption time (>15 minutes) and a water-repellent degree of 75 (AATCC photographic scale) and 2.5 respectively (ISO scale) showing an acceptable hydrophobic effect. The functionalization treatment based on mixture of ZnO/SiO_2 nanoparticles led to obtaining an efficient cotton substrate for the rejection and protection against the oily substances which exhibit an oil repellency degree of 6. Also, the functionalization treatments did not significantly change the surface morphology of the fibres, suggesting that the bulk properties of the cotton fibres remained undamaged.

Keywords: *flower-like ZnO nanoparticles, SiO_2 nanoparticles, cotton fabric, water repellency, oil repellency*

Materiale hibride pe bază de nanoparticule de ZnO și SiO_2 ca acoperiri de hidrofobizare pentru materiale textile

Acest studiu prezintă o strategie de obținere a materialelor textile cu efect hidrofob/oleofob prin aplicarea unor acoperiri hibride bazate pe un amestec de nanoparticule ZnO flower-like și nanoparticule SiO_2 modificate organic (ORMOSIL). Dispersiile obținute pe baza ambelor tipuri pe nanoparticule, sunt stabile, cu o distribuție unimodală de particule de SiO_2 cu forma cvazisferică mai mică, cu dimensiunea medie de 158 nm și, respectiv, cu o distribuție bimodală, cu un domeniu larg al mărimii particulelor, cu dimensiuni medii cuprinse între 144 nm și 435 nm pentru nanoparticulele de ZnO flower-like. Dispersiile pe bază de ZnO/SiO_2 NPs au fost apoi aplicate pe țesături din 100% bumbac la scară de laborator, prin metoda fulardării în două faze succesive. Țesăturile din bumbac funcționalizate au fost evaluate în ceea ce privește modificările morfologiei de suprafață, gradul de alb și capacitatea de respingere a apei și a uleiurilor. Materialele textile dezvoltate au prezentat o capacitate de umectare scăzută, cu valori ridicate ale timpului de absorbție a apei (>15 minute) și o capacitate de respingere a apei de 75 (scara fotografică AATCC) și respectiv 2,5 (scara ISO), prezentând un efect hidrofob acceptabil. Tratamentul de funcționalizare bazat pe amestecul de nanoparticule de ZnO/SiO_2 a dus la obținerea unui substrat eficient din bumbac pentru respingerea și protecția împotriva substanțelor uleioase, care manifestă un grad de respingere a uleiului de 6. De asemenea, tratamentele de funcționalizare nu au modificat în mod semnificativ morfologia de suprafață a fibrelor, ceea ce sugerează că proprietățile în vrac ale fibrelor de bumbac au rămas nedeteriorate.

Cuvinte cheie: *nanoparticule de ZnO flower-like, nanoparticule de SiO_2, țesătură din bumbac, capacitatea de respingere a apei, capacitatea de respingere a uleiurilor*

INTRODUCTION

Textile materials present a wide applicability in numerous domains, through the introduction of superhydrophobicity on fibrous structures. This finishing process represents an ideal candidate for oil/water mixture separation and protection equipment development, but also to manufacture antibacterial and self-cleaning products. In this regard, functional coatings aim to improve the properties and performance of textile substrates as well as to introduce novel functions [1]. Based on previous research studies, for an enhanced protection of textile materials from water and other solvents, modified nanoparticles have been used to obtain hydrophobic and oleophobic properties achieving long-lasting resistance [2–3]. Zinc oxide (ZnO) has already been considered an outstanding chemical compound for textile functionalization due to its unique chemical and physical properties, environmental friendliness, biocompatibility, and low price. According to literature, ZnO nanoparticles

(ZnO NPs) were used in combination with hydrophobic or oleophobic precursors to provide multifunctional properties, such as antimicrobial, UV-protective, and hydrophobic/oleophobic properties on textile surfaces [4]. To improve these properties, the entrapment of the air in the space between the rough features has been promoted by creating certain micro/nano-roughness structures. The increase in surface roughness can be achieved by the development of micro/nanostructures such as micro/nanoparticles, micro/nano flower-like structures, nanowires and nanorods [5]. In this regard, flower-like ZnO NPs promote an increased hydrophobicity and oleophobicity compared to the nanorod morphology [6].

Furthermore, silica nanoparticles (SiO_2 NPs) represent another type of nanoparticles applied for the development of hydrophobic/oleophobic surfaces. Therefore, by generating functional groups on the surface of SiO_2 NPs, these specific properties are improved. The hydroxyl functional groups (-OH) on the surface of silica nanoparticles control nanoparticles growth and hence, act as a proper support material for nanoparticles deposition [7]. Moreover, organically modified silica (ORMOSIL) hydrophobic thin films have shown great potential for the functionalization of textile materials and other supports due to their good mechanical and thermal stability. ORMOSIL materials are commonly preferred due to their unique features, such as flexibility and stability at atmospheric conditions, which cannot be accomplished by organic polymers or glasses. In addition, different changes can be accomplished through the modification/substitution of the organic group on the ORMOSIL, leading to certain improvements regarding the physical and chemical properties of the resulting surfaces (e.g. wettability). The aim of this study was to develop hydrophobic/oleophobic cotton fabrics by applying hybrid materials based on flower-like ZnO NPs and organically modified SiO_2 NPs (ORMOSIL).

EXPERIMENTAL PART

Materials

Zinc nitrate hexahydrate – $Zn(NO_3)_6 \cdot H_2O$ reagent grade 95% (Sigma Aldrich Chemie, Germany), sodium hydroxide (NaOH, >98%, Sigma Aldrich Chemie, Germany), cetyltrymethyl ammonium bromide (CTAB, >99%, Sigma Aldrich Chemie, Germany) reagent for molecular biology, tetraethoxysilane (TEOS, 98%, Sigma Aldrich Chemie, Germany), triethoxy(octyl) silane (OTEOS, 97%, Sigma Aldrich Chemie, Germany), ammonia (33% solution, Sigma Aldrich Chemie, Germany) were used without further purification or treatment. Double distilled water and ethanol (absolute, Reactivul SA) were employed as solvents. Bleached plain weave 100% cotton fabric with weight per unit area of 254 g/m^2 was used for the functionalization process.

Synthesis of flower-like ZnO nanoparticles

ZnO NPs were synthesized using a surfactant free hydrothermal method [8] with some modifications. Briefly, 20 ml of 0.1 M solution of Zn nitrate hexahydrate ($ZnNO_3 \cdot 6H_2O$) was mixed with 20 ml of 0.6 M solution of CTAB, under magnetic stirring, in a 100 ml vial, at 85°C. To the resulted mixture, a volume of 10 ml of NaOH solution 0.3 M was added dropwise, under vigorous stirring. The previous clear solution turned milky while the NaOH solution was added. Further, the dispersion was sealed in a in vial and left for reaction at temperature, under magnetic stirring for 12 h. After the natural cooling at room temperature, the obtained white precipitate was separated by centrifugation, washed three times with distilled water and absolute alcohol. The ZnO nanopowder was then dried at 105°C for 4 h.

Synthesis of organo-modified SiO_2 nanoparticles

The synthesis of SiO_2 NPs was performed by using a procedure modified in our laboratory, based on Stöber method, i.e. hydrolysis and condensation of silane compound in basic catalysis [9]. A volume of 1 ml of 33% ammonia solution was added to 15 ml of ethanol in a vial and heated at 50°C. A TEOS solution with 2.25 M concentration was prepared by dissolving silane derivative in ethanol. 2 ml of the above solution was added into the vial in one step, under vigorous magnetic stirring. The formation of SiO_2 NPs was proved when the solution became slightly turbid. The temperature and stirring were maintained for 2 h to allow particles maturation. Then, 1 ml of organo-modified silica reagent OTEOS was added dropwise (0.5 M solution in ethanol). The dispersion was left for aging under temperature and stirring for another 2 h for the formation of the organo-modified nanoparticles. The modified SiO_2 NPs were separated by centrifugation and washed with ethanol to remove the unreacted compounds.

Immobilization of ZnO and SiO_2 NPs on the textile materials

In order to avoid the aggregation of nanoparticles during the functionalization of the textile materials, the ZnO and SiO_2 dispersions were prepared separately and mixed just before the textile treatment. A dispersion of 2% ZnO NPs in distilled water was prepared by mixing the ZnO nanopowder with water, under magnetic stirring, followed by sonication in a bath for 10 minutes (Branson, 50W). The modified SiO_2 NPs were dispersed in a 0.002 M solution of polydimethyl siloxane as hydrophobization polymeric agent.

ZnO and SiO_2 NPs dispersions were deposited separately by padding method on the laboratory padder (ROAKES, UK) in successive phases on the surface of textile materials, in the following conditions: 5 passes of the textile material, 2 barr squeezing pressure, with a wet pick-up rate of 85%. After each impregnation operation, the treated textile materials

were then subjected on the drying operation at 100°C for 3 minutes. The drying process of the impregnated textile materials was carried out on the drying/curing/heat-setting/vaporization unit, model TFO/S 500 mm (ROACHES, UK). The sequence of the constituent operations of functionalization process are the following: padding with ZnO NPs dispersions → drying → padding with SiO_2 NPs dispersed in polydimethyl siloxane → drying → functionalized textile materials.

Methods

Dynamic light scattering (DLS)

For the characterization of the size and size distribution of the obtained dispersions, the dynamic light scattering (DLS) technique was used. Measurements were performed using a Zetasizer Nano instrument (Malvern).

X-ray diffraction (XRD)

Crystallinity and phase identity of the ZnO nanopowders were investigated using X-ray diffraction on a Shimadzu XRD 7000 instrument.

Scanning electron microscopy (SEM)

The size and morphology of ZnO and SiO_2 NPs and respectively the surface morphology of textile treated samples was investigated by a FEI Quanta 200 Scanning Electron Microscope (Netherlands) with a GSED detector, at different magnification and accelerating voltage of 12.5 kV – 20 kV.

Whiteness degree of treated samples

In order to assess the influence of the functionalization treatments on the textile materials appearance, the 100% cotton fabrics were tested before and after treatments in terms of whiteness degree according to the SR EN ISO 105-J01:2003 standard.

Assessment of water-repellent properties

For the assessment of water-repellent properties, the treated samples with hybrid coatings based on ZnO/SiO_2 NPs were tested from the wettability point of view, according to the drop test method (STAS 12751-89 standard), surface wetting resistance – Spraytest (SR EN ISO 4920:2013 standard)

Assessment oil-repellent properties

The oil repellence of the PES samples was determined under static conditions using hydrocarbon resistance test (SR EN ISO 14419:2010 standard) with eight hydrocarbon liquids in a series of decreasing surface tension. Paraffin oil was denoted with the rating number 1 and n-heptane was given the rating number 8. Drops of the standard test liquids were placed on the fabric surface and observed for wetting. The repellence rating was the highest numbered test liquid that did not wet the fabric in 30 seconds.

RESULTS AND DISCUSSION

Dynamic light scattering (DLS)

Figure 1 shows the DLS diagrams of the obtained ZnO and SiO_2 NPs dispersions, presenting small dimensions and, in the case of SiO_2 nanoparticles, good monodispersity.

The average size of the SiO_2 NPs is 158 nm, with no other signal at higher values. In the case of ZnO NPs, the size distribution is bimodal, indicating the presence of two populations, with average size at 144 nm and 435 nm. Moreover, ZnO NPs exhibit a broad particle size distribution, demonstrated by the polydispersity index of 0.444 and the high value of width of the peaks. The large range of nanoparticle size is due to the formation of the flower-like aggregated of smaller ZnO sheets, while the hydrothermal synthesis of such complex morphologies is very difficult to control.

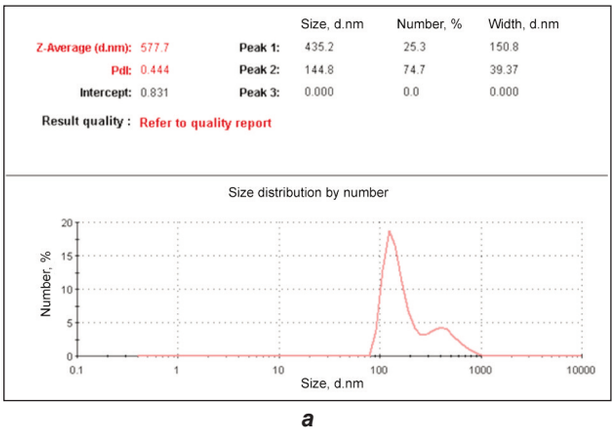
X-ray diffraction (XRD)

The result of the diffractograms is specific to the phase of hexagonal wurtzite for all ZnO samples (figure 2).

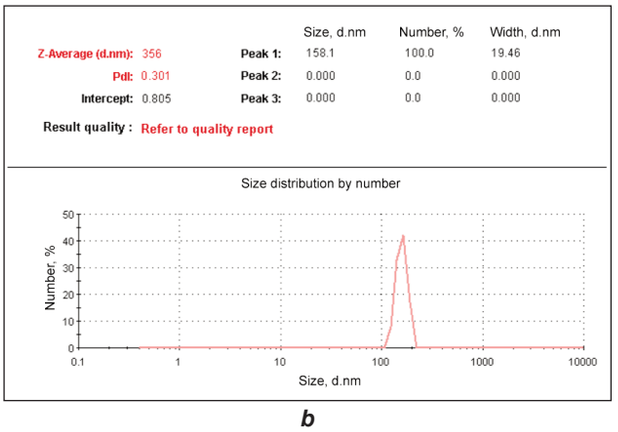
The XRD peaks are sharp and intense, indicating that the nanopowders are highly crystalline. The diffractogram recorded for SiO_2 NPs (data not shown) contains no evident peaks, suggesting the amorphous phase of the silica nanoparticles.

Scanning electron microscopy (SEM)

The SEM image (figure 3, *a*) reveals that ZnO NPs exhibit flower-like morphology, with pellets (sheets)



a



b

Fig. 1. Size and size distribution of: *a* – ZnO NPs; *b* – SiO_2 NPs obtained according the procedure described above

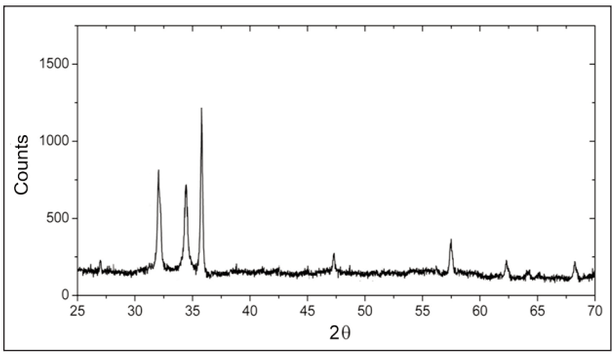
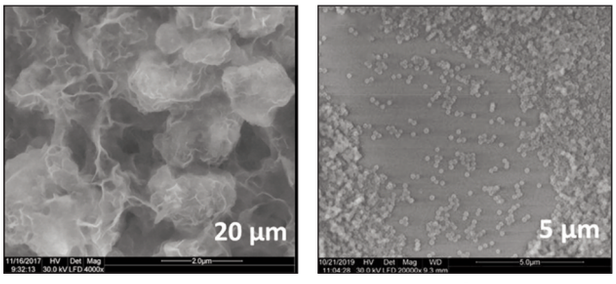


Fig. 2. The XRD diffractogram for the ZnO nanopowder

converged in a center. Some distinct sheets, unassociated are also present, corresponding to the particles with smaller size observed in DLS diagram. Figure 3, *b* presents a SEM micrography of SiO_2 NPs, where it can be observed that the nanoparticles exhibit an increased monodispersity and quasi spherical shape.



a *b*

Fig. 3. SEM images for: *a* – ZnO NPs; *b* – SiO_2 NPs

The surface morphology of cotton fibres untreated and treated with hybrid coatings based on ZnO flower-like/SiO_2 NPs organically modified (ORMOSIL) is shown in figure 4. The obtained micrographs reveal that the surface of the cotton fibres was not changed greatly by the subsequent coating process, therefore, the fibre bulk properties remained undamaged. The untreated cotton fabric showed a smooth and clean surface. The electronic images recorded for the treated fabric also show that the surface of the cotton fibers is covered with a relatively large number of ZnO/SiO_2 NPs with different sizes, distributed as an uneven layer of agglomerated particles. Moreover, the SEM images reveal a hierarchical rough structure, which can contribute to the hydrophobic behavior of the cotton substrate.

Whiteness degree of treated samples

The values obtained for the whiteness degree of 100% cotton fabric before and after the functionalization treatment are shown in table 1.

The values obtained for the whiteness degree, both on the Berger and CIE scales, reveal the fact that the hydrophobization/oleophobization combined treatment does not significantly change the appearance of the treated textile material. This indicates the high transparency of the hybrid ZnO/SiO_2 NPs based coating, which is very beneficial for the retention of the original color expression on source colorful fabric.

Table 1

WHITENESS DEGREE OF TREATED SAMPLE		
Sample	**Whiteness degree**	
	Berger	**CIE**
Untreated	65.07	66.8
ZnO/SiO_2 NPs	65.55	66.92

Assessment of water- and oil-repellent properties

The values obtained for wetting capacity, surface wetting resistance and oil repellency are presented in table 2.

The results presented in table 2 show that the application of hybrid coatings provided both water- and oil-repellent properties to the cotton fabric. The textile material treated with hybrid coatings has a low wetting capacity, with high values of water absorption time (> 15 minutes), showing an acceptable hydrophobic effect. Treated samples tested through the superficial wetting test (Spraytest), have shown a hydrophobic effect characterized by the partial wetting of the test specimen, with a rating of 2.5 on the ISO scale and 75 on the AATCC photographic scale, being considered an acceptable water repellent degree, which was obtained under the conditions of the selected experimental protocol. Fabric samples exhibit an oil repellency degree of 6, which defines the 100% cotton fabric textile treated with ZnO/SiO_2 NPs as an efficient substrate for the rejection and protection against oily substances.

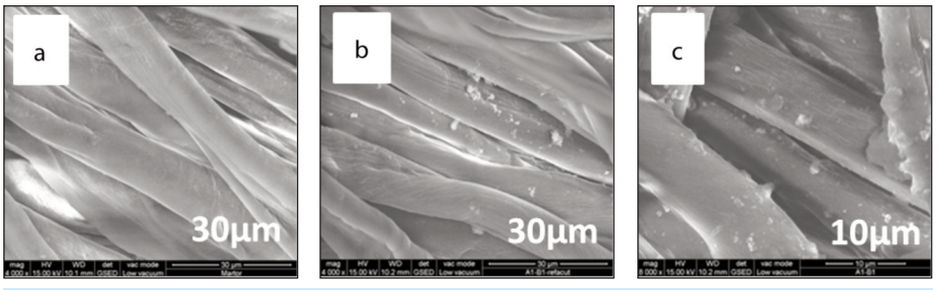


Fig. 4. SEM images of: *a* – the native cotton fibers at low-magnification; *b* – treated cotton fabric with hybrid coatings based on ZnO/SiO_2 NPs at low magnification; *c* – treated cotton fabric with hybrid coatings based on ZnO/SiO_2 NPs at higher magnification

Table 2

WATER AND OIL REPELLENCY			
Characteristic		**Sample**	
		Untreated cotton fabric	Functionalized cotton fabric
Wettability (s)		Immediate	900
Wetting resistance	ISO scale	0	2.5
	AATCC photographic scale	0	75
Oil repellency		0	6*

Note: *Rating is the highest numbered test liquid which did not wet the fabric in 30 seconds; name of the highest numbered test liquid: n-decane – C10 with Rating 6.

CONCLUSIONS

Hybrid materials based on the mixture of ZnO and SiO_2 nanoparticles have been studied as cost effective, ecological coating for textiles hydrophobization. The prepared SiO_2 NPs have quasi spherical shape, while ZnO NPs possess flower-like morphology. The nanoparticles combination, with different dimensions and shapes, allow a suitable roughness to obtain the increase regarding contact angle values, thus, increasing the hydrophobicity at low nanoparticle concentration and low hydrophobic polymer concentration in the coating material. The colloidal systems of both SiO_2 and ZnO NPs are stable, according to the DLS diagrams and facilitate a simple procedure for the textile treatment, without sonication or other methods of dispersion as preliminary steps.

The hydrophobization/oleophobization combined treatment achieved with hybrid coatings based on flower-like ZnO/SiO_2 NPs organically modified (ORMOSIL) does not significantly change the appearance of the treated textile material. The surface of the cotton fibers was not changed significantly by the subsequent coating process, while the fibre bulk properties remained undamaged. The fabric samples exhibited a 75 water-repellent degree and a 6 oil repellency degree.

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