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Bacterial Cellulose Membrane with Functional Properties

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Cellulose Membrane with Functional Properties

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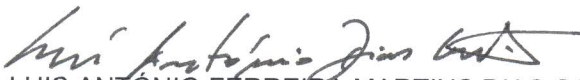
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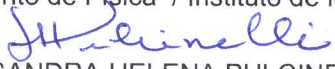
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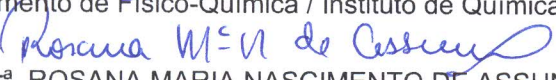
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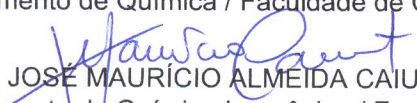
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4.2. National Conferences: 5

4.3. Poster presentation: 11

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4.5. Oral presentation: 2

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- Publications in Journals

1) Pereira, C.; Alves, C.; Monteiro, A.; Magen, C.; Pereira, A.; Ibarra, A.; Ibarra, M.; Tavares, P.; Araujo, J.; Blanco, G.; Pintado, J.; Carvalho, A.; Pires, J.; Pereira, M. F. R. and Freire, C. Design novel hybrid materials by one-pot co-condensation: from hydrophobic mesoporous silica nanoparticles to super-amphiphobic cotton textiles. **ACS Applied Materials & Interfaces**, v. 3, p. 2289-2299, 2011.

2) Ribeiro, L. S.; Pinto, T.; Monteiro, A.; Soares, O. S. G. P.; Pereira, C.; Freire, C. and Pereira, M. F. R. Silica Nanoparticles Functionalized with a Thermochromic dye for Textile Applications. **Journal of Materials Science**, v. 14, p. 5085-5092, 2013.

3) Monteiro, A.; Jarrais, B.; Rocha, I. M.; Pereira, C.; Pereira, M.F.R. and Freire, C. Efficient immobilization of montmorillonite onto cotton textiles through their functionalization with organosilanes. **Applied Clay Science**, v. 101, p. 304-314, 2014.

4) Pinto, T.; Costa, P.; Sousa, M. C.; Sousa, C. A. D.; Monteiro, A.; Pereira, C.; Soares, O. S. G. P.; Silva, C. S. M.; Pereira, M. F. R.; Coelho, P. J. and Freire, C. Naphthopyran-

based silica nanoparticles as new high performance photo responsive materials, **ACS Applied Materials & Interfaces**, v. 8, p. 7221-7231, 2016.

5) Monteiro, A. S.; Domeneguetti, R. R.; Man, M. W. C.; Barud, H. S.; Teixeira-Neto, E. and Ribeiro, S. J. L. Bacterial Cellulose-SiO₂@TiO₂ Organic-Inorganic Hybrid Membrane with Self-Cleaning Properties. **Journal of Sol-Gel Science and Technology**, V.1, p. 2-11, 2019.

- Patents

Silva, C.; Monteiro, A.; Tavares, D.; Vieira, R.; Silva, F. Self-Cleaning Composite Material, respective Method of Obtention and Uses Thereof. **EP 3009558 A2**. Centro de Nanotecnologia e Materiais, Funcionais e Inteligentes (CeNTI), 2016-04-20.

6. Awards

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“Have the courage to follow your heart and intuition. They somehow know what you truly want to become.”

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ABSTRACT

This work reports the development of economic and environmentally friendly Bacterial Cellulose Membrane (BCM) with functional properties.

The spherical mesoporous silica nanoparticles with average particle size around 51 ± 4 nm, obtained by sol-gel method and spherical silica nanoparticles with heterogeneous particles size distribution (20-40 nm) obtained through agro-industrial waste were prepared and functionalized by in situ and post-grafting methodology, respectively, with alkoxysilanes with easy-cleaning properties and natural dye obtained through natural extracts, namely curcuma. Anatase $\text{TiO}_2@ \text{SiO}_2$ spherical nanocomposites prepared by the sol-gel method, have also been developed. Subsequently, these functional nanomaterials and the organosilanes 1,4 – bis(triethoxysilyl)benzene (BTEB), Bis(triethoxysilylpropyl)disulfide (BTPD) and 1,2-Bis(triethoxysilyl)ethane (BTSE), were successfully incorporated into BCM, by in situ and post-grafting methodologies.

In the BCM functionalized with BTEB, BTPD and BTSE, spherical silica nanoparticles with porous structure and heterogeneous particle size, were formed on the cellulose fibers. The surface repellency of the functionalized BCM with silica nanoparticles containing easy-cleaning properties was remarkably enhanced. This BCM displaying phobicity to water, toluene, cyclohexane and artificial sweat. Specifically, the BCM functionalized by in situ and post-grafting with $\text{SiO}_2@ \text{F}_{13}\text{TES}$, displayed a surface almost superhydrophobic ($> 150^\circ$). Methyl violet 2B dye decomposition measurements showed that the BCMW- $\text{SiO}_2@ \text{TiO}_2$ (BCM functionalized in wet state) presented a good self-cleaning performance showing fast Methyl violet 2B dye decomposition in 30 minutes. BCM with yellow-orange coloration from curcuma with good resistance to washing and high chemical stability have been developed.

This versatile biomaterial emerge as a promising substrate with high added value being able possibly allow their application in several areas.

Keywords: Functional bacterial cellulose membrane; organic-inorganic hybrids; silica nanoparticles; $\text{SiO}_2@ \text{TiO}_2$ (Anatase) nanocomposites; sol-gel method; reuse of agro-industrial waste; easy-cleaning properties; photocatalytic activity; self-cleaning properties; natural-based color properties.

Resumo

Este trabalho descreve o desenvolvimento de membranas de celulose bacterianas (BCM), econômicas e ecologicamente amigáveis com propriedades funcionais.

Nanopartículas de sílica esféricas com tamanho de partícula de cerca de 51 ± 4 nm, obtidas pelo método sol-gel e nanopartículas de sílica com tamanho de partículas heterogêneo, extraídas da casca de arroz, foram preparadas e funcionalizadas pelas metodologias *in situ* e *post-grafting*, respectivamente, com alcóxissilanos com propriedades easy-cleaning e curcuma. Nanocompósito de anatase $\text{SiO}_2@\text{TiO}_2$ preparado pelo método sol-gel, também foi desenvolvido.

Posteriormente, estes nanomateriais funcionais e os organosilanos 1,4 – bis(trietoxissilil)benzeno (BTEB), Bis(trietoxissililpropil)disulfeto (BTPD) and 1,2-Bis(trietoxissilil)etano (BTSE), foram imobilizados com sucesso na BCM, segundo as metodologias *in situ* e *post-grafting*.

Na BCM funcionalizada com os organosilanos BTEB, BTPD e BTSE, nanopartículas de sílica esféricas com estrutura porosa e distribuição de tamanho de partícula heterogêneo, foram formados nas fibras de celulose. A repelência da BCM funcionalizado com nanopartículas de sílica contendo propriedades de limpeza facilmente melhorada notavelmente. BCM apresenta fobicidade à água, tolueno, cicloexano e solução de suor artificial. Especificamente, a BCM funcionalizada com a amostra $\text{SiO}_2@\text{F}_{13}\text{TES}$ segundo as metodologias *in situ* e *post-grafting*, apresentam uma superfície quase superhidrofóbica ($> 150^\circ$). As medições de decomposição do corante metil violeta 2B, mostraram que a amostra BCMW- $\text{SiO}_2@\text{TiO}_2$ (BCM funcionalizada no estado molhada) apresentou um bom desempenho de auto-limpeza (decomposição do corante metil violeta 2B em 30 minutos). BCM com coloração amarelo alaranjado, proveniente da curcuma, com boa estabilidade química também foi desenvolvida.

Esse versátil biomaterial surge como um substrato promissor, com alto valor agregado, podendo ser aplicado em diversas áreas.

Palavras-Chave: Membrana de celulose bacteriana funcional; híbridos orgânicos-inorgânicos; Nanopartículas de sílica; Nanocompósito $\text{SiO}_2@\text{TiO}_2$ (anatase); método sol-gel; reutilização de resíduos agro-industriais; propriedades de fácil limpeza; atividade fotocatalítica; propriedades de auto-limpeza; propriedades de coloração natural.

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NOTATION AND GLOSSARY

List of abbreviations

AFM	- Atomic Force Microscopy
BCM	- Bacterial Cellulose Membrane
BTPD	- Bis(triethoxysilylpropyl)disulfide
BET	- Brunauer-Emmett-Teller
BTEB	- 1,4 – bis(triethoxysilyl)benzene
BTSENE	- 1,2-Bis(triethoxysilyl)ethylene
BTSE	- 1,2-Bis(triethoxysilyl)ethane
BCMW	- Bacterial Cellulose Membrane Wet
BCMD	- Bacterial Cellulose Membrane Dry
CA	- Contact angle
CTAC	- Aqueous hexadecyltrimethylammonium chloride solution solution
C ₈ TMS	- Octyltrimethoxysilane
C ₁₆ TMS	- Hexadecyltrimethoxysilane
Cur	- Curcuma
CPMAS	- Cross-polarization magic angle spinning
DLS	- Dynamic Light Scattering
F ₁₃ TES	- Tridecafluorooctyltriethoxysilane
FTIR-ATR	- Attenuated Total Reflectance Fourier Transform Infrared
MNs	- Mesoporous silica nanoparticles
MV	- Methyl Violet 2B
NLDFT	- Non-local density functional theory
PDI	- Polydispersion indexes by DLS
PG	- Post-grafting
RMN	- Solid-State Nuclear Magnetic Resonance
SNs	- Silica nanoparticles
SEM	- Scanning Electron Microscopy
STEM	- Scanning Transmission Electron Microscopy
TEA	- Triethanolamine
TGA	- Thermogravimetric Analysis
TEOS	- Tetraethylorthosilicate
THF	- Tetrahydrofuran

TEM - Transmission Electron Microscopy

Wt - Weight

XRD - X-ray Diffraction

XPS - X-ray photoelectron spectroscopy

XRFA - X-ray fluorescence

List of variables

A_{BET} - Specific surface areas

CrI – Relative degree of crystallinity

d_{DLS} - Average hydrodynamic diameters by DLS

d_{SEM} – Average particle size by SEM

d_{TEM} – Average particle size by TEM

d_{pore} - Pore size

I_{002} – Maximum intensity of the (002) plane diffraction

I_{am} – Intensity of the amorphous halo

V_{meso} - Porous volumes

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Preface

Framework and presentation of the project

Over the last decades, the design of high performance functional substrates with enhanced properties has been the subject of intense research, offering promising improvements in a plethora of scientific and technological areas.

Development of value added, functional, cost-effective and innovative products is one of the key strategies to increase the competitiveness of industrial sectors dealing with cellulose. The development of Bacterial Cellulose Membranes (BCM) with functional and innovative properties, to enhance its properties and performance, has been one growing field of interest in recent years. Our research group have accumulated experience in the preparation of functional BCM and in the development of nanomaterials with functional/engineered properties.

The development of this project aims to overcome the limitations and environmental problems, namely the color fastness, the contamination of the effluents, significant reduction of cleaning actions and reduction demand of the agro-industrial waste, extracting silica nanoparticles of these (high value-added material), thus transforming an environmental impact into a circular economy, developing economic and environmentally friendly BCM with natural colored based and cleaning surface.

The collaboration with Doctor Michel Wong Chi Man and his research group in the laboratory of Molecular Architectures and Nanostructured Materials (AM2N) at the Institut Charles Gerhardt Montpellier (ICGM) at the Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM), during the research internship abroad, BEPE (November 2017 to November 2018), was fundamental and had a high added value in this project given good expertise in synthesis and functionalization of hybrid silica-based functional nanomaterials and silsesquioxanes.

The results obtained in this project will open new avenues for the design of smart and innovative cellulose membrane.

Objective

The main purpose of this thesis consists in the production of economic and environmentally high performance BCM with functional properties. In this context, the PhD research activity can be summarized in the following objectives:

- a) Preparation and characterization of silica nanoparticles from rice husk;
-

- b) Preparation, characterization and evaluation of silica nanoparticles (obtained from sol-gel method and rice husk) with easy-cleaning properties;
- c) Preparation and characterization of silica nanoparticles, from rice husk, with natural colored properties;
- d) Preparation and characterization of anatase $\text{SiO}_2@\text{TiO}_2$ nanocomposites;
- e) Preparation, characterization and evaluation of functional BCM with easy-cleaning, self-cleaning and natural colored properties, obtained through the immobilization by in situ and post-grafting, of the functional organic-inorganic hybrid materials;
- f) Preparation and characterization of BCM functionalized with organic silicon source 1,4 – bis(triethoxysilyl)benzene (BTEB), Bis(triethoxysilylpropyl)disulfide (BTPD) and 1,2-Bis(triethoxysilyl)ethane (BTSE).

Organization of the thesis

This thesis is divided into **10 chapters**.

The **chapter 1** is devoted to introduce bacterial cellulose membrane, their preparation, properties and applications; silica sources (silica produced from living organisms – biogenic silica or synthesized from sol-gel method; and the functional properties developed in this work (easy-cleaning, self-cleaning and natural-based colored properties).

The procedures, materials and reagents used for the preparation of the functional nanomaterials and functional BCM, as well as the instrumentation and procedures used in the characterization and evaluation of the functional materials obtained are described in the **chapter 2**.

In the **chapter 3** and **chapter 4** are presented the results and respective discussion of characterization of the silica nanoparticles with easy cleaning properties, prepared and functionalized by sol-gel method, as well as of the silica nanoparticles obtained from rice husk with easy-cleaning and natural-based colored properties. The evaluation of functional properties is also presented.

The results and respective discussion of characterization of the anatase $\text{SiO}_2@\text{TiO}_2$ nanocomposites are presented in the **chapter 5**.

From **chapter 6** to **chapter 8** are presented the results and respective discussion of characterization of the BCM functionalized with the prepared functional materials and whose characterization has been presented from **chapter 3** to **chapter 5**. The evaluation of functional properties before and after wash fastness tests is also presented.

In the **chapter 9** the results and respective discussion, by means of the characterization techniques used of the BCM functionalized with 1,4 – bis(triethoxysilyl)benzene (BTEB), Bis(triethoxysilylpropyl)disulfide (BTPD) and 1,2-Bis(triethoxysilyl)ethane (BTSE) are presented.

The final considerations of the work developed, as well as the future outlook, are presented in **chapter 10**.

Lastly, the photographs of the functional BCM samples and FTIR-ATR of BCM functionalized by post-grafting with silica nanoparticles obtained by sol-gel method, are presented in **annex 1** and **annex 2**, respectively.

CHAPTER 1

Introduction

1. Introduction

1.1. Bacterial cellulose membrane

Cellulose ($C_6H_{10}O_5$) is a naturally occurring homopolysaccharide formed by a linear chain of monosaccharide β -D-glucose linked by $\beta(1\rightarrow4)$ bond. The repeating unit is cellobiose formed by the union of two glucose molecules (**Figure 1**) [1-3].

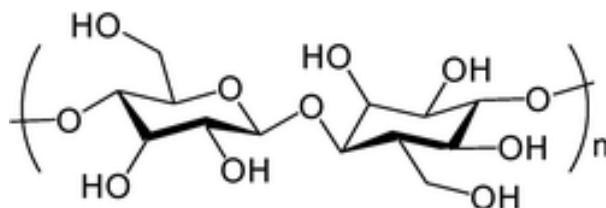


Figure 1 - Chemical structure of cellulose [2].

This biomaterial is obtained through the biosynthesis induced by a few strains of bacteria, including the *Gluconacetobacter xylinus* (formerly named *Acetobacter xylinus*). This microorganism is a gram-negative bacteria, non-pathogenic and non-photosynthetic, capable to convert glucose, glycerol and others organic substrates into cellulose within a few days [1, 2].

The biochemical process of cellulose synthesis by this microorganism consists of three main steps: (i) polymerization of glucose residues in β -1-4 glucan, (ii) extracellular secretion of linear chains, and (iii) organization and crystallization of glucan chains through hydrogen bonds and van der Waals forces [3]. The anhydroglucose units and various BC fibrils interact closely with each other to form a crystalline structure through internal and external hydrogen bonds, resulting in the compaction of fibers. After BCM synthesis, the membrane is further processed to remove bacterial cells, organic acids, salts as well as residual sugars and other components of the culture medium, which could be integrated within the cellulose network (**Figure 2**).

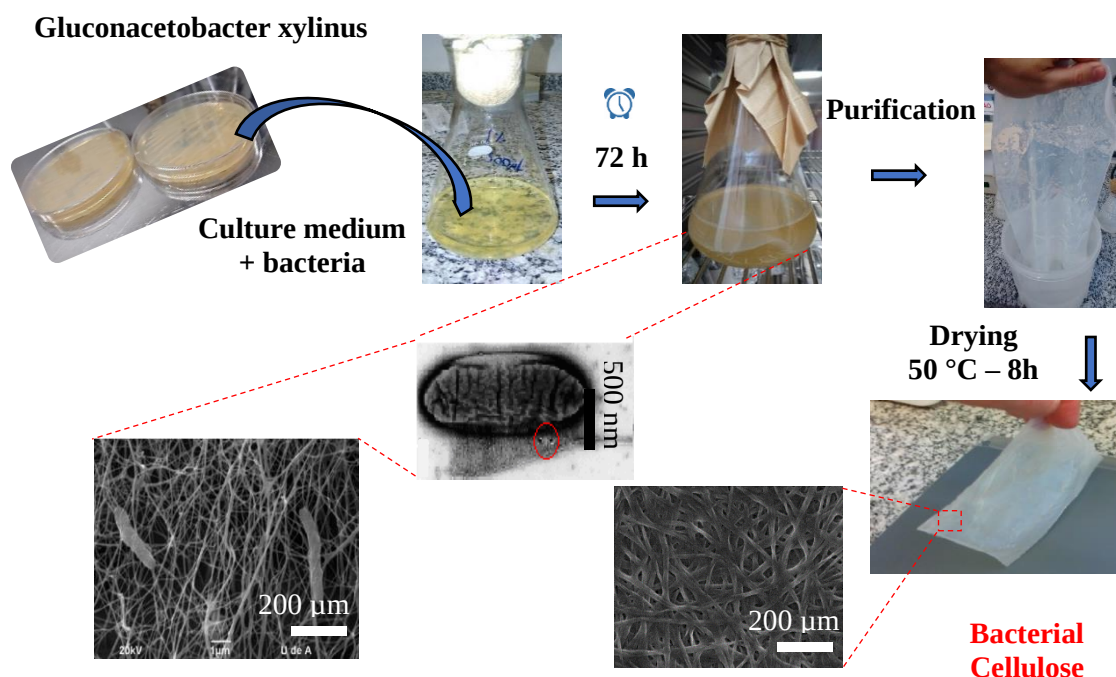


Figure 2 – Representative scheme of preparation of Bacterial Cellulose [own authorship].

Unlike plant cellulose, Bacterial Cellulose Membrane (BCM) is produced in the pure form, devoid of lignin, hemicellulose, pectin, or any other compound present in the plant pulp and does not contain components of animal origin. In addition, it has superior mechanical properties compared with plant cellulose (crystallinity – plant cellulose (56% - 65%) vs bacterial cellulose (65 – 79%) and young's modulus - plant cellulose (5.5 – 12.6 GPa) vs bacterial cellulose (15.0 – 30.0 GPa) [1-4].

The thin nanofibers of 20–100 nm diameter, with a large surface area per unit, combined with the hydrophilic nature of BC (hydroxyl groups), results in high water absorption capacity, better adherence, and increased moisture content. These properties, combined with the distinct physical and mechanical properties of the molecule, including its insolubility, rapid biodegradability, tensile strength, elasticity, durability, nontoxic and non-allergenic features, make BCM ideal for a variety of important applications in different fields including in the cosmetics area, as a stabilizer of emulsions, in the Medicine, as temporary artificial skin for therapy of burns and ulcers, among others areas [4, 5]. Indeed, with the presence of a large number of hydroxyl groups within their structure, these building blocks represent a unique platform for significant surface modification to graft a myriad of functional molecules using various chemistries, with

functional properties, namely, easy-cleaning and self-cleaning, make BCM ideal for the design of several functional products with high added value [5].

There are two main strategies to implant these modifications, in situ and post-grafting. In situ modification is to modify BCM during bacterial cell culture by varying the culture conditions, adding additional materials. In contrast, post-grafting modification of BCM is carried out after the BCM has been formed (**Figure 3**) [5].



Figure 3 –Schematic representation of preparation of BCM modifications methods: (A) in situ and (B) post-grafting [5].

1.2. Silica

1.2.1. Properties and applications

Silica, SiO_2 , is the most abundant chemical compound in the earth's crust (~ 60 wt%) [6]. The structural unit of silica is tetrahedron (SiO_4), in which each silicon atom, in central position, is coordinated by four oxygen atoms, joined by siloxane (Si-O-Si)

bridges. This arrangement allows the formation of a three-dimensional crystal lattice through the sharing of tetrahedral oxygen with neighboring groups. Silica contains silanol groups (Si-OH), (4-5 OH/nm² groups), giving it surface reactivity and sites of immobilization or efficient interaction/functionalization with various chemical species [6-8]. Si-OH groups can be classified into three types depending on how they are arranged: isolated silanols (where there is only one OH group attached to a silicon atom); vicinal (where there are two OH groups attached to two atoms) and geminal (in which two OH groups are attached to the same silicon atom), as shown in **Figure 4** [6-8].

Silica is a versatile material with a wide spectrum of applications for industry, improving the performance of the developed technologies and the products obtained due to its excellent properties such as thermal and mechanical stability, chemically inert, optical transparency and surface chemistry [6, 7].

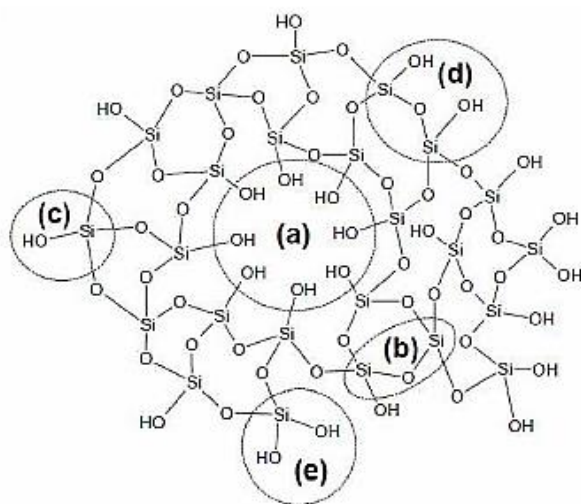


Figure 4 – Silica structure. (a) silica pore; (b) siloxane group; (c) isolated silanol group; (d) vicinal silanol group and (e) geminal silanol group [6].

1.2.2. Silica Source

Silica can be of natural or synthetic origin. They can be classified as natural crystalline silicas (ex: quartz), synthetic crystalline silicas (ex: Keatite), natural amorphous silicas (ex: biogenic silica and vitreous silica) and synthetic amorphous silicas (ex: fused silica, pyrogenic, precipitated, colloidal or gel) [9].

i. Synthetic amorphous silica – sol-gel method

Silica is synthesized through the sol-gel technological process. This process involves the synthesis of an inorganic polymer network at low temperatures, the gel being formed from a colloidal suspension or by hydrolysis and condensation of a precursor in solution [9-11]. The most commonly used precursors in the sol-gel method are metal or semi-metallic alkoxides, as they are easily hydrolyzable, soluble in organic media and easily purified [12]. The most widely used is tetraethylorthosilicate (TEOS), which being immiscible in water, requires the addition of an alcohol capable of homogenizing the solution [13].

This method involves hydrolysis and subsequent condensation of the precursor. In hydrolysis reactions, the alkoxide (OR) group of the precursor is replaced by the silanol group (Si-OH), forming in parallel an alcohol, due to the nucleophilic attack of the oxygen atom of the water hydroxyl group (**Figure 5A**). Condensation reactions form dimers, linear trimers, cyclic and polymeric species with siloxane bonds (Si-O-Si). These reactions may occur in aqueous medium when the network is formed with simultaneous production of water, or medium alcohol when an alcohol is produced (**Figure 5B and 5C**). Hydrolysis and condensation reactions only occur in the presence of an acid or base catalyst as they are very slow and incomplete [10, 11].

The morphology and textural properties of the materials obtained are strongly influenced by several reaction parameters such as pH, temperature, reaction time, agitation, reagent concentration, nature and concentration of catalysts and type of solvent [10, 11].

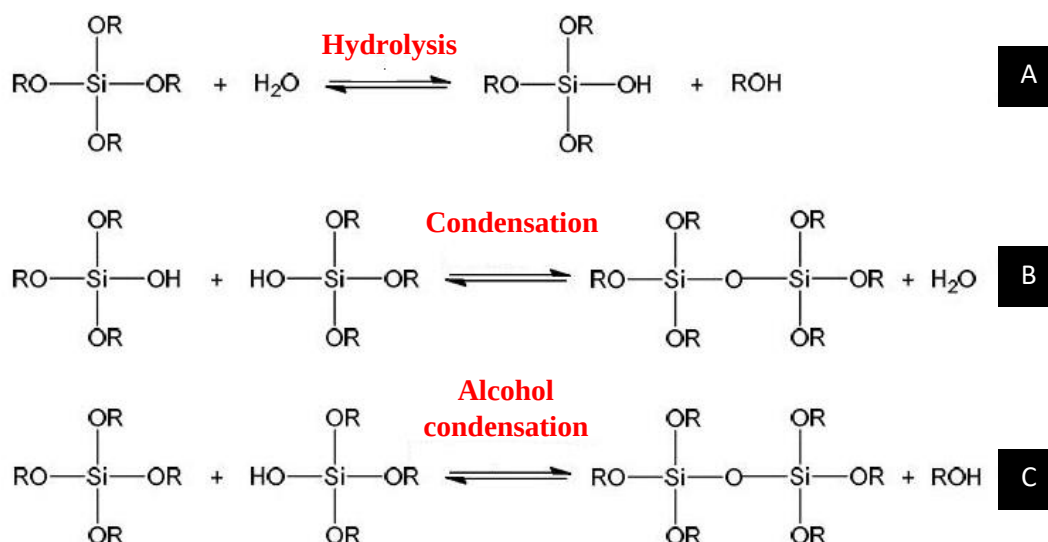


Figure 5 - Hydrolysis and condensation reactions that occur during the sol-gel method [13].

The sol-gel process presents as main advantages: the high purity and homogeneity of the inorganic materials and/or hybrid produced; the relatively low reaction temperature and the possibility of controlling the size and morphology of the particles as well as influencing the characteristics of the material through the experimental parameters such as reagent concentration, pH, temperature and reaction time [9, 14]. However, it also has some disadvantages leading to an environmental impact, namely: the toxicity and non-biodegradable reagents; use of catalysts; energy costs and high costs of reagents used during the process. The synthesis of TEOS is expensive and generates undesirable products such as hydrogen chloride gas [15] World production of TEOS is estimated to range from 23 thousand tons to 32 thousand tons a year [16].

Nowadays, other more economical and ecological possibilities emerge that include extracting silica from agro-industrial waste.

ii. Natural amorphous silica – biogenic silica

Biogenic silica is all the silica that is produced from living organisms such as plants and animals [17].

In general, the biosilification process occurs through the absorption and accumulation of the silicic acid monomer in the polymerization of monomeric units until formation of stable nuclei and spherical particles for formation of branched chains [18].

The bioaccumulation of silica by plants aims at increasing resistance against pathogenic fungi and improving the photosynthetic rate [19]. In all plants, silica is absorbed through the roots as orthosilicic acid Si(OH)_4 . Due to its immunological and structural reinforcement character, silica is bioaccumulated mainly in the stems and leaves [19, 20].

1.2.3. Agro-industrial waste

The agro-industrial sector generates large amounts of solid waste resulting from processing, treatment of raw materials and disposal of its by-products. Handling and improper disposal in places such as soil, water and air can lead to pollution. This pollution causes problems that potentiate impacts on the environment and human health, because its high abundance, caused by excessive production, raises questions related to the accumulation of waste and consequent disposal in landfills.

Many of these agro-industrial wastes, considered without any commercial value, have silica in their composition. **Table 1** shows some abundant and biodegradable wastes as potential source of silica.

Table 1 - chemical composition of some agro-industrial wastes as a potential source of silica.

Waste		Ashes% (wt/wt)	SiO ₂ % (wt/wt)	Ref.
Rice	Peel	15,0-28,0	95,0-98,0	[21]
Peanut	Peel	3,1	27,7	[21]
	Straw	8,3		[22]
Coconut	Peel	3,1	69,3	[21]
Coffee		0,9-4,1	13,5-16,6	[21]
Wood		0,5	12,8	[23]
Bean	Straw	4,30	-	[23]
	Stem	4,61	-	[22]
	Pod	6,65	-	
Corn	Stem	3,43	-	[23]
	Leaf	3,53	-	
	Straw	1,58	-	
Olive	Pit	1,7	30,8	[24]
Sugar cane	Stem	3,23	-	[23]
	Leaf	3,45	-	[23]
Hazelnut	Peel	1,4	27,3	[24]
Nut	Peel	2,8	9,9	[24]
Wheat	Peel	9,9	43,2	[25]
Lupine bean	Peel	2-3	-	[25]

From the analysis of **Table 1**, it is possible to verify that the percentage of silica is higher in the rice husk ashes, therefore, this residue shows to be a great potential as an unlimited source of silica. The main constituents of the rice husk are cellulose, hemicellulose lignin (72-85% (wt/wt)) and silica (15-28% (wt/wt)). Generally, about 25% (wt/wt) of the rice husk is converted to ash whose composition is metal oxides (SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, K₂O), wherein about 85-90% (wt/wt) is SiO₂ amorphous [26].

The FAO (Food and Agriculture Organization) forecast for world rice production in 2018 was 772.5 million tons (1.3% higher than 2017), with 90% produced and consumed in Asian countries [25]. In Brazil, the estimated production for the same year was 12.1 million tons, which can generate about 435.0 thousand tons of silica, considering that the husks make up 22% of the rice and that they have an average content of 18% of silica [25].

1.2.4. Reuse of silica from agro-industrial waste

Different approaches have been developed for the extraction of silica from agroindustrial wastes. In order to obtain silica with a high degree of purity, a purification and heat treatment it is necessary.

The heat treatment conditions are defined by thermogravimetric analysis of the waste. Specifically, rice husk has an organic decomposition temperature of 700 ° C (see **chapter 4 – section 4.1.2**).

Many authors have shown that rice husk purification treatment with HCl, HNO₃, H₂SO₄, NaOH and NH₄OH solutions, followed by heat treatment, has proven to be an effective way to remove impurities and metal oxides, producing completely white silica ash with a high purity (90-95% silica) [27-29]. Other forms include the direct extraction of silica in basic medium. Generally, the authors use a NaOH solution to obtain a silicate solution (precursor), followed by the addition of an acid (H₂SO₄) to precipitate the silica. [30].

In order to develop a more ecological and economical method and more effective in removing impurities and metal oxides, this work reports the development of a hydrothermal process to obtain silica from rice husk. Hydrothermal treatment will allows the expansion of the rice husk cellulosic fibers and solubilizes part of the lignin, contributing to the fast and effective access of the acid in the impurities [30].

1.2.5. Mesoporous silica nanoparticles

Mesoporous (pore diameter between 2 nm and 50 nm - classification according IUPAC (International Union of Pure and Applied Chemistry)) [26] silica nanoparticles are a class of versatile nanomaterials with tremendous potential for a broad spectra of applications, including catalysis [31], controlled drug delivery [32] and surface coatings [33]. Their high specific surface areas, ordered structure, and tunable pore sizes are some of their remarkable features. The ability to incorporate specific organic functional groups onto their surface through covalent bonding is another key parameter to engineer their properties in route to the target applications [31].

Bein *et al.*, developed a one-pot strategy for the synthesis of mesoporous silica nanoparticles with small size (40-60 nm), narrow particle size distributions, very high specific surface areas, and high colloidal stability. Their method is based on the use of a polyalcohol, triethanolamine (TEA) , which acts as a base, as a complexing agent for silicate precursors and as an encapsulator for mesoporous particles, thus regulating the

alkoxides hydrolysis/condensation rates and limiting the particles growth and aggregation [33].

1.3. Functional properties

Since the birth of nanotechnology, new challenges emerged in various areas of research toward the design of hybrid materials and technological processes [33]. The design of high performance functional materials with enhanced properties, has been the subject of intense research, offering promising improvements in a plethora of scientific and technological areas.

The silica nanoparticles is promising nanomaterial for the development of functional substrates with a view on a variety of technological applications owing to their remarkable properties, namely, adsorption capacity, optical transparency, high thermal, mechanical stability and tunable surface chemistry [33, 34].

1.3.1. Functionalization of silica nanoparticles

The surface functionalization of silicates can change the chemical and physical properties of these materials dramatically. There are two major ways to functionalize the surface of silica nanoparticles: co-condensation and post-grafting (**Figure 6**).

Post-grafting is a method to modify an as-synthesized inorganic material surface by anchorage of functional groups to the surface of material. In the process of grafting silica nanoparticles, the surface silanol groups (Si-OH), which can be present in high concentration, act as convenient anchoring points for organic functionalization [33-35]. Surface functionalization with organic groups by grafting is most commonly carried out by silylation. The original structure of the porous support is generally maintained after grafting. In this method, the external surface is more accessible and is functionalized predominantly over the internal pore surface. The functional groups on the external surface are also more accessible in subsequent reactions, leading to reduced selectivities in processes that benefit from pore confinement [32-37].

Co-condensation method is another strategy to functionalize silica nanoparticles surface by sol-gel chemistry between tetraalkoxysilane and one or more organoalkoxysilanes with Si-C bonds. The co-condensation offers several advantages because it is an one-pot methodology, provides a more homogeneous distribution of the organic moieties throughout the material and controls the silica nanoparticles morphology. [31, 32, 35, 36].

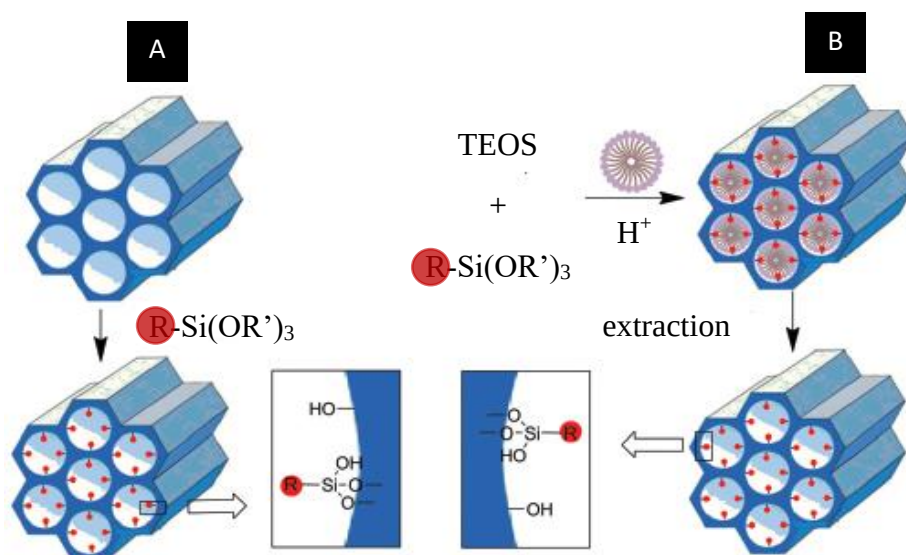


Figure 6 – Schematic illustration of the modification of MSNs by (A) post-grafting and (B) co-condensation methodology [35 and own authorship].

1.3.2. Easy-cleaning properties

One of the most fascinating property in nature is easy-cleaning properties, existing on the lotus leaf and butterfly wings, for example. This property is also known as lotus effect. The surface of these materials are always kept clean because they repel contaminants deposited therein. This action is possible due to the existence in the structure of lotus leaf of micro and nanoscale roughness and superhydrophobic epicuticular waxes with low surface energy (static contact angle $> 150^\circ$ and dynamic contact angle of 0°) (**Figure 7**) [37, 38].

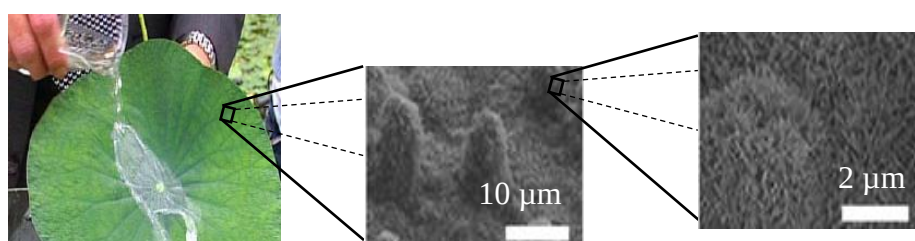


Figure 7 – Lotus leaf structure with easy-cleaning properties [37 and own authorship].

The requirements for the production of surfaces with easy-cleaning properties, it is the result of the synergy between two factors: an increase of the nanoscale surface roughness imparted for example by the silica nanoparticles combined with compounds with low surface free energy [33].

In this way, in the present work, to promote easy-cleaning properties, silica nanoparticles were functionalized by in situ and by post-grafting, with organosilanes with different surface energy and consequently with different degrees of easy of cleaning, to obtaining BCM with different degrees of repellency, for different applications. The organosilanes used were as follows: octyltrimethoxysilane (C_8TMS), hexadecyltrimethoxysilane ($C_{16}TMS$) and with fluoroalkoxysilane, the tridecafluorooctyltriethoxysilane ($F_{13}TES$) (see the structure of these organosilanes in **Table 2, chapter 2, section 2**).

BCM with easy-cleaning properties can be used as artificial temporary skin for wounds and burns, for example. BCM with this property, able to repel sweat, will provide greater cleaning and wound healing.

The easy-cleaning property is evaluated by measuring the contact angle (CA) between the drop of the test liquid and the substrate surface. If the CA is less than 90° , the surface is hydro/oleophilic (**Figure 8A**); between 90° and 150° , the surface is hydro/oleophobic (**Figure 8B**), equal or superior than 150° , the surface is superhydro/oleophobic (**Figure 8C**) [37, 38].

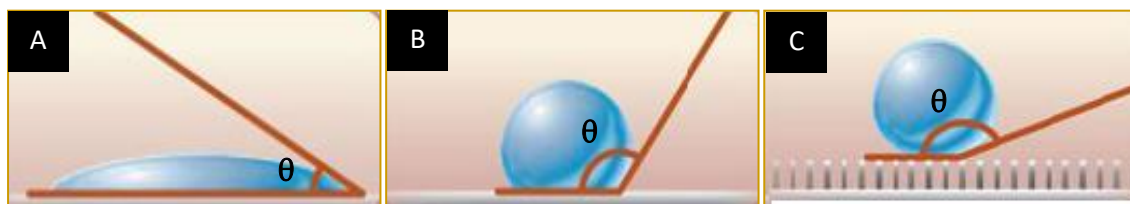


Figure 8 – Schematic representation of a surface (A) hydro/oleophilic ($0^\circ < \theta < 90^\circ$), (B) hydro/oleophobic ($90^\circ < \theta < 150^\circ$) e (C) superhydro/oleophobic ($\theta > 150^\circ$) [37].

1.3.3. Self-cleaning properties

Substrates with self-cleaning technology have the capacity to degrade dirt, odour and microorganisms through a photocatalytic process (**Figure 9**), allowing a reduction of cleaning actions and increase of the durability of the substrates [39].

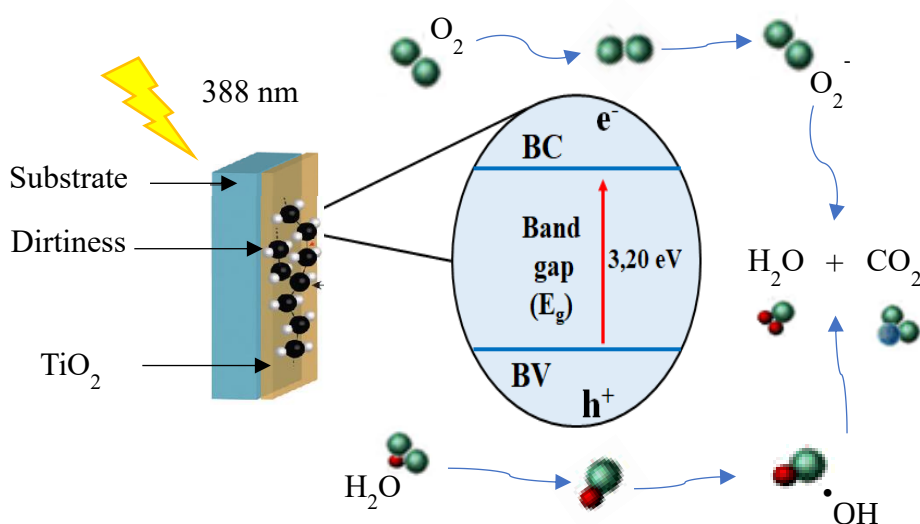


Figure 9 – Representative scheme of the photocatalytic process [own authorship].

The titanium dioxide (TiO₂) is the most used among the photocatalysts based on benefits-cost ratio, as well as due to its suitable electronic and optical properties and good chemical stability [40].

The Anatase TiO₂ has the highest photoactivity among different crystal phases of TiO₂, rutile and brookite (**Figure 10**) [41, 42]. The rutile phase is thermodynamically stable, but the metastable anatase phase that is generally formed at low temperature, for example, by sol-gel processing [43], transforms to rutile by heating or even by mechanical grinding [44]. The anatase-to-rutile phase transformation (from a metastable phase to a stable one), is markedly influenced by the nature and the amount of cation impurities [44, 45] and anion impurities [46] present in the system, grain size [44], and preparation conditions such as reaction atmosphere. To resolve most of these problems, TiO₂ can be coated on the surface of thermally stable, low cost and high surface area core materials [46, 47]. SiO₂ is one of the best core materials for preparing the core@shell nanoparticles. SiO₂-TiO₂ heterogeneous system often exhibits better photocatalytic activity than TiO₂

alone [48] due to the improved stability of silica-supported anatase and presence of oxygen vacancies in the supported titania as well as due to the improved adsorption of the reactants near the active centers [49].

In the present work, the BCM with self-cleaning properties was developed by the immobilization of the $\text{SiO}_2/\text{TiO}_2$ nanocomposite in BCM.

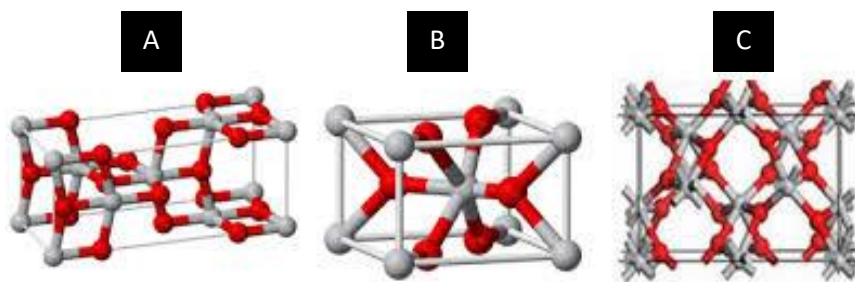


Figure 10 - Crystalline structures of titanium dioxide. A: Anatase, B: rutile and C: brookite [50].

1.3.4. Natural-based colored properties

Economic and environmentally friendly BCM with natural colored was another property developed. This functional BCM, with a view to being applied, for example, in the textile industry, as artificial textiles and highly absorbent materials, or in paper industry [51], overcome the limitations and environmental problems, namely the color fastness and the contamination of the effluents.

Currently it becomes imperative forward the industry for alternatives of dyeing more sustainable. In this context, this project intend to overcome these challenges, by the development of colored BCM of natural base, with high value added, through an innovative process, more economical and environmentally sustainable. These gains will be achieved by replacing synthetic dyes by natural dyes, that will be covalently bonded to the BCM through silica nanoparticles, obtained from agro-industrial waste.

Silica nanoparticles acts as linker between dye and the BCM structure, and allow to obtain better color parameters, such as uniformity, intensity and solidity [52, 53].

The natural dye used in this project was the curcuma. Curcuma (**Figure 11A**) is a yellow-orange, aromatic substance extracted from the plant named *Crocus Sativa*. The

coloring matter exists in the plant stamens. The yellow-orange color is due to crocin, which is a glycosated carotenoid, whose aglycone is crocetin (**Figure 11B and 11C**) [54, 55]. This dye is one of the most powerful chemopreventive and anticancer agents. Its biological effects range from antioxidant, anti-inflammatory to inhibition of angiogenesis and is also shown to possess specific antitumoral activity [41]. These properties will add value in the BCM, extending therefore their use to a wide range of highly sophisticated applications.

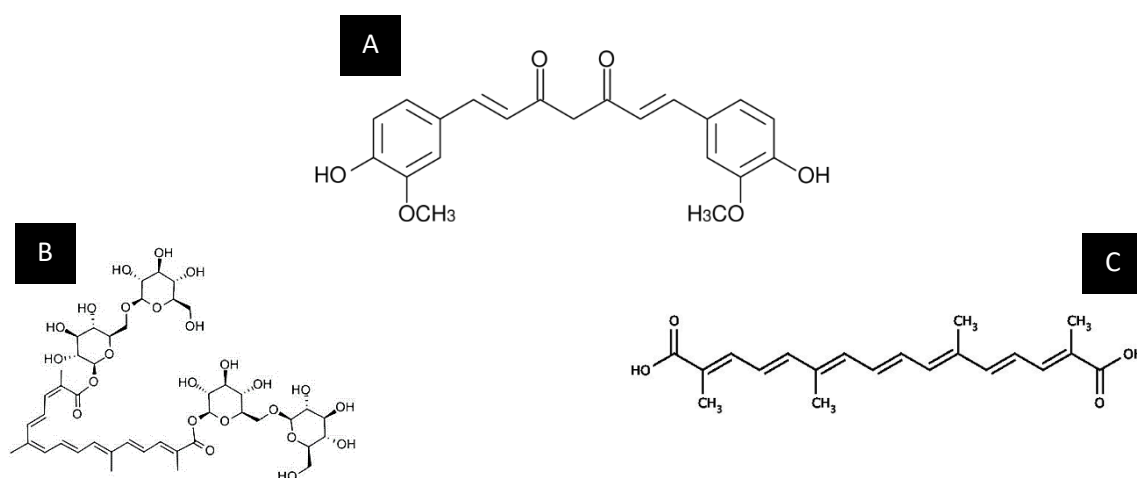


Figure 11 - Chemical structure of (A) curcuma (B) crocin and (C) crocetin.

CHAPTER 2

Experimental

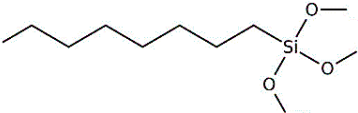
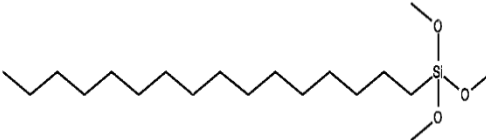
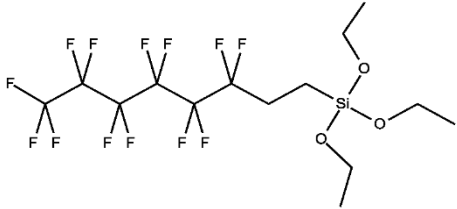
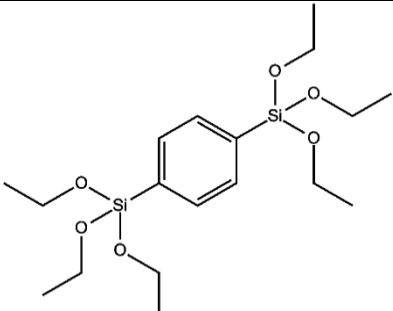
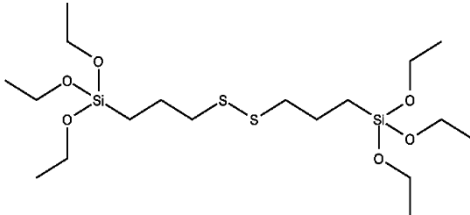
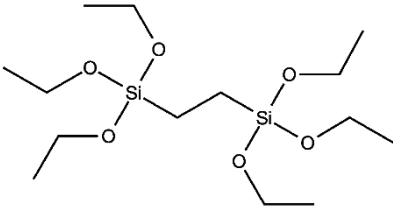
2. Experimental

The procedures, materials and reagents used for the preparation of functional nanomaterials and functional BCM and the instrumentation and procedures used in the characterization and evaluation of the materials obtained is described below.

To promote easy-cleaning properties, silica nanoparticles were functionalized with alkoxysilanes with long alkyl chain, namely, Octyltrimethoxysilane (C_8TMS), Hexadecyltrimethoxysilane ($C_{16}TMS$) and with fluoroalkoxysilane, the Tridecafluorooctyltriethoxysilane ($F_{13}TES$).

BCM was functionalized with three different organosilanes, 1,4 – bis(triethoxysilyl)benzene (BTEB), Bis(triethoxysilylpropyl)disulfide (BTPD) and 1,2-Bis(triethoxysilyl)ethane (BTSE). All organosilanes were purchased, with the exception of BTEB, which was synthesized (**section 2.2**). The **Table 2**, summarizes the organosilanes used with the respective structure.

Table 2 – Organosilanes used in the functionalization.

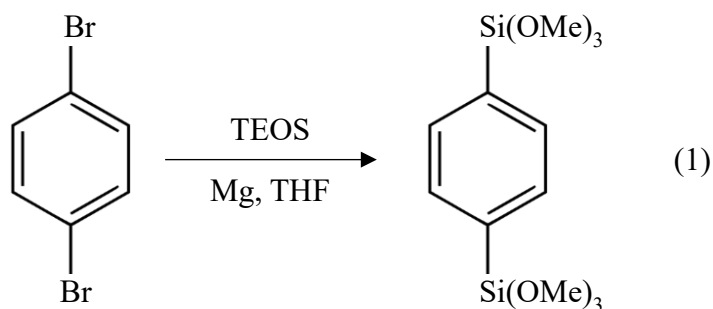
Organosilane	Abbreviation	Structure
Octyltrimethoxysilane	C ₈ TMS	
Hexadecyltrimethoxysilane	C ₁₆ TMS	
Tridecafluorooctyltriethoxysilane	F ₁₃ TES	
1,4 – bis(triethoxysilyl)benzene	BTEB	
Bis(triethoxysilylpropyl)disulfide	BTPD	
1,2-Bis(triethoxysilyl)ethane	BTSE	

2.1. Materials and reagents

Triethanolamine, TEA ($\geq 99.5\%$), aqueous hexadecyltrimethylammonium chloride solution, CTAC (25 wt%), tetraethylorthosilicate, TEOS ($\geq 99\%$), ammonium nitrate (analytical grade), Titanium tetraisopropoxide, TIP (97%), nitric acid (70%), octyltrimethoxysilane, C₈TMS (96%), hexadecyltrimethoxysilane, C₁₆TMS ($\geq 85\%$), tridecafluorooctyltriethoxysilane, F₁₃TES (98%), hydrochloric acid (37%, analytical grade), lactic acid ($\geq 85\%$), 1,2-dibromoethane (99%), 1,4-dibromobenzene (98%), tetrahydrofuran, THF ($\geq 99.9\%$, analytical grade), acetic acid (99.7%), sodium hydroxide (analytical grade), sodium chloride (analytical grade) and curcuma were supplied from Sigma-aldrich. Yeast extract was from Kasvi, peptone G was from Acumedia and d-glucose anhydrous (analytical grade), disodium hydrogen phosphate (analytical grade), citric acid (analytical grade), magnesium sulfate heptahydrate (analytical grade), and phosphate monopotassium (analytical grade) were purchased from Synth. Bis(triethoxysilylpropyl)disulfide, BTPD (analytical grade) was supplied from Alfa chemistry and 1,2-Bis(triethoxysilyl)ethane, BTSE (95%, analytical grade) from Alfa Aesar. Ethanol (99.8%, analytical grade) was purchased from Lac and toluene (analytical grade), cyclohexane (analytical grade), toluene (analytical grade) and hexane (95%, analytical grade) were purchased from Sigma-Aldrich. Ultrapure water (Milipore, specific resistivity: 18 M Ω cm) was used throughout the experiments. The rice husk was purchased from *Novarroz*, Oliveira de Azeméis, Portugal.

2.2. Preparation of 1,4-bis(triethoxysilyl)benzene (BTEB)

Organic silicon source 1,4-bis(triethoxysilyl)benzene (BTEB) was prepared by the method reported in the literature [56, 57]. The reaction (1) was carried out under nitrogen by use of a vacuum line and solvents dried.



To a mixture of magnesium turnings (15.0 g) in 50.0 cm³ of THF (0.62 mol) under nitrogen 20 drops of 1,2-dibromoethane were added, under vigorous stirring during 5 min. To this solution, 450 cm³ of TEOS (2.02 mol) in 250 cm³ of THF (3.09 mol) were added and the mixture was brought to reflux. Afterward, a solution of 26.1 cm³ of 1,4-dibromobenzene (20.4 mmol) in 100.0 cm³ of THF (1.23 mol) was added dropwise for 2 h. Within 30 min of initiating the addition, the reaction became mildly exothermic. After the completion of the addition of dibromide, the grey-green mixture was kept at reflux for 2 h at 60 °C and then at room temperature for 12 h. 200.0 cm³ of hexane was added to precipitate any remaining magnesium salts in solution, and the mixture was quickly filtered under nitrogen to afford a clear, light brown solution. Hexane was removed in vacuum, and the remaining TEOS was distilled off in vacuum leaving a brown oil. The oil was distilled (135 °C) to give a clear colorless oil. ¹H NMR (CDCl₃) δ 7.67 (s, 4 H, ArH), 3.84 (q, 12 H, OCH₂CH₃), 1.22 (t, 19 H, OCH₂CH₃).

2.3. Part I. preparation of functional hybrid nanomaterials

Mesoporous silica nanoparticles obtained from sol-gel method and silica nanoparticles obtained from agro-industrial waste, namely rice husk, were prepared and functionalized by in situ and post-grafting methodology, respectively, with alkoxysilanes with easy-cleaning properties and natural dye obtained through natural extracts, namely curcuma. Anatase SiO₂@TiO₂ spherical nanocomposites prepared by sol-gel method, have also been developed. The preparation is described below.

2.3.1. Preparation of mesoporous silica nanoparticles with easy-cleaning properties by sol-gel method

Mesoporous silica nanoparticles with easy-cleaning properties, were synthesized by co-condensation between TEOS and C₈TMS or C₁₆TMS or F₁₃TES (see the structure of these organosilanes in **Table 2**), using TEA as base and CTAC as template, following procedures adapted from literature [58].

Figure 6B and **Figure 12** illustrates the procedure used. In the case of F₁₃TES:TEOS molar ratio of 1:3, a stock solution containing 64.0 cm³ of water (3.55 mol), 10.5 cm³ of ethanol (0.179 mol), and 10.4 cm³ of 25 wt % CTAC solution (7.86 mmol) was stirred for 10 min at room temperature. To this solution 4.1 cm³ of TEA (0.031 mol) were added (pH 11). Afterward, 60 cm³ of this solution were heated to 60 °C, and then 4.35 cm³ of TEOS (19.5 mmol) and 2.5 cm³ of F₁₃TES (6.5 mmol) were

simultaneously added under vigorous stirring. The reaction mixture was stirred at 60 °C for 2 h and then cooled to room temperature. Finally, ethanol was added and the resulting silica nanoparticles were isolated by centrifugation (20 min at 14 °C and 16000 rpm), followed by template extraction. Template removal was performed by refluxing the silica nanoparticles twice in 150 cm³ of an ethanolic solution of ammonium nitrate (0.25 M) for 1 h and twice in 150 cm³ of an ethanolic solution of hydrochloric acid (0.14 M) for 1 h. Afterward the silica nanoparticles were separated by centrifugation, washed/centrifuged with ethanol twice, and finally a part was redispersed in ethanol while the remaining was dried at 80 °C for 12 h.

The final molar composition of the reagents in the reaction mixtures was 1 TEOS:0,3 F₁₃TES/C₈TMS/C₁₆TMS:0,27 CTAC:1 TEA:137 water:6.2 ethanol. A molar ratio of TEOS:TEA of 1:1 was chosen to minimize the particle size [58, 59]. Unfunctionalized silica nanoparticles (SiO₂) were prepared as reference, under identical experimental conditions, without additional organosilane C₈TMS, C₁₆TMS or F₁₃TES. **Table 3** summarizes the samples obtained.

Table 3 - Mesoporous silica nanoparticles.

Organosilane	Sample
-	SiO ₂
C ₈ TMS	SiO ₂ @C ₈ TMS
C ₁₆ TMS	SiO ₂ @C ₁₆ TMS
F ₁₃ TES	SiO ₂ @F ₁₃ TES

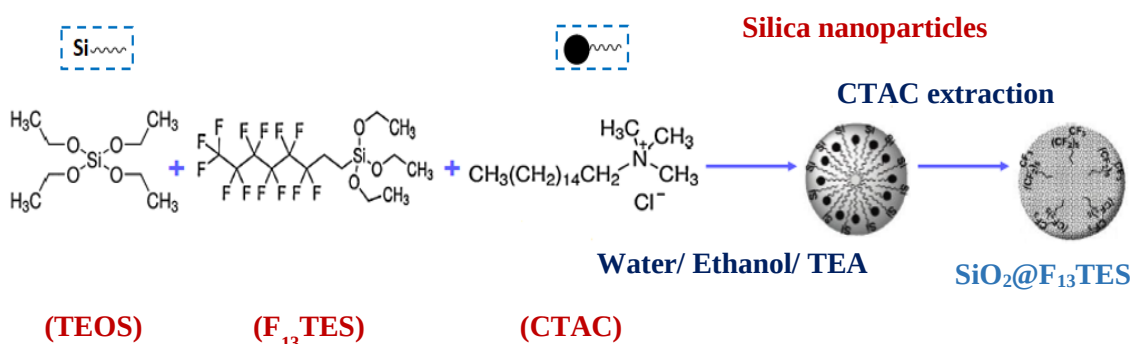


Figure 12 – Schematic representation of the preparation of $\text{SiO}_2@\text{F}_{13}\text{TES}$ sample by co-condensation methodology [own authorship].

2.3.2. Preparation of functional silica nanoparticles from rice husk

Silica nanoparticles obtained from agro-industrial waste, namely rice husk, have been functionalized by post-grafting methodology with organosilane F_{13}TES , to obtain silica nanoparticles with easy-cleaning properties, and with natural-based colored dye (curcuma) to obtain natural-based colored silica nanoparticles.

i. Preparation of silica nanoparticles obtained from rice husk

For the preparation of silica nanoparticles from rice husk, a pre-treatment of the agro-industrial waste followed by a heat treatment was performed. Pre-treatment included 4 stages: **sifting**, in order to remove visible impurities and homogenize waste size; **washing**, in order to eliminate impurities and metal oxides; **drying** and **milling** with a knife mill followed of a ball mill, in order to obtain a larger contact area during heat treatment.

Two methods were tested in the washing process during pre-treatment. Initially, the rice husk was pre-treated with water and hydrochloric acid (10% (wt/wt)), for 1 h at room temperature (**method A**). The resulting sample will be referred to as $\text{SiO}_2\text{-rice-1}$. In order to obtain silica nanoparticles with high purity and develop a more sustainable, ecological and economic process, the pre-treatment was optimized, having proceeded to a hydrothermal treatment, in which the rice husk was pre-treated with water and hydrochloric acid (5% (wt/wt)) at high pressures and temperatures (150 °C for 1 h) followed by heat treatment (**method B**). This method is described below. 10 g of rice

husk in 200 cm³ of milipore water (11.1 mol) remained under vigorous stirring during 1 h at room temperature. Afterward, the agro-industrial residue was filtered and transferred to a hydrothermal reactor (**Figure 13**) together with 100 cm³ of milipore water. In turn, the hydrothermal reactor was placed inside an oven at 150 °C for 4 h. The rice husk was recovered by filtration, and washed with milipore water remained under vigorous stirring during 1 h at room temperature. Afterward, the rice husk was dried at 110 °C for 12 h and then, ground with a ball mill apparatus (400 rpm during 20 min). In a last stage, the heat treatment was carried out. The conditions were defined through the thermogravimetric analysis of the rice husk ((from 30 to 700 °C under an oxygen atmosphere, at a heating rate of 5°C/min and a stay at 700 °C for two hours) (**chapter 4 – section 4.1.2**)). The resulting sample will be referred to as SiO₂-rice.

Hydrothermal treatment allows the expansion of the rice husk cellulosic fibers and solubilizes part of the lignin, contributing to the fast and effective access of the acid in the impurities [58].

Table 4 summarizes the samples obtained with the variables studied in the pretreatment.



Figure 13 – Hydrothermal reactor [own authorship].

Table 4 – Silica nanoparticles from rice husk.

Pre-treatment		Rice husk	Ashes
Pre-treatment	Method		
-	-	Rice-0	SiO ₂ -rice-0
HCl (10% (wt/wt))	A	Rice-1	SiO ₂ -rice-1
HCl (5% (wt/wt)) and hydrothermal treatment	B	Rice	SiO ₂ -rice

ii. Preparation of silica nanoparticles from rice husk with easy-cleaning properties

The functionalization of silica nanoparticles obtained from rice husk, SiO₂-rice, with organosilane F₁₃TES was performed by silylation, according to a methodology described by *García et al.* [60]. The functionalization was carried out under nitrogen with a vacuum line and dried solvents. 0.500 g of SiO₂-rice (previously dried in an oven at 120 °C for 1 h, under vacuum) was dispersed in 50.0 cm³ dry toluene (0.472 mol) and afterwards, 2.5 mmol of organosilane F₁₃TES was added. The final dispersion was refluxed for 24 h under argon atmosphere. The resulting material was isolated by centrifugation (20 min at 14 °C and 16000 rpm), washed by reflux with dry toluene (2 x 50.0 cm³) for 1 h and then dried at 80 °C for 12 h. The ratio of SiO₂-rice:organosilane was 500 mg:2.5 mmol. The resulting sample will be referred to as SiO₂@F₁₃TES-rice.

Figure 6A and **Figure 14** illustrates the procedure used in this methodology.

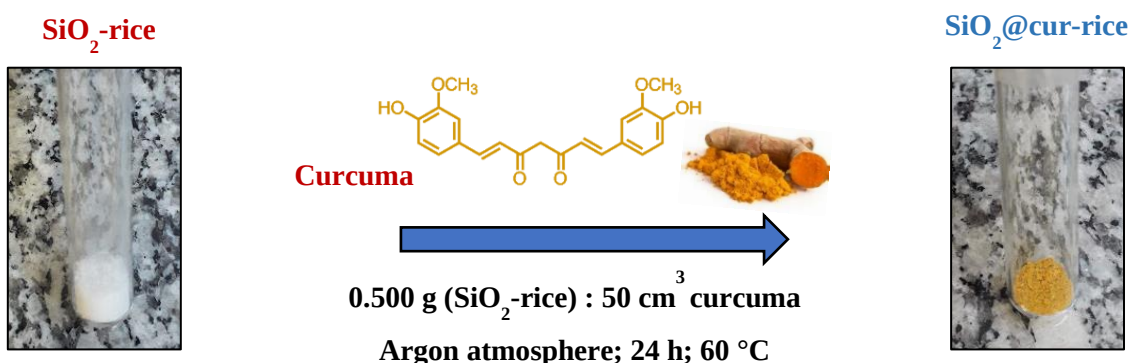


Figure 15 – Schematic representation of the preparation of $\text{SiO}_2\text{@cur-rice}$ by post-grafting methodology [own authorship].

2.3.3. Preparation of anatase $\text{SiO}_2\text{@TiO}_2$ nanocomposites

The preparation of $\text{SiO}_2\text{@TiO}_2$ nanocomposites was performed following the procedures adapted from literature [42, 61] and described below.

i. Preparation of titanium dioxide sols

For the preparation of TiO_2 sol, 5 mL of titanium tetraisopropoxide (TIP) (3.52 mmol) was added dropwise to 100 mL acidic water (55.5 mmol) containing 1 mL nitric acid (15.7 mmol) and 10 mL acetic acid (0.181 mol) under vigorous stirring (800 rpm). The mixture was stirred for 16 h at 60 °C (pH = 1-2) [42, 61]. The resulting sample is denoted as TiO_2 .

ii. Preparation of silica nanoparticles

The synthesis of SiO_2 nanoparticles is described in **section 2.3.1**.

iii. Preparation of $\text{SiO}_2\text{@TiO}_2$ nanocomposites

1 g of as-prepared SiO_2 nanoparticles, was added to TiO_2 sol and dispersed in an ultrasonic bath for 15 min. The $\text{SiO}_2\text{-TiO}_2$ mixture was kept for 12 h to form SiO_2 supported TiO_2 spherical nanocomposites (pH = 3-5). The resulting sample is denoted as $\text{SiO}_2\text{@TiO}_2$. The final molar composition of the reagents was SiO_2 : TIP : water : nitric acid : acetic acid = 1 : 0.21 : 3.3 : 1 : 10. 10 mL of the colloidal sol sample, was separated

by centrifugation and dried at 80 °C for 12 h, for subsequent physicochemical characterization [61]. **Figure 16** illustrate the procedure used in this methodology.

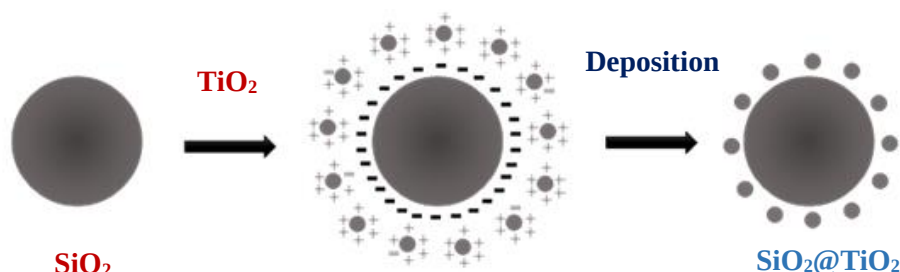


Figure 16 – Schematic representation of the formation mechanism of $\text{SiO}_2@\text{TiO}_2$ nanocomposite [own authorship].

2.4. Part II. Preparation of Functional Bacterial Cellulose Organic-Inorganic Hybrid Membranes

The nanomaterials previously prepared were incorporated into BCM, following two different methodologies: in situ and post-grafting. BCM was also be functionalized with four different organic silicon sources, BTEB, BTPD and BTSE.

In in-situ functionalization of BCM, the culture medium composition was changed according to materials used. On the other hand, in post-grafting functionalization, the BCM was modified after the BCM has been formed in culture medium (**Figure 17**).

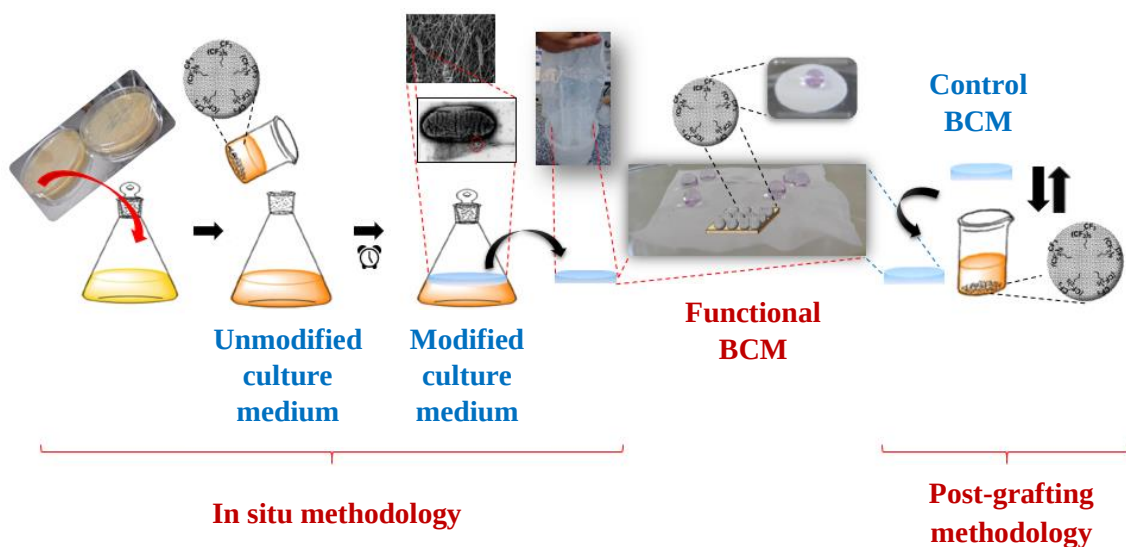


Figure 17 - Schematic representation of the preparation of bacterial BCM with easy-cleaning properties [own authorship].

2.4.1. Preparation of bacterial cellulose membranes

BCM were prepared following the procedures adapted from literature [51]. The strain used was *Gluconacetobacter xylinus* (ATCC23760) supplied by André Tobello Foundation, Campinas-SP, Brazil. An aliquot of the bacterium *Gluconacetobacter xylinus* (ATCC23760) was replicated to a sterile solid medium plate HS (Hestrim-Schramm) containing 12 g of glucose (0.067 mol), 3 g of yeast extract, 3 g of peptone G, 1.62 g of disodium hydrogen phosphate (0.011 mol), 0.69 g of citric acid (3.59 mmol), 15 g of agar and 585 mL of milipore water (32.5 mol). After growth time, the microorganism was inoculated into sterile liquid culture medium consisting of 50 g of glucose (0.277 mol), 4 g of yeast extract, 0.73 g of magnesium sulphate heptahydrate (2.96 mmol), 2 g of monopotassium phosphate (0.015 mol), 20 mL of ethanol (0.342 mol) and 980 mL of milipore water (54.4 mol) and maintained for 72 h in an oven with air circulation with constant temperature at 28 °C. Subsequently, the BCM produced were purified, in which was subjected to exchange water 5 times per day for 3 days; heated in water at 80 °C for 50 min; immersed in 100 mL of an ethanolic solution of sodium hydroxide (0.1 M) at 80 °C during 50 min and washed again with milipore water until pH 7.0.

BCM was dried at 80 °C for 24 h. The resulting dried sample is denoted BCMD (**Figure 18B**). The resulting non-dried sample is noted as BCMW (**Figure 18A**).

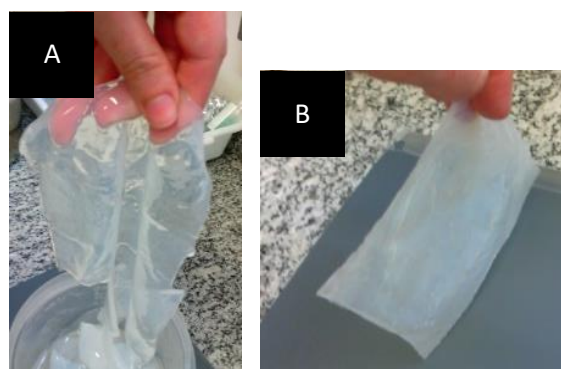


Figure 18 - Illustrative figure of (A) non-dried sample, BCMW and (B) dried sample, BCMMD [own authorship].

2.4.2. Functionalization of bacterial cellulose membranes by in situ methodology

The preparation of bacterial cellulose organic-inorganic hybrid membranes by in situ methodology (**Figure 17**), following similar procedures as those indicated in “**section 2.4.1**”, with the exception the addition of 10% of material, in the liquid culture medium, at the same time as the microorganism. The **Table 5** summarizes the samples obtained.

Table 5 - BCM functionalized by in situ methodology.

Material	BCM sample
SiO ₂	BCM@SiO ₂
SiO ₂ @C ₈ TMS	BCM@SiO ₂ @C ₈ TMS
SiO ₂ @C ₁₆ TMS	BCM@SiO ₂ @C ₁₆ TMS
SiO ₂ @F ₁₃ TES	BCM@SiO ₂ @F ₁₃ TES
SiO ₂ -rice	BCM@SiO ₂ -rice
SiO ₂ @F ₁₃ TES-rice	BCM@SiO ₂ @F ₁₃ TES-rice
SiO ₂ @cur-rice	BCM@SiO ₂ @cur-rice
BTEB	BCM@5% BTEB
BTEB	BCM@BTEB
BTPD	BCM@BTPD
BTSE	BCM@BTSE

2.4.3. Functionalization by post-grafting methodology

BCM_W (wet) and BCM_D (dried) were functionalized by post-grafting methodology (**Figure 17**) with silica nanoparticles obtained from sol-gel method with easy-cleaning properties (SiO₂@C₈TMS, SiO₂@C₁₆TMS and SiO₂@F₁₃TES) and anatase SiO₂@TiO₂ nanocomposites (SiO₂@TiO₂).

In total, 15-cm (length) x 5-cm (width) rectangular pieces (average weight = 0.3 g) of pristine BCM_W and BCM_D were used. Before the chemical modifications, pristine BCM_D pieces were dried under vacuum at 80 °C overnight. Posteriorly, nanomaterials were deposited by dip-coating, where BCM_W and BCM_D were dipped into the silica nanoparticles suspension for 5 min and then dried at 80 °C for 8 h. The resulting samples are summarized in the **Table 6**.

Table 6 - BCM functionalized by post-grafting methodology.

Material	BCM sample
SiO ₂	BCM@SiO ₂ _PG
SiO ₂ @C ₈ TMS	BCM@SiO ₂ @C ₈ TMS_PG
SiO ₂ @C ₁₆ TMS	BCM@SiO ₂ @C ₁₆ TMS_PG
SiO ₂ @F ₁₃ TES	BCM@SiO ₂ @F ₁₃ TES_PG
SiO ₂ @TiO ₂	BCM _D @SiO ₂ @TiO ₂ _PG
SiO ₂ @TiO ₂	BCM _W @SiO ₂ @TiO ₂ _PG

2.5. Physicochemical Characterization

The functional nanomaterials and functional BCM were characterized by several characterization techniques, in order to evaluate their physicochemical properties.

2.5.1. Morphological characterization

Morphological study of the functional nanomaterials and functional BCM was performed by the following characterization techniques: Scanning Electron Microscopy (**SEM**), Transmission Electron Microscopy (**TEM**); Scanning Transmission Electron Microscopy (**STEM**) and Atomic Force Microscopy (**AFM**). Average particle size of the

functional nanomaterials and functional nanomaterials incorporated into the BCM was obtained by **SEM** (d_{SEM}) and **TEM** (d_{TEM}).

SEM micrographs of the SiO_2 , TiO_2 , $\text{SiO}_2@\text{TiO}_2$ nanocomposite and BCM functionalized with $\text{SiO}_2@\text{TiO}_2$ nanocomposites were performed using a high-resolution environmental scanning electron microscope (JEOL JSM7500-F model). Samples SiO_2 and $\text{SiO}_2@\text{TiO}_2$ were analyzed in powder, while sample TiO_2 was analyzed in solution (an aliquot was deposited on the carbon tape attached to the support and dried under vacuum for 8 hours) and covered with a 1 nm thick carbon layer. SEM of the others samples were performed at *L'Institut Européen des Membranes (IEM)*, Montpellier, France, using a high-resolution environmental scanning electron microscope (Hitachi S4800 model) and an energy-dispersive X-ray spectrometer (Oxford Instruments X-Max^N SDD), respectively. The samples were analyzed with coating of 1 nm thick carbon layer.

TEM micrographs were performed at *Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM) Montpellier, France*, using a Philips CM30T electron microscope with a LaB6 filament as the source of electrons, operated at 80 kV to minimize beam damage. All the samples were dispersed in high purity ethanol under sonication and a drop of the colloidal suspension was placed on a holey carbon TEM grid and left to dry at ambient conditions.

The average particle size and standard deviations of nanomaterials were calculated from the diameters of 100 and 50 particles randomly selected from SEM and TEM micrographs, respectively, and using the ImageJ software.

STEM images of $\text{SiO}_2@\text{TiO}_2$ nanocomposite were collected at the Brazilian Nanotechnology National Laboratory (LNNano), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, Brazil, in a JEOL-JEM 2100F operated at 80 kV.

AFM measurement of functional BCM was performed using a Dimension Icon scanning probe microscope equipped with Nanoscope V controller (Bruker) at *Departamento Ingeniería Química y del Medio Ambiente, Universidad del País Vasco, Españã*. Tapping mode (TM) was employed in air using an integrated tip/cantilever (125 μm in length with ca. 300 kHz resonant frequency). Typical scan rates during recording were 0.9-1.1 line/s using a hybrid scan head with a maximum range of $100 \times 100 \mu\text{m}$. Different regions of the samples were scanned to ensure that both morphology of the investigated materials are the representative one.

The average hydrodynamic diameters (d_{DLS}) and polydispersion indexes (PDI) of the hybrid silica nanoparticles and $TiO_2@SiO_2$ nanocomposite were obtained by Dynamic Light Scattering (**DLS**) measurements. These measurements were performed at 20 °C, using a Malvern Zetasizer NanoZS compact scattering spectrometer with a 4.0 mW He-Ne laser (633 nm wavelength) at a scattering angle of 170° using a Malvern Dispersion Technology Software 6.01. All measurements were repeated five times for each sample to verify the reproducibility of the results. Stable samples were prepared by dilution of the ethanolic colloidal suspensions of the materials.

2.5.2. Thermal characterization

The thermal behavior of functional materials, rice husk and functional BCM was analyzed by thermogravimetric analysis (**TGA**). TGA of the BCM functionalized with $SiO_2@TiO_2$ nanocomposites were obtained with a SDT 2960 from TA-Instruments. This sample was heated from 50 to 700 °C under oxygen atmosphere, 200 mL min⁻¹, at heating rate of 5 °C min⁻¹. The thermograms of the others samples, were carried out on Q50 V6.7 Build 203 from TA-Instruments at *ENSCM*. Samples were heated from 50 to 900 °C under an oxygen atmosphere, 60 mL min⁻¹, at a heating rate of 10 °C min⁻¹.

2.5.3. Textural characterization

The textural properties of nanomaterials and functional BCM were studied by Nitrogen adsorption-desorption isotherms at -196 °C and X-Ray diffraction (**XRD**). Nitrogen adsorption-desorption isotherms at -196 °C of the silica nanoparticles obtained by sol-gel method were measured in an automatic apparatus Micromeritics ASAP 2020 V3.01 H at *ENSCM*. Before the adsorption experiments the samples were degassed at 120 °C under vacuum during 3 h to avoid decomposition of organic groups and at a pressure lower than 0.133 Pa. The specific surface areas (A_{BET}) were calculated from the Brunauer-Emmett-Teller (BET) model and the porous volumes (V_{meso}) were estimated from the t-method, using a dehydroxylated silica as reference material. The pore size (d_{pore}) and pore size distributions were calculated from the adsorption branch of the isotherms by using the non-local density functional theory (NLDFT) equilibrium model of N₂ on silica and assuming cylindrical pores.

The crystal phase of $SiO_2@TiO_2$ nanocomposite solid powder extracted and functional BCM was studied by **XRD**. The X-Ray Diffraction measurements were

performed at room temperature with a Siemens D5000 Diffrac Plus XRD commander diffractometer, using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and Bragg-Brentano $\theta/2\theta$ configuration. The X-Ray Diffractograms of the functional BCM were recorded at room temperature on a diffractometer Rigaku Geigerflex D/Max-c equipped with a CuK α radiation monochromator ($\lambda = 1.5405 \text{ \AA}$) at university of Franca (UNIFRAN), Franca, Brazil. The diffractograms were registered with 2θ values ranging from 5 to 75°, at a resolution of 0.05°.

2.5.4. Chemical characterization

Silica-based nanomaterials and BCM were further characterized by the following techniques: Attenuated Total Reflectance Fourier Transform Infrared (**FTIR-ATR**) Spectroscopy; ^{29}Si Cross-polarization magic angle spinning (CPMAS) and ^{13}C CPMAS Solid-State Nuclear Magnetic Resonance (**NMR**); X-ray photoelectron spectroscopy (**XPS**); X-ray fluorescence (**XRFA**) and Raman spectroscopy. These characterization techniques allowed a qualitative and quantitative analysis of the samples, as well as to evaluate the functionalization efficiency in the functionalized samples.

The **FTIR-ATR** spectra were collected with a Bruker Vertex 70 spectrophotometer in the range of 650-4000 cm^{-1} , with 4 cm^{-1} resolution and 16 scans.

^{13}C CPMAS and ^{29}Si CPMAS of hybrid silica nanomaterials, were recorded at *ENSCM*, on a 9.4 T Bruker Avance 400 spectrometer, at a spinning rate of 9 kHz for carbon and 5 kHz for silicon. ^{13}C CPMAS and ^{29}Si CPMAS NMR of BCM@BTEB were recorded on a Varian Inova 300, at a spinning rate of 9 kHz for carbon and 5 kHz for silicon. This sample was ground in a ball mill apparatus (400 rpm during 2 minutes).

The **XPS** measurements of silica-based nanomaterials and functional BCM were performed in a Thermo Scientific ESCALAB 250 spectrometer equipped with monochromatic Al K α radiation (1486.6 eV) with the X-ray source being operated at 150 W. The powdered samples were pressed into pellets and stuck on a double-sided adhesive conducting carbon tape prior to the XPS studies. Electrostatic charging effects were corrected by using the co-axial charge neutralizer developed by Kratos, and the binding energy scale was calibrated by using C 1s band at 284.8 eV (C-H/C-C) as internal reference. The XPS spectra were deconvoluted with the XPSPEAK 4.1 software, using non-linear least squares fitting routine after a Shirley-type background subtraction. The

surface atomic percentages were calculated from the corresponding peak areas and using the sensitivity factors provided by the manufacturer.

The TiO₂ and SiO₂ contents in the SiO₂@TiO₂ sample and SiO₂ contents in the rice husk were obtained by **XRFA** at the department of Chemistry, University of São Paulo (USP) São Carlos, Brazil, using a benchmark MiniPal4 (PANalytical) spectrometer in energy dispersive mode. The semiquantitative determination of TiO₂ and SiO₂ was performed using the standardless analysis package Omnian (PANalytical). All the measurements were acquired after a total measurement time of 840 s and were done in triplicate.

Raman spectra of BCM@BTEB, BCMD@SiO₂@TiO₂_PG and BCMW@SiO₂@TiO₂_PG were obtained with a Labram HR 800, Horiba Jobin Yvon Raman Spectrometer, equipped with He-Ne 632.81 nm laser and CCD (DU420A-OE-325 model) detector. The spectra were acquired with a laser power of 150 mV using an integration time of 300s and 20 runs per measurement.

2.6. Evaluation of Easy-Cleaning and Self-Cleaning properties

2.6.1. Easy-Cleaning properties

The easy-cleaning properties, of the nanoparticles and the BCM, were evaluated by measuring the contact angle (CA) between deionized water, toluene, cyclohexane, artificial sweat [49] (fingerprint liquid) and the substrate. If the CA is less than 90°, the surface is hydro/oleophilic (**figure 5A**); between 90° and 180°, the surface is hydro/oleophobic (**figure 5B**), equal or superior than 180°, the surface is superhydro/oleophobic (**Figure 5C**) [54, 55]. The CA were performed with a contact angle apparatus Dataphysics Contact Angle System OCA. The measurements were performed at room temperature, by placing a 3 µL droplet of liquid on the sample surface, with a computer-controlled liquid dispensing system. The CA were determined automatically from the images of the drop, captured with a digital video camera HS3 (high speed charge coupled device) interfaced to image-capture software, using the Laplace-Young fitting algorithm. Average CA were determined by measuring the values at three different positions on each sample surface, in the case of nanoparticles, and in ten different positions on each sample surface, in the case of BCM. The nanoparticles were analyzed as pellets. The CA measurements on the functional materials were repeated after six months, providing similar values (not shown).

The preparation of artificial fingerprint liquid following procedures adapted from literature [62]. This liquid was formulated by mixing the following substances: lactic acid 3 mL/L, acetic acid 5 mL/L, sodium chloride 10 g/L, sodium hydrogen phosphate 10 g/L, and deionized water. The solution was stirred for at least 4 h at room temperature before being used.

2.6.2. Self-Cleaning properties – photocatalytic activity

The self-cleaning properties of BCM functionalized with $\text{SiO}_2@\text{TiO}_2$ nanocomposites were evaluated by observing the decomposition of adsorbed methyl violet 2B (MV) dye. The absorbance peak of MV dye in the visible region (450-700 nm) was measured after each dosage of irradiation of UV light (5-30 min). 15 cm x 5 cm of the BCM were dipped in aqueous solution of MV dye (0.1%), for 5 min and then dried for 1 h at room temperature. Afterward, 5 cm x 5 cm of the BCM was coated with aluminum foil and then placed under UV radiation (10 cm x 5 cm). The sample-lamp distance was 7 cm. A solar light simulator system, based on a Xe 150-W lamp, the range of emission wavelength between 290 and 400 nm (UVA and UVB) (16S-150W model, Solar Light, Inc., Philadelphia, USA) and a UV-Vis spectrometer (Carry 5000 model) was used. **Figure 19** illustrate the procedure used.

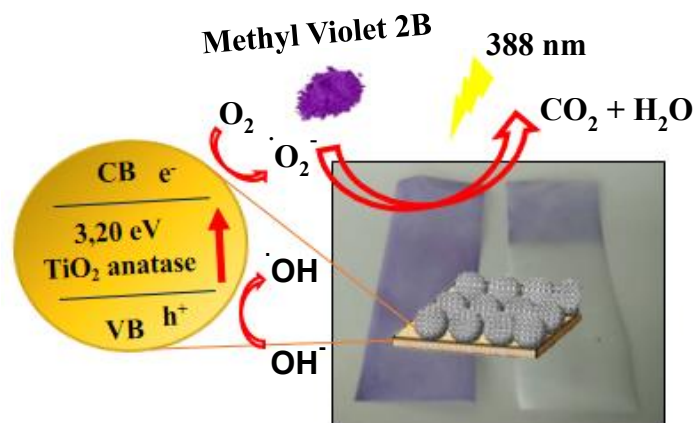


Figure 19 - Schematic representation of the evaluation of self-cleaning properties of BCM [own authorship].

2.7. Resistance to washing of functional bacterial cellulose membrane

In order to evaluate the stability of the materials on the BCM, the bacterial cellulose organic-inorganic hybrid membranes, were placed in water in an ultrasonic bath at room temperature for 20 min and then dried at 50 °C for 8 h. Subsequently, the functional properties were evaluated.

The contact angle measurements and photocatalytic activity on the functional BCM were repeated after six months, providing similar values.

This assessment is an important criterion for the validation of the obtained product.

PART I

Characterization of Functional Hybrid Nanomaterials

CHAPTER 3

Silica Nanoparticles
with Easy-Cleaning
Properties by
Sol-gel Method

3. Silica Nanoparticles with easy-cleaning properties by sol-gel method

The prepared silica nanoparticles with easy-cleaning properties by sol-gel method were characterized by SEM, TEM, DLS, EDS, N₂ adsorption-desorption isotherms at -196 °C, FTIR-ATR, ²⁹Si CPMAS and ¹³C CPMAS Solid-State NMR, TGA, XPS and contact angle. The results and respective discussion, by means of the characterization techniques used, are presented in this chapter.

3.1. SEM, TEM and DLS

In **Figure 20** and **Figure 21** are represented the SEM and TEM micrographs, respectively, of the SiO₂, SiO₂@C₈TMS, SiO₂@C₁₆TMS and SiO₂@F₁₃TES samples. In the SEM micrograph of each sample is identified (red square) where the EDS analysis (**Figure 23**) was performed. The **Figure 22** are illustrated the particles size distribution histograms, of these samples, determined by SEM image analysis. Additionally, in the **Table 7**, are summarized the average particle size estimated by SEM and TEM images analysis and DLS, as well as the polydispersion indexes (PDI) by DLS.

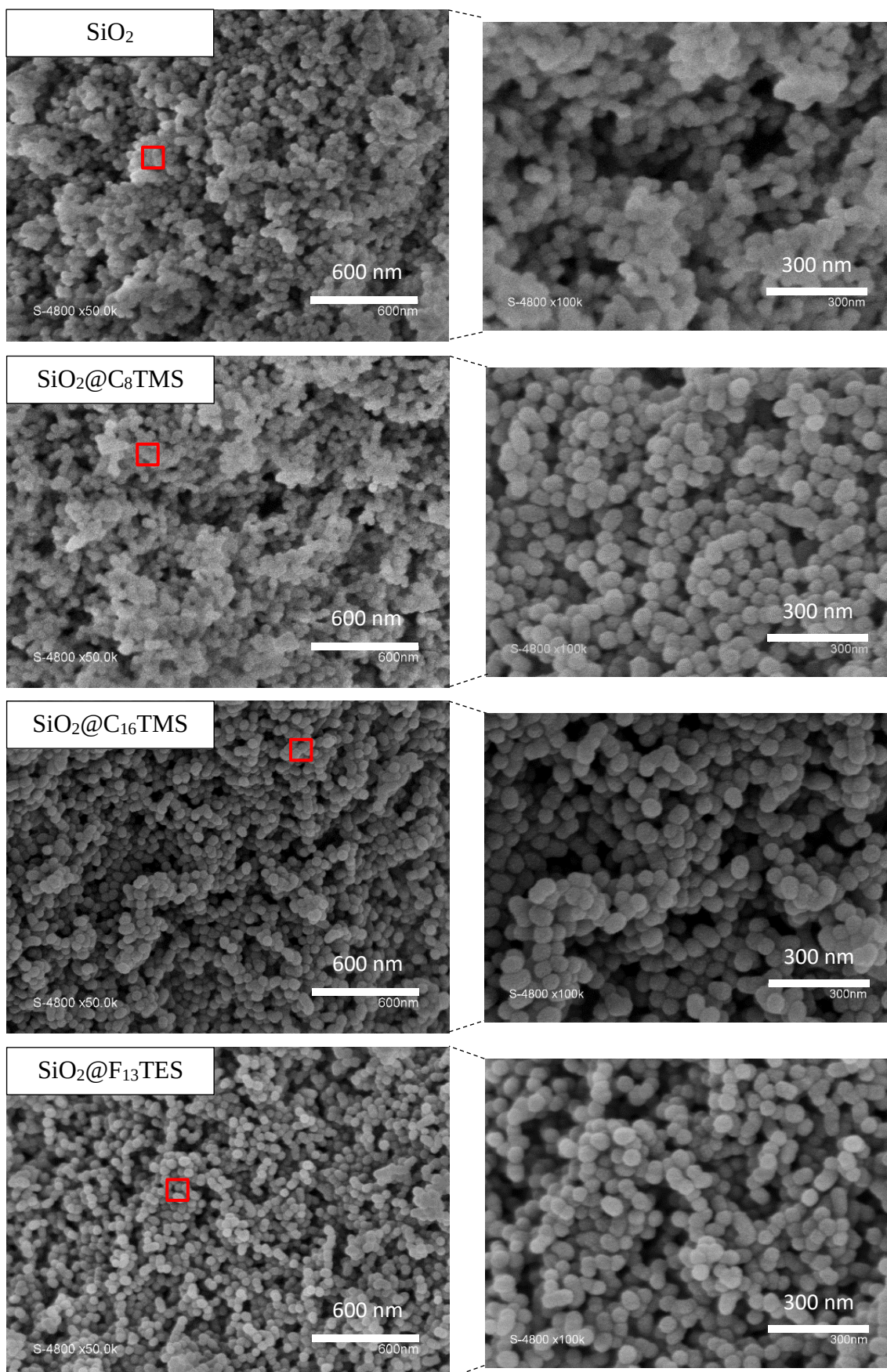


Figure 20 – SEM micrographs of SiO_2 , $\text{SiO}_2@\text{C}_8\text{TMS}$, $\text{SiO}_2@\text{C}_{16}\text{TMS}$ and $\text{SiO}_2@\text{F}_{13}\text{TES}$ nanomaterials.

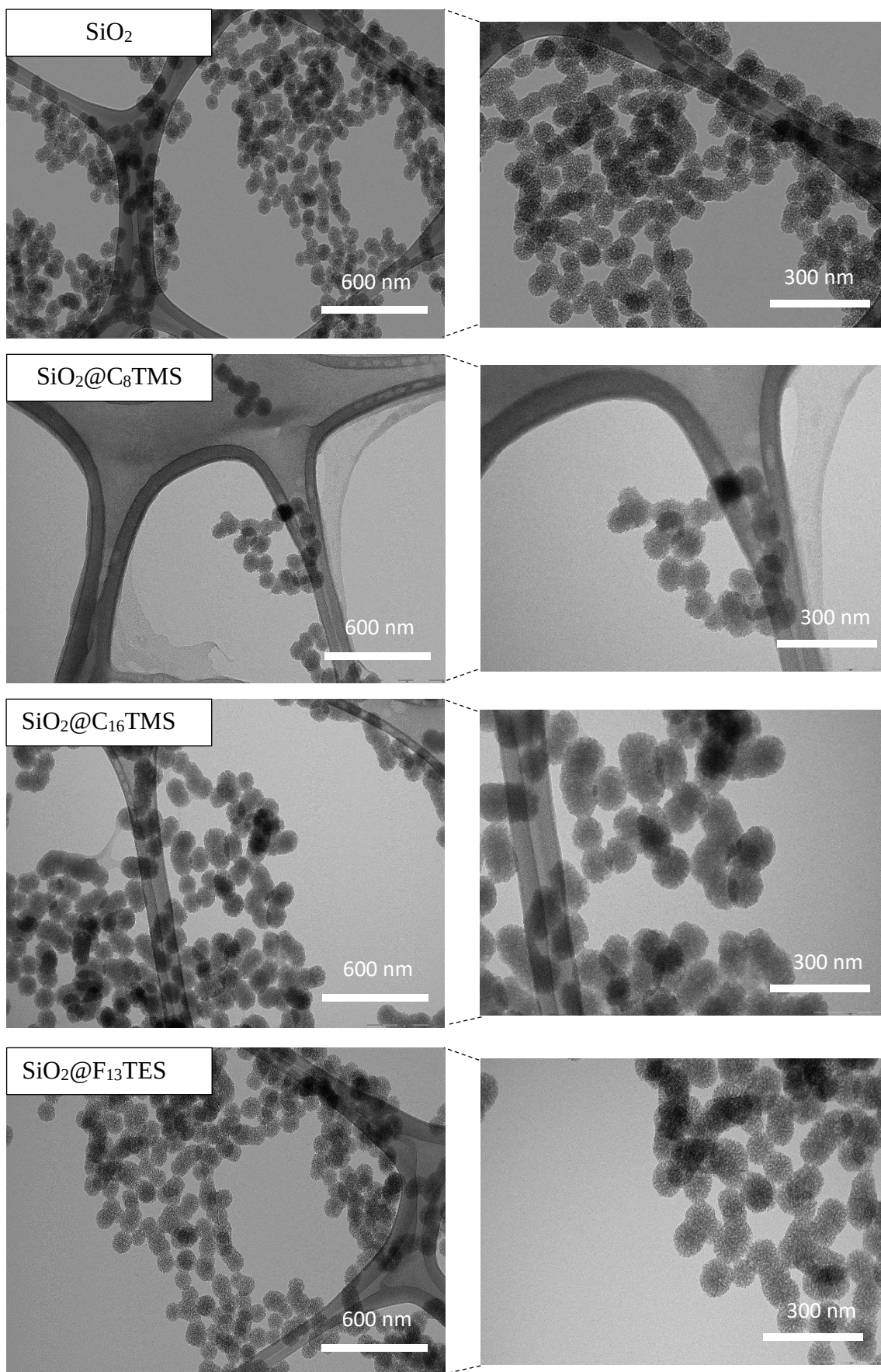


Figure 21 – TEM micrographs of SiO₂, SiO₂@C₈TMS, SiO₂@C₁₆TMS and SiO₂@F₁₃TES nanomaterials.

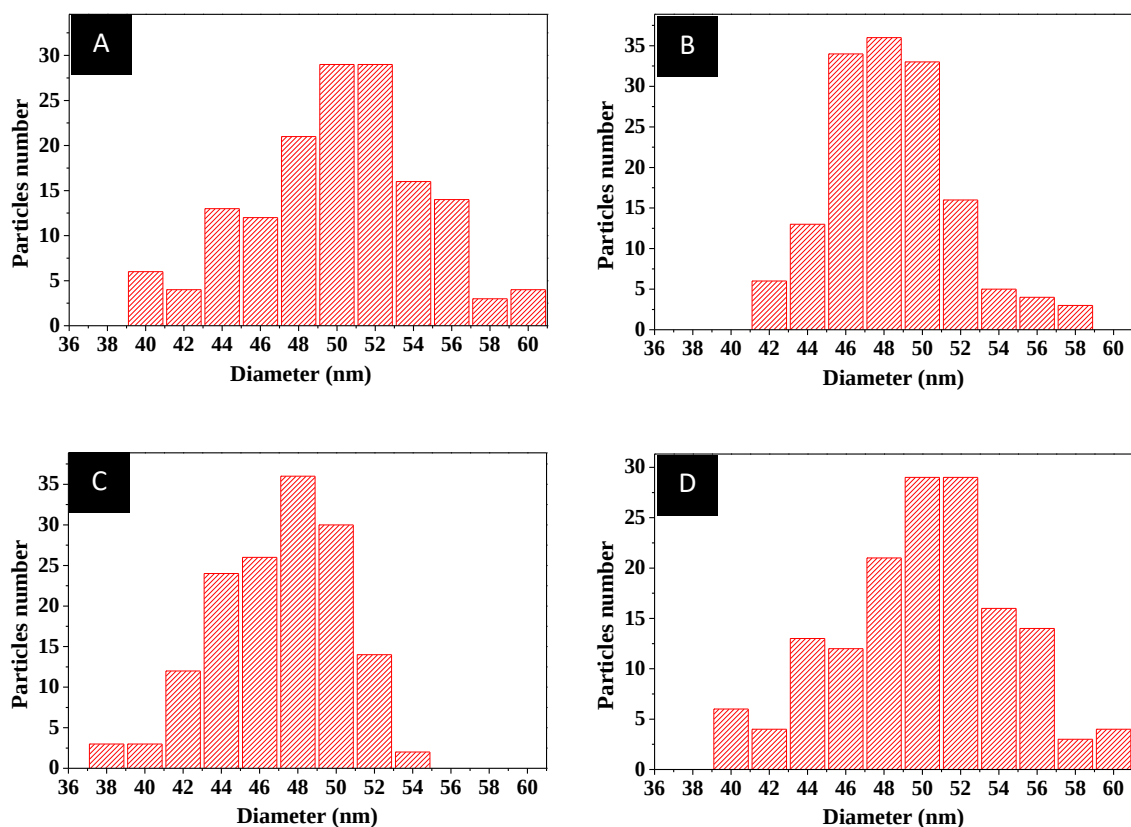


Figure 22 – Particles size distribution histograms of (A) SiO₂, (B) SiO₂@C₈TMS, (C) SiO₂@C₁₆TMS and (D) SiO₂@F₁₃TES nanomaterials, determined from SEM images analysis.

Table 7 – Average particle size estimated by SEM (d_{SEM}), TEM (d_{TEM}) and average hydrodynamic diameter (d_{DLS}) and polydispersion index (PDI) by DLS of the mesoporous silica-based nanomaterials.

Material	Particle size (nm)			
	d_{SEM}	d_{TEM}	DLS	
			d_{DLS}	PDI
SiO ₂	51 ± 4	52 ± 4	68 ± 2	0.15
SiO ₂ @C ₈ TMS	48 ± 3	49 ± 3	61 ± 3	0.14
SiO ₂ @C ₁₆ TMS	48 ± 4	50 ± 2	62 ± 4	0.07
SiO ₂ @F ₁₃ TES	51 ± 4	51 ± 3	71 ± 4	0.08

The SEM and TEM images (**Figure 20** and **Figure 21**) show that all the nanomaterials are composed of nearly spherical nanoparticles with a wormhole-type mesoporous structure and particle size around 50 ± 4 nm, which is comparable to the values obtained by Bein *et al.* (45-60 nm) [58], with narrow size distributions. In all samples, a degree of monodispersion was achieved. The preservation of the almost-spherical shape and nanosize independently of changing the organosilane is noteworthy. DLS analysis (**Table 7**) confirmed that all samples present excellent colloidal stability and corroborates the particle size trend observed by SEM and TEM (**Table 7**). Nevertheless, the average hydrodynamic diameters are always higher than the discrete particle sizes estimated by electron microscopy techniques [33, 58, 59].

3.2. EDS

In the **Figure 23** are illustrated the EDS spectra (inset: atomic percentages of C, O, Si and F), obtained during SEM experiment. In **Figure 20**, in the micrograph of each sample, is identified (red square) where the EDS analysis was performed.

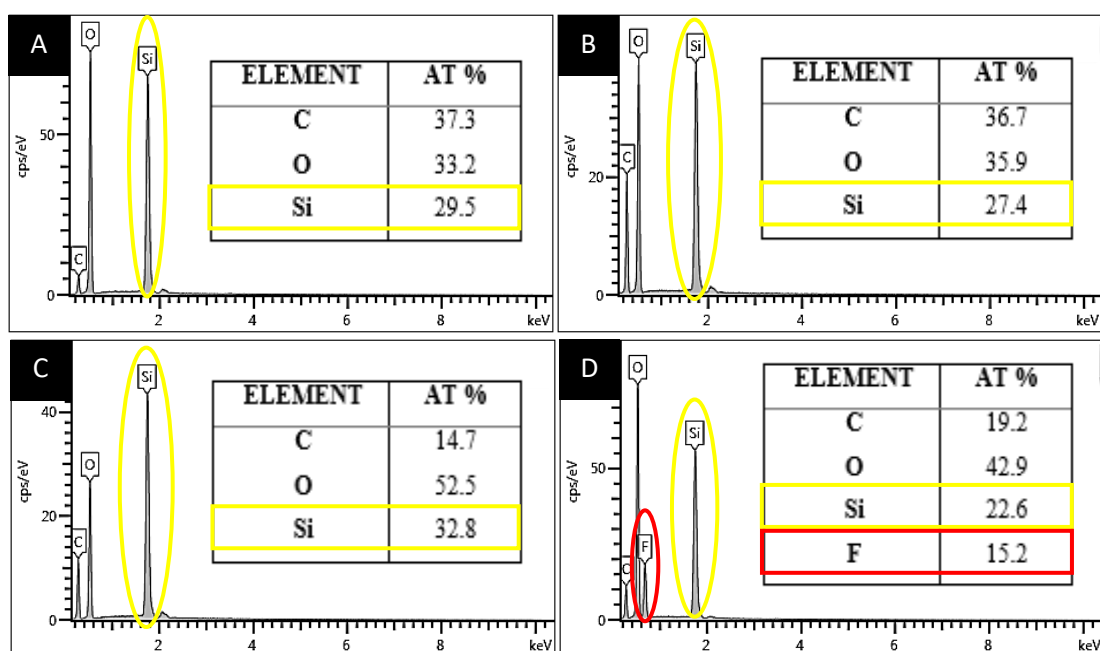


Figure 23 - EDS spectra of SiO₂ (A), SiO₂@C₈TMS (B), SiO₂@C₁₆TMS (C) and SiO₂@F₁₃TES (D) nanomaterials, obtained during SEM experiments.

The EDS spectra confirm the incorporation of organosilane C₈TMS and C₁₆TMS with the increasing of C atomic ratio compared to the control (SiO₂), and F₁₃TES with the increasing of carbon atomic ratio and the presence of F. The presence of carbon in the sample SiO₂ may, in part, be due to the esterification of the silica nanoparticles surface during the template extraction procedure in acidified ethanolic medium (this is verified by FTIR-ATR, **Figure 25**) and also the carbon layer deposited on the silica nanoparticles to increase conductivity during the SEM analysis.

3.3. N₂ adsorption-desorption isotherms at -196 °C

In **Figure 24** are represented the N₂ adsorption-desorption isotherms at -196 °C of the (A) SiO₂, (B) SiO₂@F₁₃TES, (C) SiO₂@C₁₆TMS and (D) SiO₂@C₈TMS samples. The nanomaterials exhibit type IV isotherms, which are characteristic of mesoporous materials.

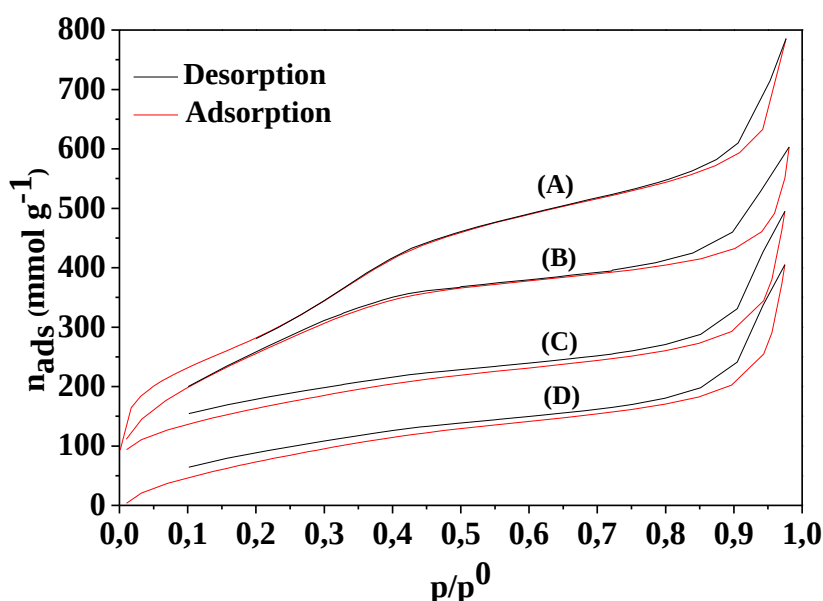


Figure 24 - N₂ adsorption-desorption isotherms at -196 °C of (A) SiO₂, (B) SiO₂@F₁₃TES, (C) SiO₂@C₁₆TMS and (D) SiO₂@F₁₃TES nanomaterials.

The **Table 8**, presents the N₂ adsorption-desorption isotherms data, namely the specific surface area BET (**A_{BET}**), calculated from the BET model, pore volumes (**V_{meso}**), estimated from the *t*-method and the pore size (**dpore**), determined by the method DFT of the mesoporous silica-based nanomaterials.

Table 8 - Textural properties of the Mesoporous Silica-Based Nanomaterials.

Material	N ₂ adsorption-desorption isotherms data		
	A _{BET} (m ² g ⁻¹)	V _{meso} ^[a] (cm ³ g ⁻¹)	dpore ^[b] (nm)
SiO ₂	1079	1.01	4.5
SiO ₂ @C ₈ TMS	248	0.23	3.7
SiO ₂ @C ₁₆ TMS	423	0.62	3.9
SiO ₂ @F ₁₃ TES	1006	0.85	3.3

^[a] Mesoporous volume. ^[b] NLDFT pore diameter (maximum of the NLDFT pore size distribution).

The specific surface area (**A_{BET}**), pore volumes (**V_{meso}**) and pore size (**dpore**) of the functionalized silica nanoparticles, decrease compared to the control (SiO₂), confirming the incorporation of the organosilanes. The pore size distributions show an increase in the pore diameter ongoing from SiO₂@C₈TMS to SiO₂@C₁₆TMS. The pore enlargement differs from the tendency reported in literature for other mesoporous silicas functionalized by co-condensation [36, 37, 63]. However, in those studies organosilanes with short alkyl chains were incorporated. Consequently, the increase of the pore size is probably related to increase the carbon chain and to the long hydrophobic chains and the interactions between organosilane, TEOS, and CTAC during the co-condensation reaction.

3.4. FTIR-ATR

Figure 25 shows the vibrational spectroscopy FTIR-ATR of the mesoporous silica-based nanomaterials, **(A)** SiO₂@C₈TMS, **(B)** SiO₂@C₁₆TMS and **(C)** SiO₂@F₁₃TES (black spectrum), in the 4000-650 cm⁻¹ (left) and 1600-650 cm⁻¹ (right) range. The dotted lines highlight the characteristic peaks of organosilane. In order to evaluate the chemical modification of the silica-based nanomaterials, the vibrational spectra of the SiO₂ (blue spectrum) and the respective organosilane (red spectrum), are also presented together.

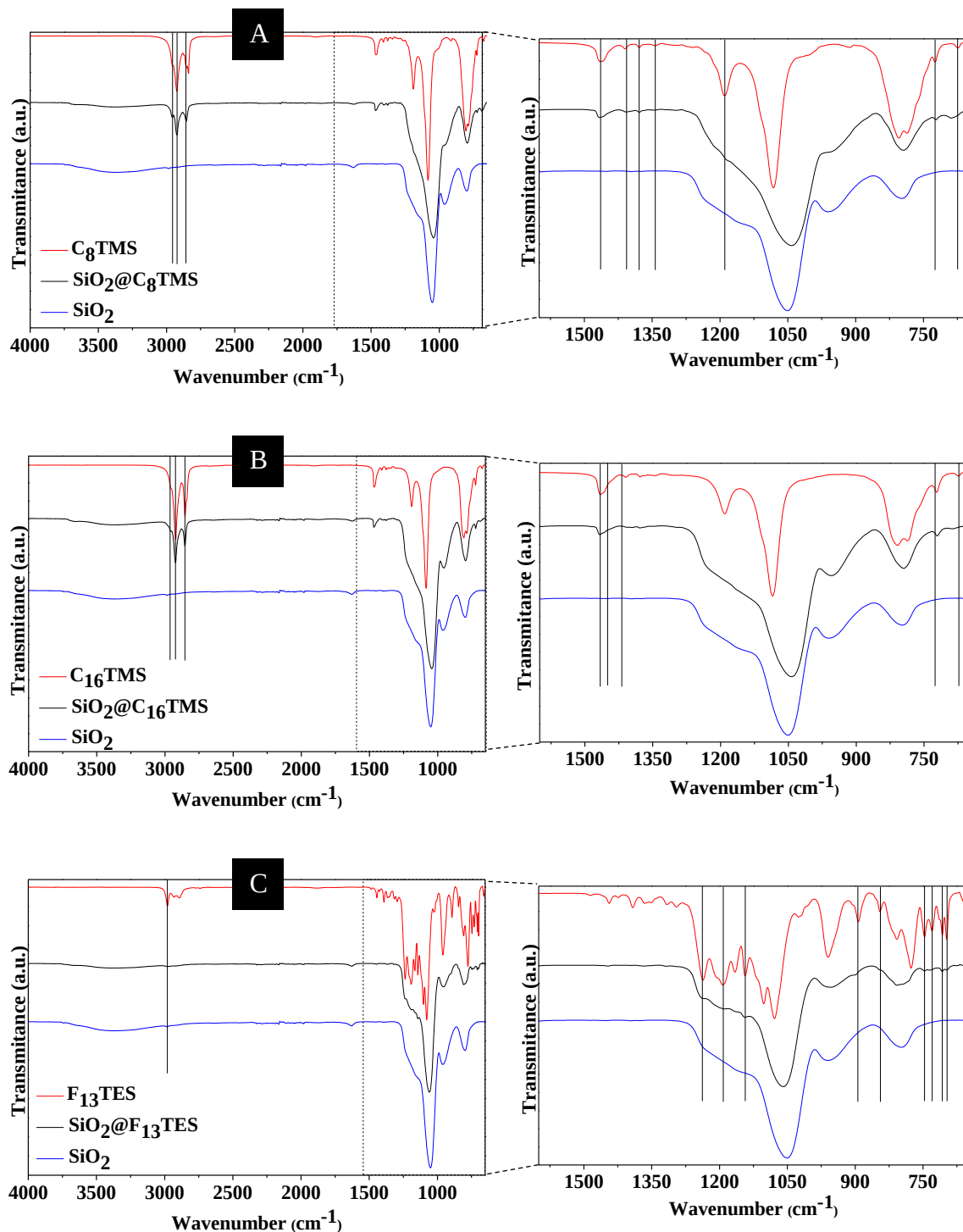


Figure 25 – FTIR-ATR spectra of **(A)** $\text{SiO}_2@\text{C}_8\text{TMS}$, **(B)** $\text{SiO}_2@\text{C}_{16}\text{TMS}$ and **(C)** $\text{SiO}_2@\text{F}_{13}\text{TES}$ nanomaterials, in the $4000\text{--}650\text{ cm}^{-1}$ (left) and $1600\text{--}650\text{ cm}^{-1}$ (right) range. The dotted lines highlight the characteristic bands of organosilane.

The infrared spectrum of SiO_2 exhibits the typical bands related to the silica network: Si-O-Si asymmetric stretching (1090 cm^{-1} with a shoulder around 1235 cm^{-1}),

Si-O stretching of Si-OH and Si-O⁻ groups (963 cm⁻¹) and Si-O-Si symmetric stretching (799 cm⁻¹) [33, 64, 65]. The spectrum also features a broad band centered around 3440 cm⁻¹ related to O-H stretching vibrations of hydrogen-bonded surface silanol groups and physically adsorbed water, with two weak shoulders around 3735 and 3654 cm⁻¹ ascribed to isolated and internal silanol groups, respectively, and a band at 1633 cm⁻¹ due to the H-O-H bending vibrations of adsorbed water [33, 65].

FTIR-ATR spectroscopy confirmed the complete removal of the template CTAC by solvent extraction, through the absence of the characteristic bands of CTAC in the spectra of the silica-based nanomaterials, namely at 1490, 1480 and 1470 cm⁻¹ ascribed to asymmetric N⁺-CH₃ deformation and C-H bending vibrations [64, 66, 67]. The weak peaks at 2982, 2936, 2906 and at 1449, 1397 and 1372 cm⁻¹ are assigned to stretching and deformation vibrations of ethoxy groups bound to silica which result from the esterification of the silica surface during template extraction with acidified ethanol [18].

The vibrational spectra of the silica-based nanomaterials, confirm the functionalization successfully. Besides displaying the characteristic bands of the SiO₂ framework (blue spectrum), are characterized by the appearance of several peaks which match well the fingerprint vibrational modes of the organosilane C₈TMS, C₁₆TMS and F₁₃TES, respectively (red spectrum), namely:

- SiO₂@C₈TMS: C-H symmetric stretching of -CH₃ (2979 cm⁻¹), C-H antisymmetric stretching of -CH₂ (2925 and 2854 cm⁻¹), C-H antisymmetric deformation of -CH₃-CH₂ (1464 cm⁻¹), C-H antisymmetric deformation of Si-CH₂ (1410 cm⁻¹), C-H symmetric deformation of -CH₂ (1379 cm⁻¹), -CH₂- deformation of (1343 and 1190 cm⁻¹) and CH₂ rocking of -CH₂- (724 and 674 cm⁻¹) vibrations [37, 64, 65];
- SiO₂@C₁₆TMS: C-H symmetric stretching of -CH₃ (2961 cm⁻¹), C-H antisymmetric stretching of -CH₂ (2922 and 2852 cm⁻¹), C-H antisymmetric deformation of -CH₃-CH₂ (1466 cm⁻¹), C-H antisymmetric deformation of Si-CH₂ (1410 cm⁻¹), C-H symmetric deformation of -CH₂ (1378 cm⁻¹) and CH₂ rocking of -CH₂- (722 and 674 cm⁻¹) vibrations [37, 64, 65];
- SiO₂@F₁₃TES: C-H symmetric stretching (2979 cm⁻¹), C-H/C-C symmetric deformation (1237-1144 cm⁻¹), C-F stretching (1237-1144 cm⁻¹) and C-F deformation (1237-1144 cm⁻¹ and 893-698 cm⁻¹ respectively) vibrations of CH₂, CF₂ and CF₃ groups [68-70].

3.5. ^{29}Si CPMAS and ^{13}C CPMAS Solid-State NMR

Figure 26 present the ^{29}Si CPMAS (A) and ^{13}C CPMAS (B) NMR spectra of the silica-based nanomaterials and the bands assignments.

The ^{29}Si CPMAS NMR spectra of all silica-based nanomaterials (**Figure 26A**), present peaks at -111 and -100 ppm, which correspond to Q^4 and Q^3 resonances, respectively, and are associated to the fully condensed silica units and to silica with one terminal silanol group; the weak Q^2 shoulder around -91 ppm, associated the geminal silanol groups, are present in the samples SiO_2 (pink spectrum) and $\text{SiO}_2@\text{F}_{13}\text{TES}$ (orange spectrum) and almost absent in the samples $\text{SiO}_2@\text{C}_8\text{TMS}$ (red spectrum) and $\text{SiO}_2@\text{C}_{16}\text{TMS}$ (blue spectrum) [58, 59, 70, 71]. In the functional silica-based nanomaterials ($\text{SiO}_2@\text{C}_8\text{TMS}$, $\text{SiO}_2@\text{C}_{16}\text{TMS}$ and $\text{SiO}_2@\text{F}_{13}\text{TES}$), two additional peaks are detected around -65 and -57 ppm which are respectively associated to T^3 and T^2 silicon environments, revealing the anchorage of C_8TMS , C_{16}TMS and F_{13}TES , respectively, through 3- and 2-fold covalent grafting [58, 59, 69, 71].

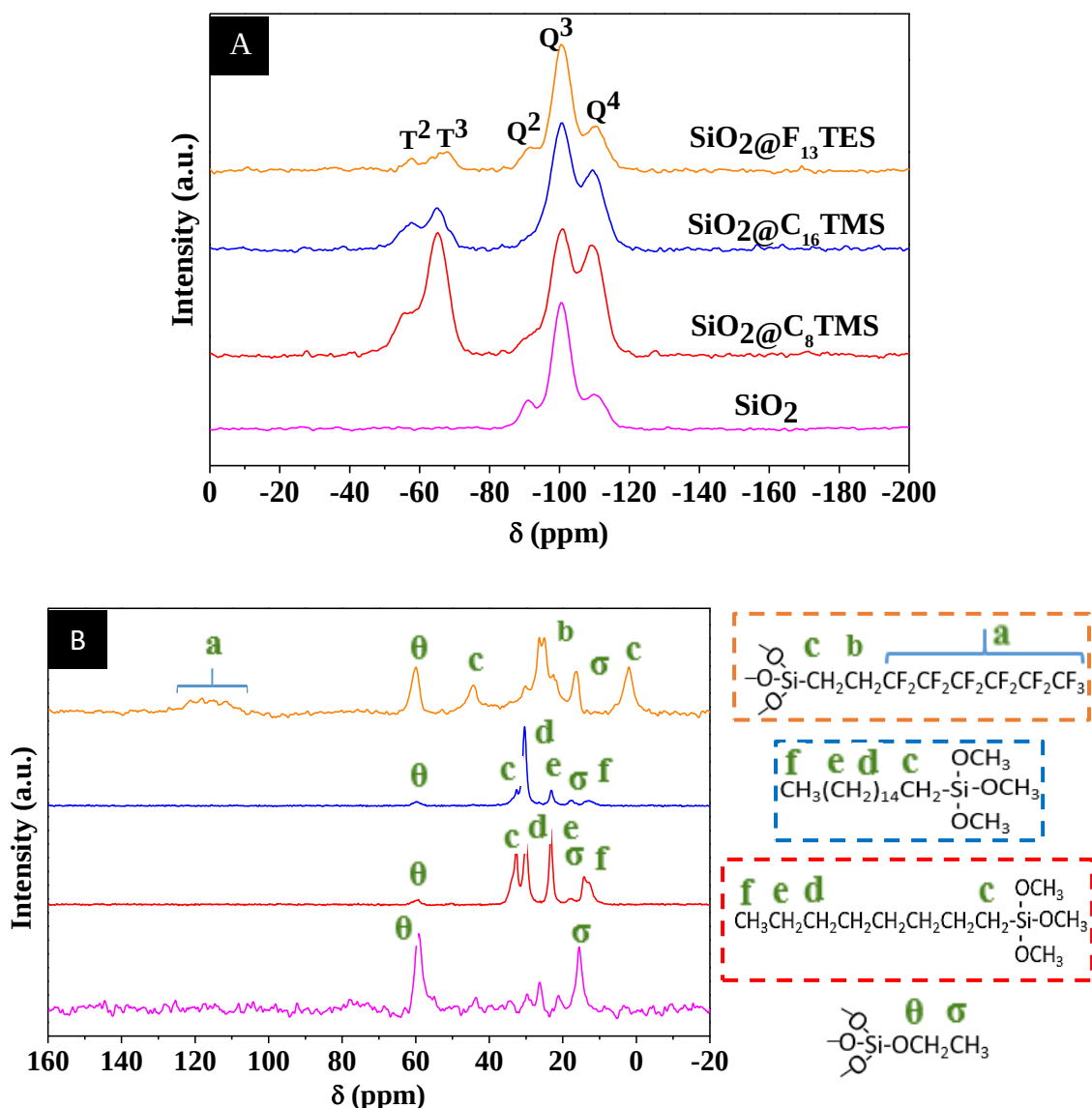


Figure 26 – (A) ^{29}Si CPMAS and (B) ^{13}C CPMAS NMR spectra of the samples: SiO_2 (pink spectrum), $SiO_2@C_8TMS$ (red spectrum), $SiO_2@C_{16}TMS$ (blue spectrum) and $SiO_2@F_{13}TES$ (orange spectrum) and the bands assignments.

The ^{13}C CPMAS NMR spectra of silica-based nanomaterials (**Figure 26B**) exhibit the characteristic chemical shifts of organosilanes C_8TMS , $C_{16}TMS$ and $F_{13}TES$ [33, 72]. The peaks at 15 (σ) and 59 (θ) ppm, present in all samples, are due to the presence of ethoxy groups generated by the incomplete hydrolysis of organosilanes [33, 72]. The absence of the characteristic resonance peaks of CTAC also proved the complete extraction of the template [55, 71].

3.6. TGA

Functionalization efficiency was also confirmed by TGA analysis. The thermograms of the pristine and functionalized SiO₂ are shown in **Figure 27**. In the **Table 9** are summarized the total and partial weight loss for each degradation level.

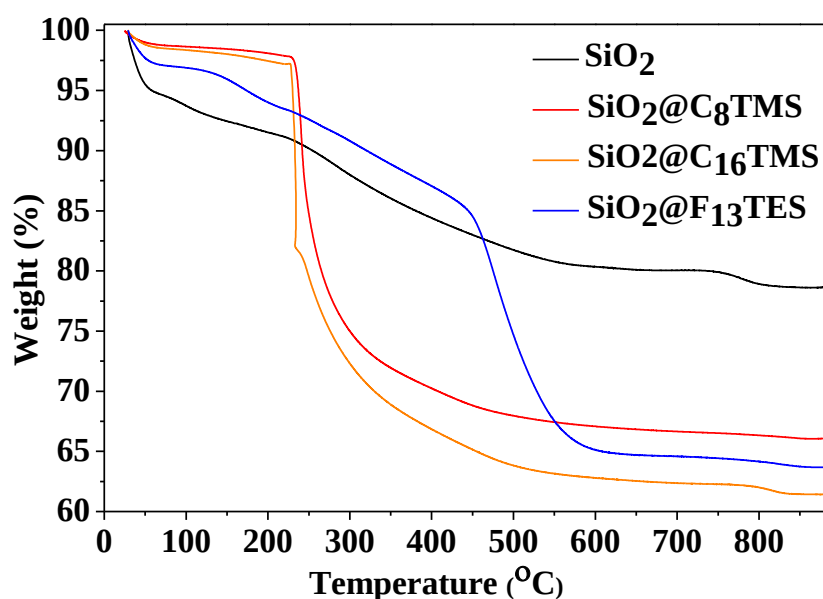


Figure 27 – Thermogravimetric curves of the samples: SiO₂ (black curve), SiO₂@C₈TMS (red curve), SiO₂@C₁₆TMS (orange curve) and SiO₂@F₁₃TES (blue curve), under O₂ atmosphere.

Table 9 – Weight loss for each degradation level obtained through the thermogravimetric curves.

Samples	1° weight loss (%)	2° weight loss (%)	3° weight loss (%)	Total (%)
SiO ₂	8.1 [29 – 178 °C]	11.8 [178 – 698 °C]	1.4 [698 – 834 °C]	21.3
SiO ₂ @C ₈ TMS	2.3 [29 – 229 °C]	31.6 [229 – 896 °C]	-	33.9
SiO ₂ @C ₁₆ TMS	2.8 [29 – 228 °C]	35.0 [228 – 780 °C]	0.8 [780 – 839 °C]	38.6
SiO ₂ @F ₁₃ TES	6.2 [29 – 205 °C]	28.9 [205 – 609 °C]	1.20 [609 – 862 °C]	36.3

The SiO₂ thermogram (**black curve**) presents an initial weight loss of 8.1% in the temperature range of 29-178 °C due to the loss of physisorbed water and ethanol from the porous structure [69, 72]. Two more weight losses of 13.2% are observed in the range of 178-834 °C, with the major weight loss rates occurring between 178-698 °C. This second and third weight losses arises from the dehydroxylation of the silica surface and from the decomposition of ethoxy moieties [58, 72].

The thermograms of the functionalized SiO₂ (**red, orange and blue curves**) present similar profiles, being possible to identify the existence of two main steps of weight losses. The first, in the temperature range of ~ 29 to 205 °C, is attributed to the removal physisorbed water, and the second one, which occurs in the range of ~ 178 to 862 °C, is associated with the decomposition of the organosilane organic chain (first and significant inflection) and with the dehydroxylation of the silica surface (second inflection) [69].

3.7. XPS

The surface atomic percentages and core-level binding energies (BEs) of the different elements determined by XPS are summarized in **Table 10** and **Table 11**, respectively.

Table 10 – Surface atomic percentages for silica-based materials obtained by XPS^[a].

Sample	Atomic (%)			
	C 1s	O 1s	Si 2p	F 1s
SiO ₂	19.2	55.5	25.3	-
SiO ₂ @C ₈ TMS	47.7	34.8	17.5	-
SiO ₂ @C ₁₆ TMS	66.4	24.4	9.2	-
SiO ₂ @F ₁₃ TES	13.5	43.6	21.1	21.8

^[a] Determined by the areas of the respective peaks in the high-resolution XPS spectra.

Table 11 - Core-level binding energy and area of each component for silica nanomaterials obtained by curve fitting of XPS spectra.

Sample	C 1s		O 1s		Si 2p		F 1s	
	BE ^[a] (eV)	Area ^[b] (%)	BE ^[a] (eV)	Area ^[b] (%)	BE ^[a] (eV)	Area ^[b] (%)	BE ^[a] (eV)	Area ^[b] (%)
SiO ₂	284.6 (1.6)	61.4	533.5 (1.4)	93.6	104.1 (1.4)	100	-	-
	286.5 (1.6)	33.9	535.5 (1.4)	6.4	-	-	-	-
	288.6 (1.6)	4.7	-	-	-	-	-	-
SiO ₂ @C ₈ TMS	284.6 (1.5)	68.6	532.9 (1.5)	93.8	103.4 (1.4)	97.8	-	-
	286.2 (1.5)	28.6	535.0 (1.5)	6.2	105.2 (1.4)	2.2	-	-
	288.3 (1.5)	2.8	-	-	-	-	-	-
SiO ₂ @C ₁₆ TMS	284.6 (1.6)	70.0	532.9 (1.4)	94.0	103.5 (1.4)	97.9	-	-
	286.1 (1.6)	24.6	535.0 (1.4)	6.0	105.4 (1.4)	2.1	-	-
	288.2 (1.6)	5.4	-	-	-	-	-	-
SiO ₂ @F ₁₃ TES	284.6 (1.6)	23.1	532.6 (1.5)	95.8	103.1 (1.8)	100	688.6 (2.1)	100
	286.0 (1.6)	14.7	534.5 (1.5)	4.2	-	-	-	-
	288.1 (1.6)	5.9	-	-	-	-	-	-
	290.8 (1.6)	44.5	-	-	-	-	-	-
	293.2 (1.6)	11.8	-	-	-	-	-	-

^[a] The values between brackets refer to the FWHM of the bands. ^[b] Relative area of each component in the different core-level regions.

In all samples, the absence of nitrogen and chlorine confirmed the efficient template extraction.

The SiO₂ sample is mainly composed by oxygen and silicon, but a small quantity of carbon (19.2%) is also detected (**Table 10**). The O 1s and Si 2p high-resolution spectra exhibit bands centered at 533.5 and 104.1 eV respectively (**Table 11**), which are typical values for lattice oxygen and silicon in pure silica [33, 34]. In the O 1s region is also observed a small shoulder around 535.5 eV, which is probably related to C-O bonds from ethoxy groups due to surface esterification. The high-resolution C 1s spectrum (**Table 11**) could be deconvoluted into three components. The main components, centered at 284.6 and 286.5 eV, are assigned to C-H/C-C and C-O bonds, respectively from the ethoxy moieties on the nanomaterials surface [34].

The increase in the atomic percentage of carbon in the samples SiO₂@C₈TMS and SiO₂@C₁₆TMS compared to sample SiO₂ and C/Si ratios increase in the order of SiO₂@C₈TMS < SiO₂@C₁₆TMS, certify the incorporation of alkyl chains (organosilanes C₈TMS and C₁₆TMS) (**Table 10**). The appearance of a strong band in the F 1s spectra at 688.6 eV and new bands in the C 1s spectra in the sample SiO₂@F₁₃TES related to C-H/C-C (284.6 eV), C-O/-CF₂-CH₂- (286.0 eV), -CF₂-CH₂- (288.1 eV), -CF₂-CF₂- (290.8 eV) and CF₃-CF₂- (293.2 eV) groups confirm the incorporation of fluoroalkyl chains (organosilane F₁₃TES) [33, 34].

3.8. Evaluation of easy-cleaning properties

The easy-cleaning properties were evaluated by measuring the contact angles. In **Figure 28** are illustrated representative photographs of deionized water, toluene, cyclohexane and artificial sweat droplets on the surface of the silica-based nanomaterials pellets and the corresponding contact angles (CA).

Sample	Liquid			
	Water	Toluene	Cyclohexane	Artificial Sweat
SiO_2				 
$\text{SiO}_2@\text{C}_8\text{TMS}$	91.0°	47.2°	39.2°	34.1°
$\text{SiO}_2@\text{C}_{16}\text{TMS}$	94.2°	66.9°	63.0°	57.7°
$\text{SiO}_2@\text{F}_{13}\text{TES}$	145.0°	97.4°	96.3°	95.5°
				 

Figure 28 - Contact angle between deionized water, toluene, cyclohexane, artificial sweat and the silica-based nanomaterials.

In the SiO_2 sample, all liquids droplets are almost immediately absorbed, demonstrating that the surface is amphiphilic. In contrast, in the functionalized silica-based nanomaterials ($\text{SiO}_2@\text{C}_8\text{TMS}$, $\text{SiO}_2@\text{C}_{16}\text{TMS}$ and $\text{SiO}_2@\text{F}_{13}\text{TES}$ samples), the CA increase in relation of the pristine SiO_2 sample. These results evidenced that the nanoparticles were functionalized successfully, proving the previous results.

This evidence are directly related to the surface chemical composition of the nanomaterials, in particular with: (1) the gradual decrease of the amount of silanol groups and physisorbed water on the nanomaterials surface and, (2) the progressive enrichment of the surface with carbon (alkyl chains, in the case of organosilanes C_8TMS and C_{16}TMS) and fluoroalkyl chains (in the case of organosilane F_{13}TES), functional entities which provide low-surface-energy and therefore promote the repellency properties to the nanomaterials [73].

Additionally, two trends are observed: the CA increases in the order $\text{SiO}_2@\text{C}_8\text{TMS} < \text{SiO}_2@\text{C}_{16}\text{TMS} < \text{SiO}_2@\text{F}_{13}\text{TES}$, reaching 149.8° (for water), in the case of $\text{SiO}_2@\text{F}_{13}\text{TES}$, a threshold value of superhydrophobic ($\text{CA} > 150^\circ$); the greater the difference between the surface tension of the liquid (water – 72.8; toluene – 28.5 and

cyclohexane – 25.0 at 20 °C (10^{-2} mN/m) and the surface energy of the silica nanoparticles, the greater the CA [33, 37].

The degree of repellency observed is due to the fact that the surface energy of fluoroalkoxysilanes, F₁₃TES is lower than alkoxysilanes, C₈TMS and C₁₆TMS and the surface energy of the organosilane C₁₆TMS is lower than organosilane C₈TMS. The Laplace force changes with the number of carbon atoms in the organosilane molecules (the higher the number of carbons in the organosilane, the lower the surface energy) [33, 37].

3.9. Conclusions

The spherical silica nanoparticles with average particle size around 51 ± 4 nm, narrow size distribution, wormhole-type mesoporous structure and high porosity were synthesized, as evidenced by DLS and morphological (SEM and TEM) and textural (N₂ adsorption-desorption isotherms at -196 °C) characterization.

The results obtained by EDS, N₂ adsorption-desorption isotherms at -196 °C, FTIR-ATR, RMN, TGA and XPS, indicate an efficient functionalization of the silica nanoparticles with the organosilanes C₈TMS, C₁₆TMS and F₁₃TES. The functionalized hybrid silica nanoparticles didn't evinced morphological and size differences in relation to pure silica.

The solid-state NMR analysis revealed that the functionalization occurred by a mechanism of anchorage through 3- and 2-fold covalent grafting.

The functionalized silica nanoparticles (SiO₂@C₈TMS, SiO₂@C₁₆TMS and SiO₂@F₁₃TES) presented phobicity to water, toluene, cyclohexane and artificial sweat, whereas the pristine silica nanoparticles (SiO₂) presented philicity to these liquids.

In view of these results, these functionalized silica-based nanomaterials are potential candidates for the development of surfaces with easy-cleaning properties. Consequently, in the second part of this work, we prepared functional BCM modified with these functionalized silica-based nanomaterials through the in situ and post-grafting methodology and investigated their repellency properties.

CHAPTER 4

Functional Silica Nanoparticles from rice husk

4. Functional Silica Nanoparticles from rice husk

Control and pre-treated rice husk were characterized by FTIR-ATR, X-ray fluorescence and TGA. The morphology and chemical composition of the silica nanoparticles from rice husk and respective functional silica nanoparticles (with easy-cleaning and natural-based colored properties) were characterized and their properties evaluated. The results and respective discussion, by means of the characterization techniques used, are presented in this chapter.

4.1. Characterization of rice husk

In **Figure 29** is represented the photograph of the rice husk without (rice-0 (**A**)) and with pretreatment (rice-1 (method A) – (**B**) and rice (method B) – (**C**)).



Figure 29 - Photographs of rice husk without (rice-0 (**A**)) and with pre-treatment (rice-1 (**B**) and rice (**C**)).

Both pre-treatments (method A and method B) (**Figure 29 (B and C)**) show a characteristic color change of the residue (amber). This evidence may be indicative that the both pre-treatment was efficient for the removal of impurities and metal oxides, being in agreement with the reported in the literature [74].

4.1.1. FTIR-ATR

Figure 30 shows the vibrational spectroscopy FTIR-ATR of **rice (blue spectrum)**, **rice-1 (red spectrum)** and **rice-0 (black spectrum)** samples in the 4000-400 cm^{-1} range.

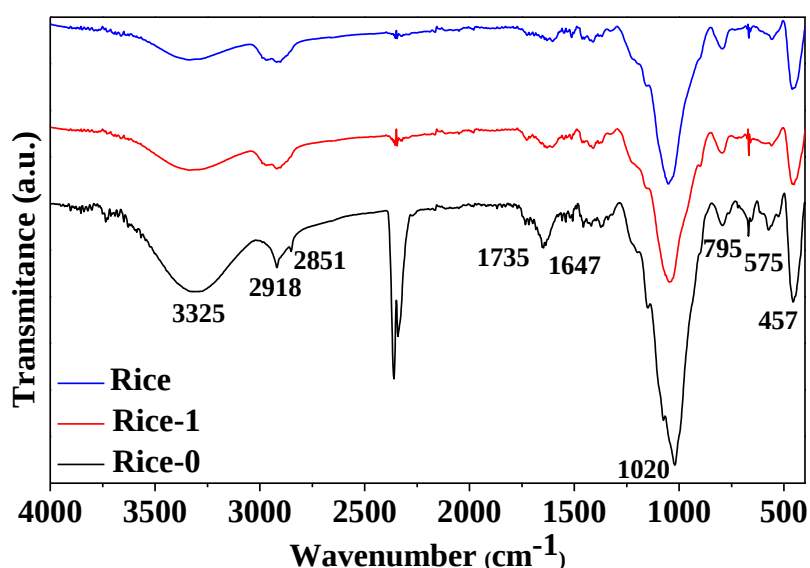


Figure 30 – FTIR-ATR spectra of Rice (blue spectrum), Rice-1 (red spectrum) and Rice-0 (black spectrum) samples, in the 4000-400 cm^{-1} range.

The FTIR-ATR spectrum of the sample Rice-0 displays the characteristic bands of this agro-industrial waste: stretching of O-H bonds of water molecules or of O-H bonds present in cellulose, lignin hemicellulose (3325 cm^{-1}), C-H symmetric stretching of $-\text{CH}_3$ (2918 cm^{-1}) and C-H antisymmetric stretching of $-\text{CH}_2$ (2851 cm^{-1}) of the cellulose, hemicellulose and lignin structure, C = C stretching of the aromatic ring of the structure of lignin, cellulose and hemicellulose (1735 cm^{-1} and 1647 cm^{-1}), symmetric stretching ($1200\text{-}1000 \text{ cm}^{-1}$) and antisymmetric stretching (795 cm^{-1}) of Si-O-Si of the silica and O-Si-O deformation of $-\text{O-Si-O-}$ (575 cm^{-1} and 457 cm^{-1}) vibrations [75].

Regardless of pre-treatment and type of pre-treatment (method A and method B), the FTIR-ATR spectrum show similar vibrational bands, with only a few differences in the wavenumber.

4.1.2. TGA

The thermograms of the samples rice-0, rice-1 (method A) and rice (method B) have an identical thermographic profile with three different weight loss levels. The TGA curves and the respective derivative of the samples rice-0 (**A**) and rice (**B**) are show in

Figure 31. In the **Table 12** are summarized the total and parcial weight loss for each degradation level for the three samples.

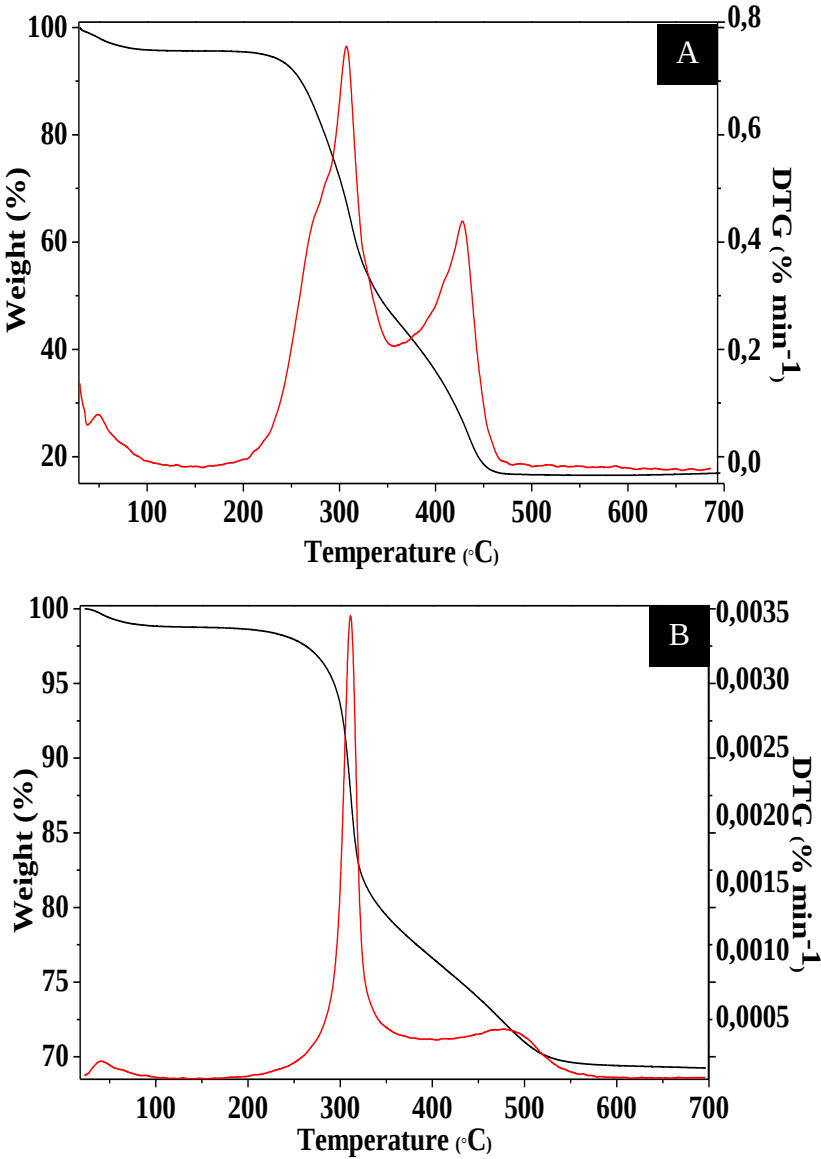


Figure 31 - TGA curves of the samples (A) rice-0 and (B) rice.

Tabela 12 – Weight loss for each degradation level obtained through the thermogravimetric curves.

Samples	Partial weight loss (%)			Total weight loss (%)	Residue coloring
	1	2	3		
Rice-0	4.2 [29-106°C]	47.9 [186 – 349 °C]	30.6 [349 – 590 °C]	82.7	Grey
Rice-1 (method A)	1.2 [22-120°C]	22.0 [174 – 397 °C]	7.4 [397 – 695 °C]	30.6	White
Rice (method B)	1.1 [23-122°C]	21.8 [171 – 395 °C]	7.1 [396 – 696 °C]	30.0	White

In the case of the thermogram of the sample rice (method B), the first degradation level (1) with an initial weight loss of 1.2% in the temperature range of 22-162 °C is due to the loss of physisorbed water; the second degradation level (2) with a weight loss of 29.2% in the temperature range of 162-556 °C is due to the devolatilization of hemicellulose and cellulose and the last degradation level (3) with a weight loss of 0.3% in the temperature range of 556-675 °C is due to the decomposition of lignin [28].

The residue resulting from the rice-1 (method A) and rice (method B) sample, after thermogravimetric analysis, showed a white colouring, suggesting that the both pre-treatment was efficient in purifying the agro-industrial waste.

The thermogravimetric analysis allowed to evaluate the thermal degradation profile of rice husk: from 30 to 700 °C under an oxygen atmosphere, at a heating rate of 5°C/min and a stay at 700 °C for two hours.

4.1.3. X-ray fluorescence

The percentage by mass of the elements, determined by X-ray fluorescence, present in samples rice-0, rice-1 (method A) and rice (method B) is summarized in **Table 13**.

Table 13 - Percentage by mass of the elements present in the samples rice-0, rice-1 and rice.

Sample	% Elements (wt/wt)						
Rice-0	SiO₂	P₂O₅	K₂O	CaO	Cr₂O₃	MnO	Fe₂O₃
	19,886	0,210	0,080	0,398	0,006	0,102	0,028
Rice-1	SiO₂	P₂O₅	K₂O	CaO	Cr₂O₃	MnO	Fe₂O₃
	20,322	0,123	0,031	0,295	0,004	0,060	0,022
Rice	SiO₂	P₂O₅	K₂O	CaO	Cr₂O₃	MnO	Fe₂O₃
	20,532	0,107	0,020	0,220	0,003	0,055	0,018

The samples presents predominantly SiO₂ in its composition (~20% wt/wt). Additionally, in a small percentage, the presence of metallic oxides is verified. The metallic oxides decreased with pre-treatment, being more significant with the hydrothermal process (method B). These results suggest that the hydrothermal process was more efficient in eliminating the metal oxides.

4.2. Characterization of silica nanoparticles from rice husk

In **Figure 32** are represented the photographs of the samples resulting of heat treatment of rice husk without (SiO₂-rice-0 (**A**)) and with (SiO₂-rice-1 (**B**) and SiO₂-rice (**C**)) pre-treatment.

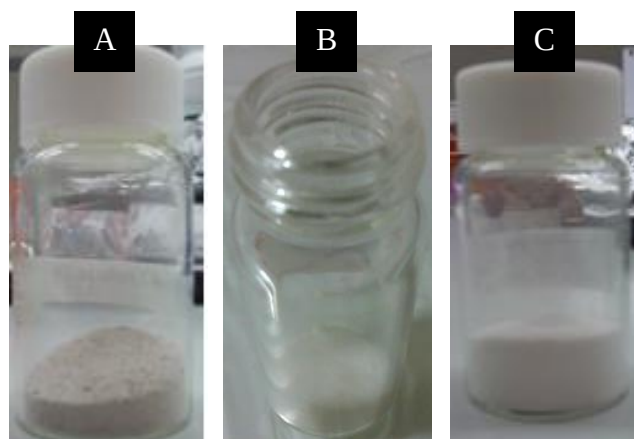


Figure 32 – photographs of the samples resulting of heat treatment of rice husk without SiO₂-rice-0 (**A**) and with SiO₂-rice-1 (**B**) and SiO₂-rice (**C**) pre-treatment.

The both pre-treatment (**Figure 32 (B)** and (**C**)) (method A and method B, respectively), allowed obtaining particles with white coloration, while the resulting sample without the pre-treatment (**Figure 32 (A)**) presented a gray coloration. This result suggests that the both pre-treatment was efficient in purifying of the rice husk, which was confirmed by FTIR-ATR and X-ray fluorescence analysis.

4.2.1. FTIR-ATR

Figure 33 shows the vibrational spectroscopy FTIR-ATR of rice husk submitted to hydrothermal pre-treatment, method B (rice) and respective sample obtained after heat treatment (SiO₂-rice) in the 4000-400 cm⁻¹ range.

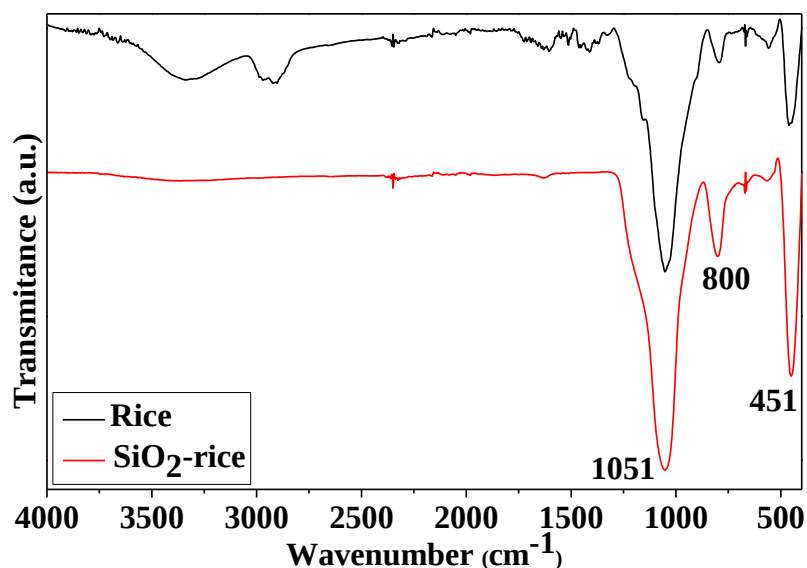


Figure 33 – FTIR-ATR spectra of Rice (black spectrum) and Rice-1 (red spectrum) samples, in the 4000-400 cm^{-1} range.

Comparing the FTIR-ATR spectra of the sample rice with the FTIR-ATR spectra of the sample SiO_2 -rice, it's possible to verify that all characteristic bands of rice husk have disappeared (presented in **section 4.1.1**), except the bands at 1051 cm^{-1} (Si-O-Si symmetric stretching vibrations), 800 cm^{-1} (Si-O-Si symmetric stretching vibrations) and 451 cm^{-1} (O-Si-O deformation vibrations of $-\text{O-Si-O}-$), characteristic of silica.

4.2.2. X-ray fluorescence

The percentage by mass of the elements, determined by X-ray fluorescence, present in samples SiO_2 -rice-1 (obtain by method A) and SiO_2 -rice (obtain by method B – hydrothermal process) is summarized in **Table 14**.

Table 14 - Percentage by mass of the elements present in the samples SiO₂-rice-1 and SiO₂-rice.

Sample	% Elements (wt/wt)		
	SiO ₂	CaO	Fe ₂ O ₃
SiO ₂ -rice-1	(98.602)	(0.610)	(0.788)
SiO ₂ -rice	(99.666)	(0.131)	(0.203)

The samples SiO₂-rice-1 and SiO₂-rice presents predominantly SiO₂ in its composition. Additionally, in a small percentage, the presence of metallic oxides (CaO and Fe₂O₃) is verified, being practically insignificant in sample SiO₂-rice. These results confirm that the hydrothermal process was more efficient in eliminating the metallic oxides of the rice husk. This process (method B) allowed to obtain silica with high purity, in a more sustainable, environmentally friendly and economical way.

The morphological and textural properties of sample SiO₂-rice are presented below.

4.2.3. TEM and EDS

In the **Figure 34** are illustrated the TEM micrographs and particles size distribution histogram, determined by TEM image analysis, of the SiO₂-rice sample. In the TEM micrograph is identified (red square) where the EDS analysis (**Figure 35**) was performed. The **Figure 35** show the EDS spectra (inset: atomic percentages of C, O and Si) of this sample.

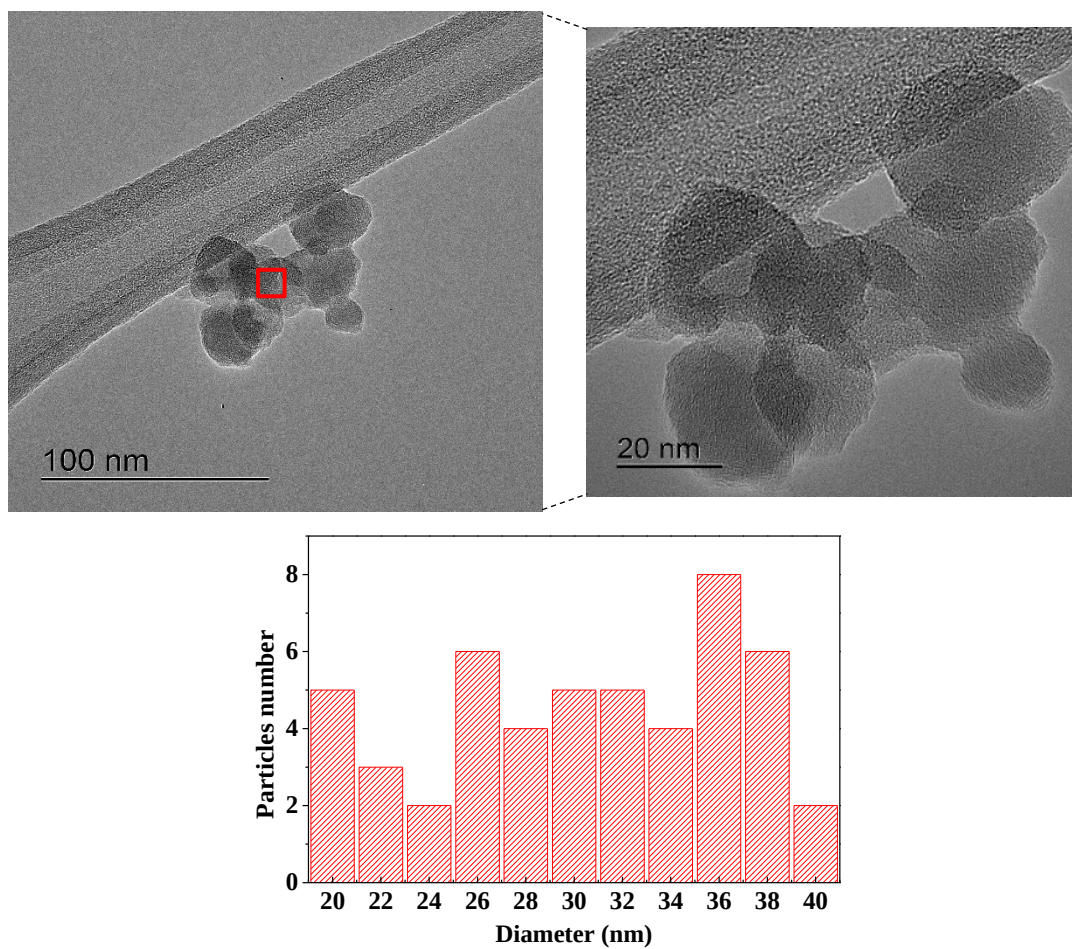


Figure 34 – TEM micrographs and particles size distribution histogram of SiO₂-rice sample.

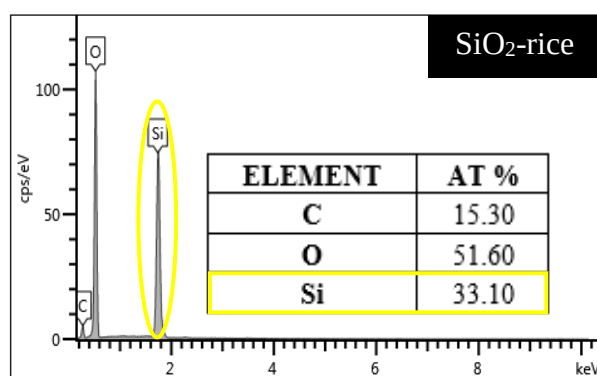


Figure 35 – EDS spectra of SiO₂-rice sample.

The TEM images and particle size distribution histogram show that the sample SiO₂-rice is composed of nearly spherical nanoparticles with heterogeneous particle size (20-40 nm). These nanoparticles exhibit porous structure, being in agreement with the results obtained by the N₂ adsorption-desorption isotherms at -196 °C (**Figure 36** and **Table 15**).

The EDS spectra from TEM experiment confirm the presence of silica through the identification of the peaks Si and O. The element C is also identified, due to the coating of the samples with this element and the tape used to fix the sample to the support.

4.2.4. N₂ adsorption-desorption isotherms at -196 °C

In **Figure 36** is represented the N₂ adsorption-desorption isotherms at -196 °C of the SiO₂-rice sample. This material exhibit type II isotherm, according to *BDDT* (Brunauer, Deming, Deming and Teller) classification, which are characteristic of non-porous, macroporous or mesoporous materials [36].

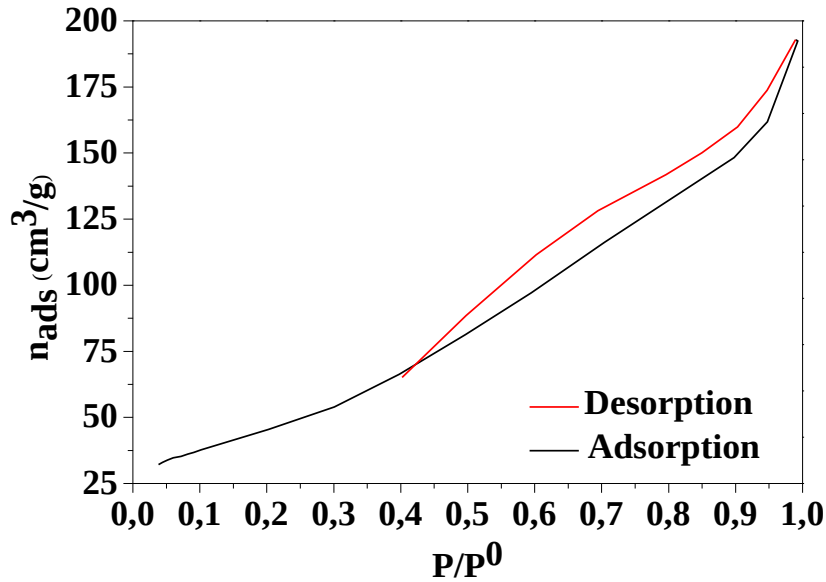


Figure 36 - N₂ adsorption-desorption isotherms at -196 °C of SiO₂-rice sample.

The **Table 15** presents the N₂ adsorption-desorption isotherms data, namely the specific surface area BET (**A_{BET}**), determined by the method BET, pore volume (**V_{pore}**),

determined by the method DFT and the pore size (**dpore**), determined by the method DFT of the SiO₂-rice sample.

Table 15- Textural properties of the SiO₂-rice sample.

Sample	N ₂ adsorption-desorption isotherms data		
	A _{BET} (m ² g ⁻¹)	V _{pore} ^a (cm ³ g ⁻¹)	d _{pore} ^b (nm)
SiO ₂ -rice	248	0.29	3.7

^a Mesoporous volume. ^b NLDFT pore diameter (maximum of the NLDFT pore size distribution).

Through the analysis of the **Table 15** it is verified that the SiO₂-rice sample present a specific surface area of 248 m² g⁻¹, pore volume of 0.29 cm³ g⁻¹ and pore size of 3.7 nm, presenting associated mesoporous.

The silica nanoparticles, SiO₂-rice, were functionalized by post-grafting methodology, with organosilane F₁₃TES, in order to obtain easy-cleaning properties (SiO₂@F₁₃TES-rice), and with curcuma (SiO₂@cur-rice).

The results by means of the characterization techniques used are presented below. In order to evaluate the modifications of the functionalized SiO₂, the results of the characterization of these nanomaterials SiO₂@F₁₃TES-rice and SiO₂@cur-rice), are presented together with the results of the characterization of the pristine silica, SiO₂-rice.

4.3. Characterization of silica nanoparticles from rice husk with easy-cleaning properties

SiO₂@F₁₃TES-rice were characterized by TEM, EDS, FTIR-ATR, ²⁹Si CPMAS and ¹³C CPMAS Solid-State NMR, N₂ adsorption-desorption isotherms at -196 °C, TGA and contact angle. The results and respective discussion, by means of the characterization techniques used, are presented below.

4.3.1. TEM-EDS

In the **Figure 37** are illustrated the TEM micrographs and particles size distribution histogram, determined by TEM image analysis, of the SiO₂@F₁₃TES-rice sample. In the TEM micrograph is identified (red square) where the EDS analysis (**Figure 38**) was performed. The **Figure 38** show the EDS spectra (inset: atomic percentages of C, O and Si) of this sample.

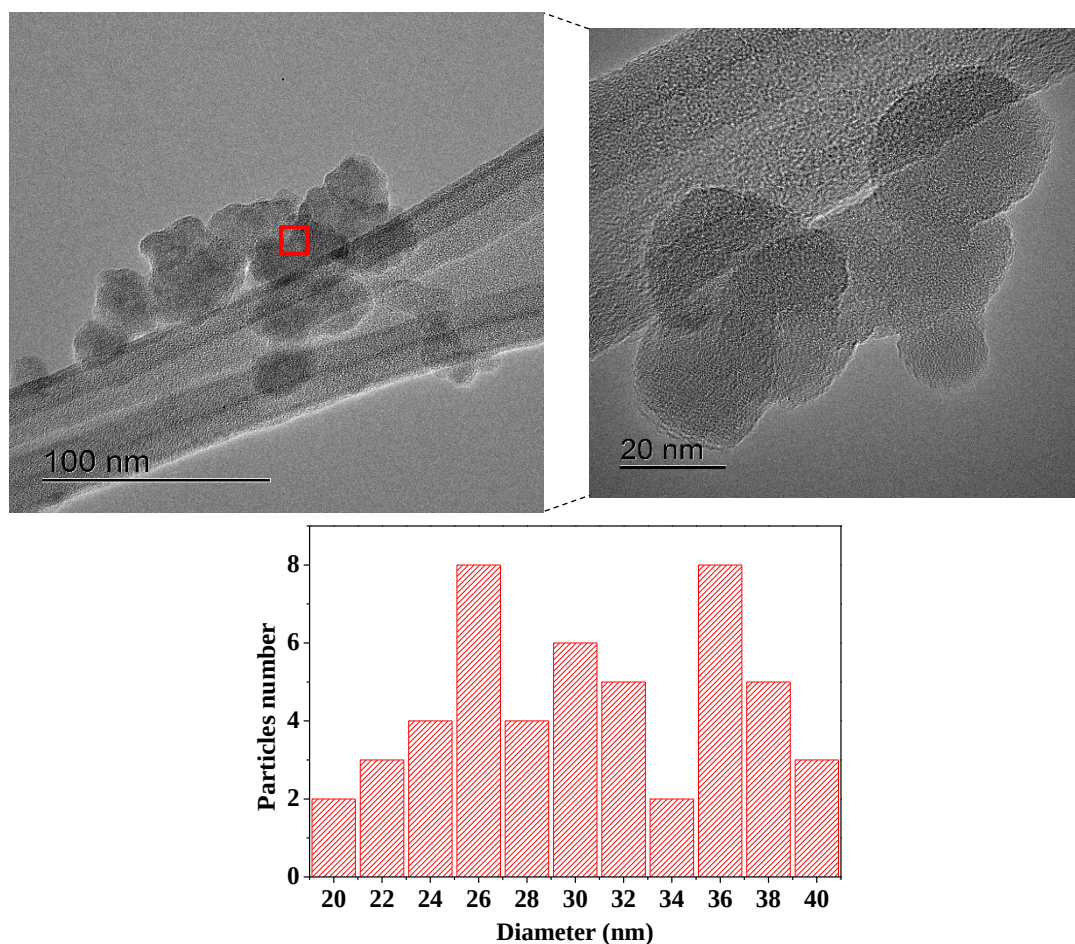


Figure 37 – TEM micrographs and particles size distribution histogram of SiO₂@F₁₃TES-rice sample.

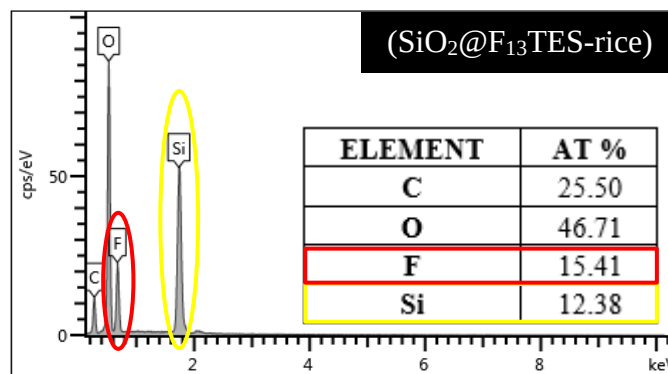


Figure 38 – EDS spectra of SiO₂@F₁₃TES-rice sample.

The TEM images and particle size distribution histogram show that after functionalization with organosilane F₁₃TES, there was a preservation of the morphology (spherical) and size (heterogeneous size, 20-40 nm) of the silica nanoparticles.

The EDS spectra from TEM analysis evidences the incorporation of organosilane F₁₃TES through the identification of the peak of F.

4.3.2. FTIR-ATR

Figure 39 shows the vibrational spectroscopy FTIR-ATR of the SiO₂@F₁₃TES-rice (black spectrum), in the 4000-400 cm⁻¹ (left) and 1600-400 cm⁻¹ (right) range. The dotted lines highlight the characteristic bands of organosilane F₁₃TES. In order to evaluate the chemical modification of the SiO₂-rice, the vibrational spectra of the SiO₂-rice (blue spectrum) and the respective organosilane F₁₃TES (red spectrum), are also presented together.

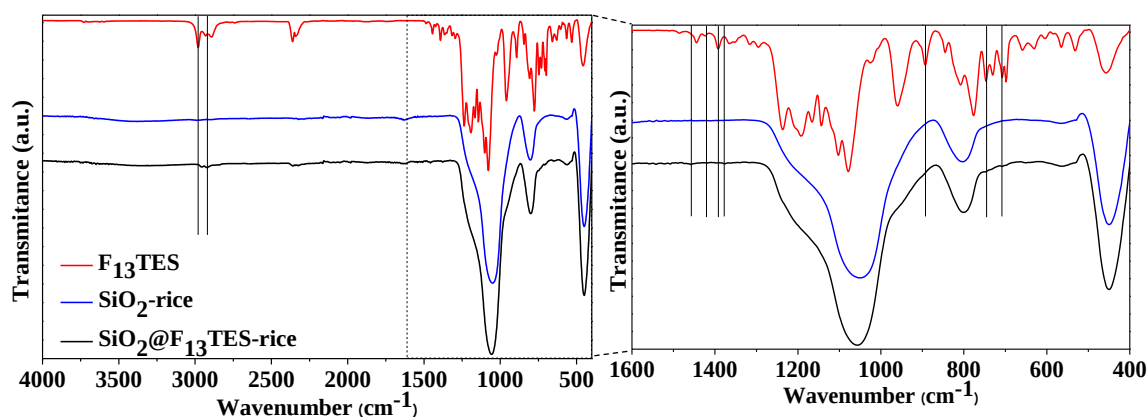


Figure 39 – FTIR-ATR spectra of SiO₂@F₁₃TES-riz, in the 4000-400 cm⁻¹ (left) and 1600-400 cm⁻¹ (right) range. The dotted lines highlight the characteristic peaks of organosilane F₁₃TES.

The vibrational spectra of the SiO₂@F₁₃TES-rice (black spectrum) confirm the functionalization successfully. Besides displaying the characteristic bands of the SiO₂ framework (blue spectrum) (description of the characteristic bands of the SiO₂ in **chapter 3, section 3.4**), the FTIR-ATR spectra is characterized by the appearance of several bands which match well the fingerprint vibrational modes of the pure organosilane F₁₃TES (red spectrum): C-H symmetric stretching (2979 and 2932 cm⁻¹), C-H/C-C symmetric deformation (1445-1367 cm⁻¹), C-F stretching (1445-1367 cm⁻¹) and C-F deformation (1445-1367 cm⁻¹ and 893-708 cm⁻¹ respectively) vibrations of CH₂, CF₂ and CF₃ groups [68-70].

4.3.3. ²⁹Si CPMAS and ¹³C CPMAS Solid-State NMR

Figure 40 present the ²⁹Si CPMAS (**A**) and ¹³C CPMAS (**B**) NMR spectra of the SiO₂-rice and SiO₂@F₁₃TES-rice and the bands assignments.

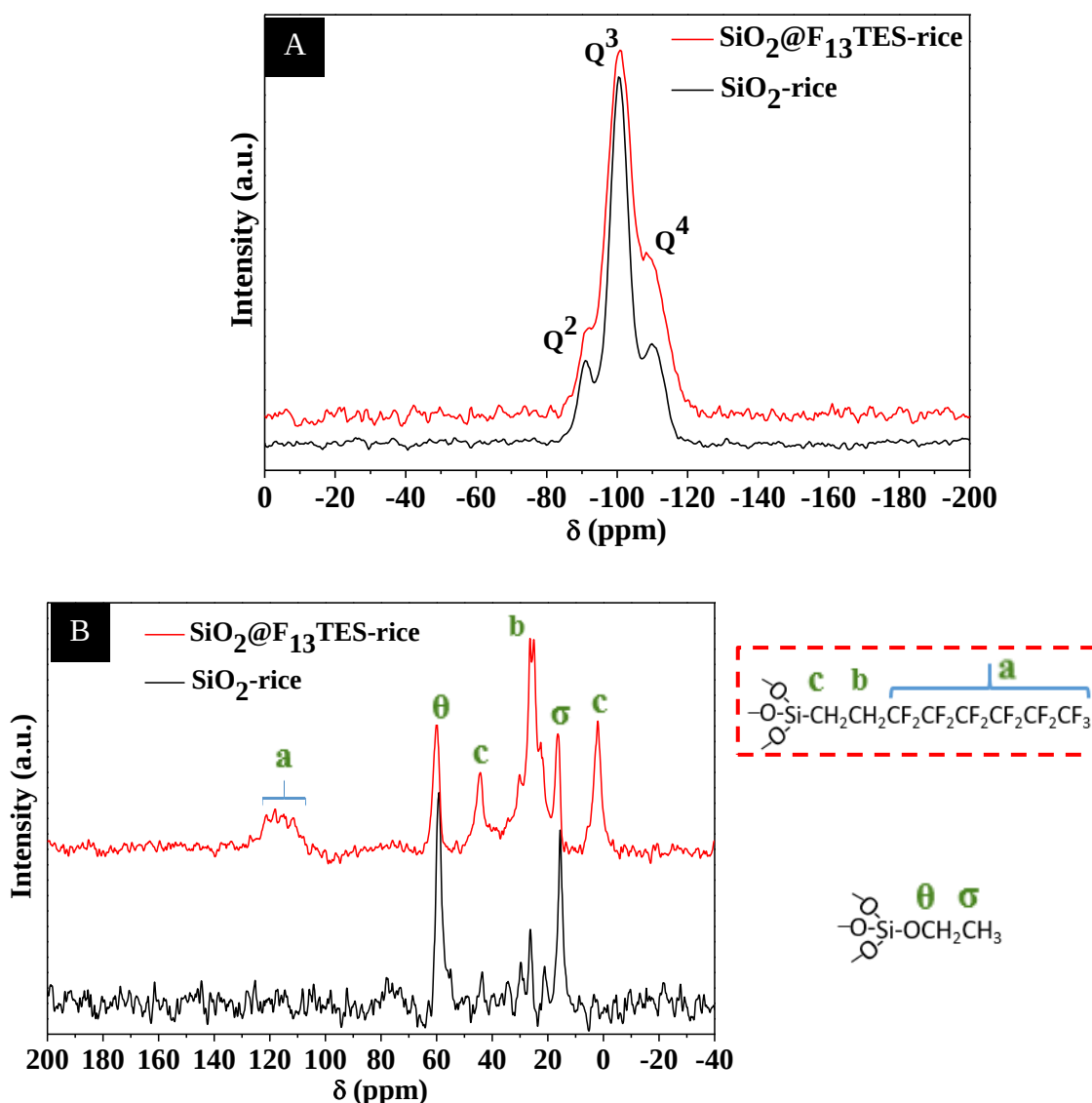


Figure 40 – (A) ^{29}Si CPMAS and (B) ^{13}C CPMAS NMR spectra of the samples: $\text{SiO}_2\text{-rice}$ (black spectrum) and $\text{SiO}_2@\text{F}_{13}\text{TES-rice}$ (red spectrum) and the bands assignments.

The ^{29}Si CPMAS NMR spectra of $\text{SiO}_2@\text{F}_{13}\text{TES-rice}$ (**Figure 40A**), present bands at -108, -101 and 91 ppm, which correspond to Q^4 , Q^3 and Q^2 resonances, respectively, and are associated to the fully condensed silica units, silica with one terminal silanol group and the germinal silanol groups [58, 59, 70].

The ^{13}C CPMAS NMR spectra of $\text{SiO}_2@\text{F}_{13}\text{TES-rice}$ (**Figure 40B**) exhibit the characteristic chemical shifts of organosilane F_{13}TES [70]. The peaks at 15 (σ) and 59 (θ) ppm, are due to the presence of ethoxy groups generated by the incomplete hydrolysis of F_{13}TES [58, 70].

4.3.4. N₂ adsorption-desorption isotherms at -196 °C

In **Figure 41** are represented the N₂ adsorption-desorption isotherms at -196 °C of the (A) SiO₂-rice and (B) SiO₂@F₁₃TES-rice. The nanomaterials exhibit type II isotherms, which are characteristic of non-porous, macroporous or mesoporous materials.

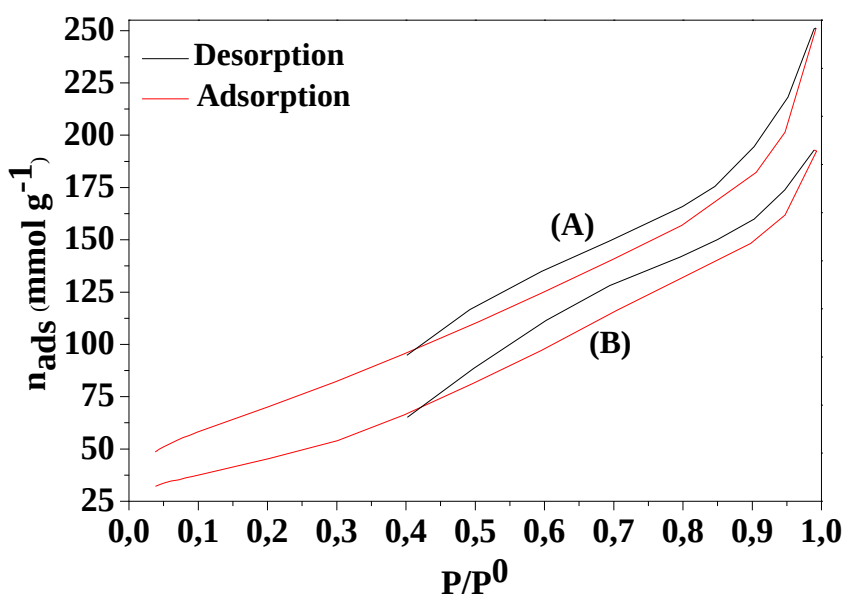


Figure 41 – N₂ adsorption-desorption isotherms at -196 °C of (A) SiO₂-rice and (B) SiO₂@F₁₃TES-rice nanomaterials.

The **Table 16** presents the N₂ adsorption-desorption isotherms data, namely the specific surface area BET (**A_{BET}**), determined by the method BET, pore volume (**V_{pore}**), determined by the method DFT and the pore size (**d_{pore}**), determined by the method DFT of the SiO₂-rice and SiO₂@F₁₃TES-rice samples.

Table 16- Textural properties of the **SiO₂-rice** and **SiO₂@F₁₃TES-rice** sample.

Sample	N ₂ adsorption-desorption isotherms data		
	A _{BET} (m ² g ⁻¹)	V _{pore} ^a (cm ³ g ⁻¹)	d _{pore} ^b (nm)
SiO ₂ -rice	248	0.29	3.7
SiO ₂ @F ₁₃ TES-rice	18	0.11	3.5

^a Mesoporous volume. ^b NLDFT pore diameter (maximum of the NLDFT pore size distribution).

Through the analysis of the **Table 16** it is verified that the specific surface area, pore volume and pore size, decrease in relation to the control (SiO₂-rice), confirming the incorporation of the organosilane F₁₃TES.

4.3.5. TGA

The thermograms of the pristine (SiO₂-rice) and functionalized SiO₂-rice (SiO₂@F₁₃TES-rice) are shown in **Figure 42**. In the **Table 17** are summarized the total and partial weight loss for each degradation level of these samples.

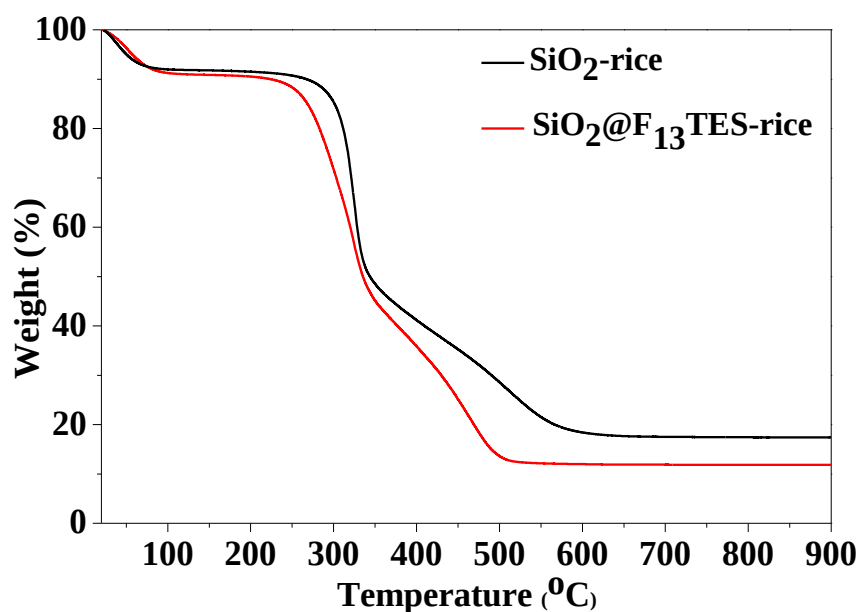


Figure 42 – Thermogravimetric curves of the samples: SiO₂-rice (black curve) and SiO₂@F₁₃TES-rice (red curve), under O₂ atmosphere.

Table 17 – Weight loss for each degradation level obtained through the thermogravimetric curves.

Samples	1° weight loss (%)	2° weight loss (%)	Total (%)
SiO ₂ -rice	9.1 [21 – 175 °C]	74.4 [175 – 682 °C]	81.5
SiO ₂ @F ₁₃ TES-rice	9.3 [21 – 176 °C]	78.8 [176 – 631 °C]	88.1

The SiO₂-rice thermogram (black curve) presents an initial weight loss of 9.1% in the temperature range of 21-175 °C due to the loss of physisorbed water from the porous structure [69, 72]. One more weight loss of 74.4% is observed in the range of 175-682°C. This second weight loss arises from the dehydroxylation of the silica surface and from the decomposition of ethoxy moieties [58, 59, 72].

The thermogram of the functionalized SiO₂-rice (SiO₂@F₁₃TES-rice) (red curve) present similar profile, being possible to identify the existence of two main steps of weight losses. The first, in the temperature range of ~ 21 to 176 °C (9.3%), is attributed to the

removal physisorbed water, and the second one, which occurs in the range of ~ 176 to $631\text{ }^{\circ}\text{C}$ (78.8%). This second weight loss in the $\text{SiO}_2@\text{F}_{13}\text{TES-riz}$ is higher than in corresponding pristine SiO_2 ($\text{SiO}_2\text{-riz}$). In this way, we can associate this second weight loss, not only the dehydroxylation of the silica surface and from the decomposition of ethoxy moieties, but also the decomposition of the organosilane organic chain, confirming the previous results. [69, 70].

4.3.6. Evaluation of easy-cleaning properties

The easy-cleaning properties were evaluated by measuring the contact angle. In **Figure 43** are illustrated representative photographs of deionized water, toluene, cyclohexane, artificial sweat droplets on the surface of the $\text{SiO}_2\text{-rice}$ and $\text{SiO}_2@\text{F}_{13}\text{TES-rice}$ pellets and the corresponding contact angles (CA).

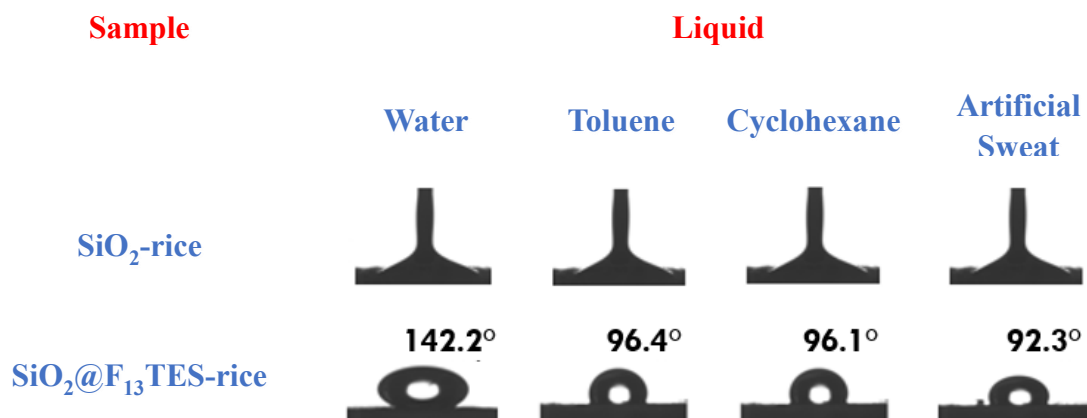


Figure 43 - Contact Angle between deionized water, toluene, cyclohexane, artificial sweat and the $\text{SiO}_2\text{-rice}$ and $\text{SiO}_2@\text{F}_{13}\text{TES-rice}$ pellets.

The easy-cleaning properties of the silica nanoparticles obtained from rice husk and functionalized with organosilane F_{13}TES by post-grafting methodology ($\text{SiO}_2@\text{F}_{13}\text{TES}$) are identical to those obtained and functionalized by co-condensation methodology ($\text{SiO}_2@\text{F}_{13}\text{TES}$ in **chapter 3, section 3.8**), present repellency to all liquids and values of contact angles very close, reaching 142.2° for deionized water, a threshold value of superhydrophobic ($\text{CA} > 150^{\circ}$). However, the contact angles of the sample

SiO₂@F₁₃TES-riz are slightly lower than those obtained by the sample SiO₂@F₁₃TES. These results were expected. In the post-grafting methodology, the distribution of functional groups often tends to be inhomogeneous. In contrast, the co-condensation methodology is able to give homogeneously distributed organic groups on the entire inner pore surfaces. This fact is directly related to the efficiency of the functional properties. [70].

These results evidenced that the nanoparticles were functionalized successfully, proving the previous results, promoting an easy-cleaning character to the nanomaterial.

4.4. Characterization of silica nanoparticles from rice husk with natural-based colored properties

SiO₂@cur-rice were characterized by TEM, EDS, FTIR-ATR, ²⁹Si CPMAS and ¹³C CPMAS Solid-State NMR and TGA. The results and respective discussion, by means of the characterization techniques used, are presented below.

In **Figure 44** are illustrated representative photographs of silica nanoparticles SiO₂-rice functionalized with curcuma (SiO₂@cur-rice), after the process of washing fastness (washed twice by sonication with ethanol during 10 min) (**Figure 44A**), and the resulting silica nanoparticles after drying at 80 °C for 12 h, SiO₂@cur-rice (**Figure 44C**). In order to visually evaluate the immobilization of curcuma on the SiO₂-rice, are presented together with the photograph of the SiO₂@curc-rice, the photographs of SiO₂-rice (**Figure 44B**) and curcuma (**Figure 44D**).

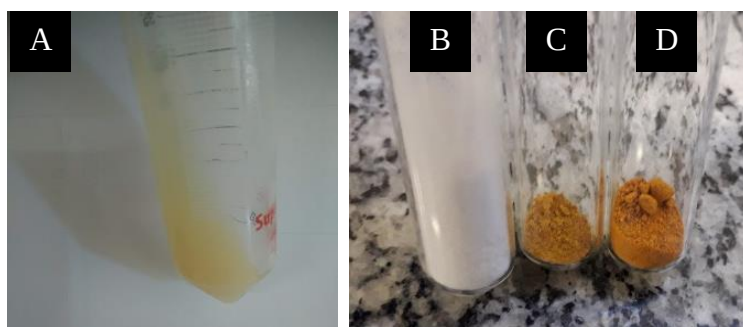


Figure 44 – Representative photographs of SiO₂@cur-rice, after the process of washing fastness (**A**), SiO₂-rice (**B**), the resulting SiO₂@cur-rice (**C**) and curcuma (**D**).

Through the analysis of **Figure 44**, it is possible to verify that the curcuma was immobilized in the SiO₂-rice successfully, presenting an identical coloring to that of curcuma (yellow-orange). The SiO₂@cur-rice, were characterized by TEM, EDS, FTIR-ATR, ²⁹Si CPMAS Solid-State NMR and TGA, in order to confirm the immobilization of curcuma.

4.4.1. TEM-EDS

In the **Figure 45** are illustrated the TEM micrographs and particles size distribution histogram, determined by TEM image analysis, of the SiO₂@cur-rice sample. In the TEM micrograph is identified (red square) where the EDS analysis (**Figure 46**) was performed. The **Figure 46** show the EDS spectra (inset: atomic percentages of C, O and Si) of this sample.

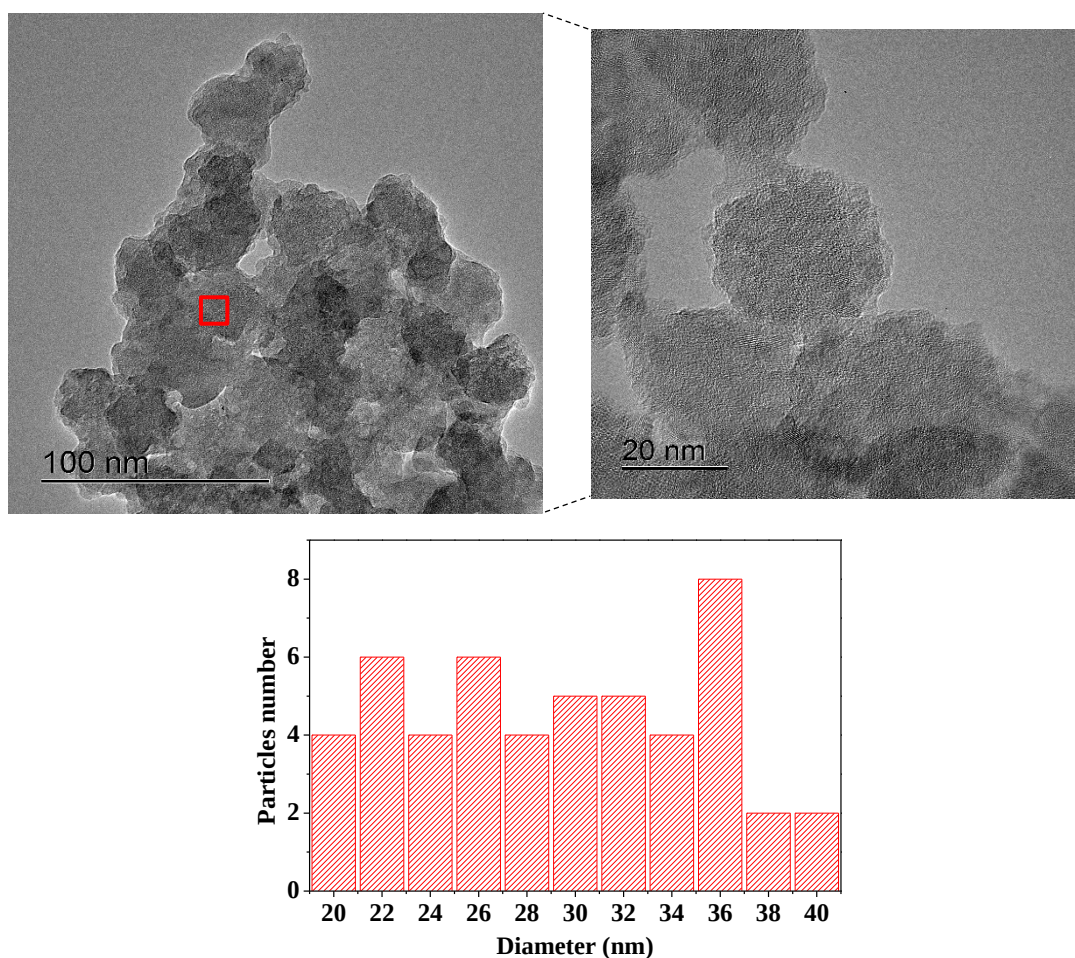


Figure 45 – TEM micrographs and particles size distribution histogram of SiO₂@cur-rice sample.

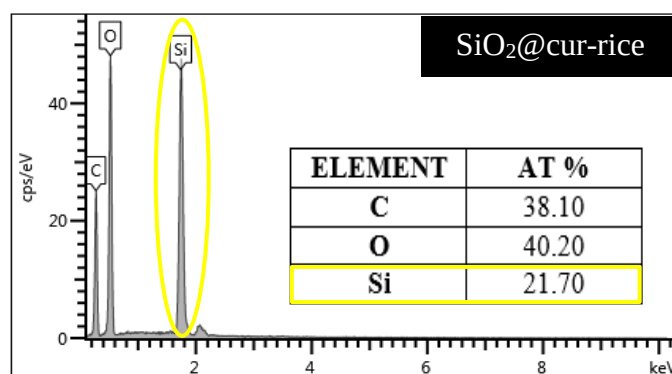


Figure 46 – EDS spectra of $\text{SiO}_2@\text{cur-rice}$ sample.

After immobilization of curcuma on silica nanoparticles, the morphology and particle size of the silica remain unchanged (spherical nanoparticles with heterogeneous particle size (20-40 nm)). The EDS spectra evidences the incorporation of curcuma with the increasing of C and O atomic ratio compared to the control, $\text{SiO}_2\text{-rice}$ (**Figure 45**).

4.4.2. FTIR-ATR

Figure 47 shows the vibrational spectroscopy FTIR-ATR of the $\text{SiO}_2@\text{cur-rice}$ (black spectrum), in the $4000\text{-}650\text{ cm}^{-1}$ (left) and $1750\text{-}650\text{ cm}^{-1}$ (right) range. The dotted lines highlight the characteristic bands of curcuma. In order to evaluate the chemical modification of the $\text{SiO}_2\text{-rice}$, the vibrational spectra of the $\text{SiO}_2\text{-rice}$ (blue spectrum) and the curcuma (red spectrum), are also presented together.

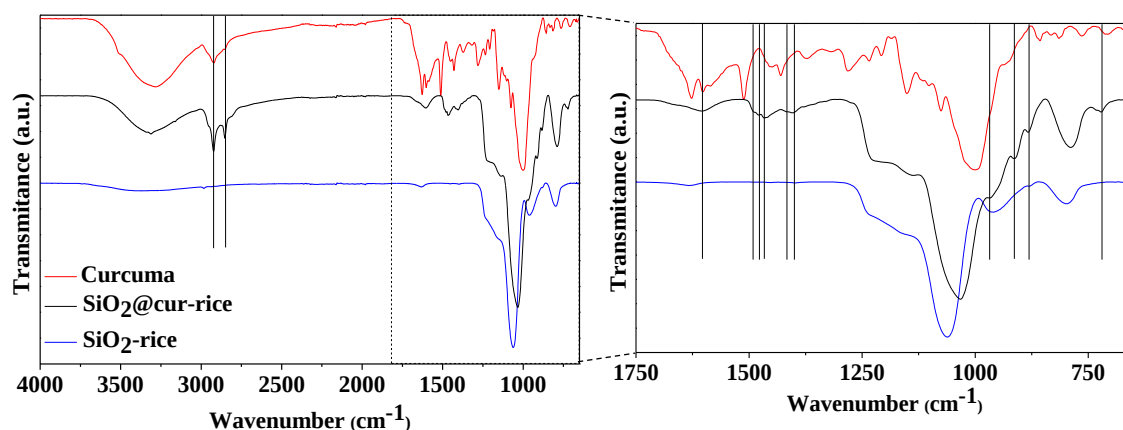


Figure 47 – FTIR-ATR spectra of SiO₂@cur-rice, in the 4000-650 cm⁻¹ (left) and 1750-650 cm⁻¹ (right) range. The dotted lines highlight the characteristic peaks of curcuma.

The vibrational spectra of the SiO₂@cur-rice (black spectrum) confirm the immobilization of curcuma on the SiO₂-rice successfully. The presence of curcuma in the vibrational spectrum of SiO₂@cur-rice is evidenced by the following bands: C=C in plane stretching (1602 and 1511 cm⁻¹), C-H antisymmetric deformation (1465 and 1453 cm⁻¹), C=C stretching and C-H deformation (1430 cm⁻¹), C-H symmetric deformation (1373 cm⁻¹) and C=C symmetric stretching (925 - 815 cm⁻¹) vibrations [69, 72].

4.4.3. ²⁹Si CPMAS Solid-State NMR

Figure 48 present the ²⁹Si CPMAS NMR spectra of the SiO₂-rice and SiO₂@cur-rice.

The ²⁹Si CPMAS NMR spectra of SiO₂-rice (black spectrum) and SiO₂@cur-rice (red spectrum), present peaks at -110 and -100 ppm, which correspond to Q⁴ and Q³ resonances, respectively, and are associated to the fully condensed silica units and to silica with one terminal silanol group; the peak Q² around -91 ppm, associated the geminal silanol groups are present in the samples SiO₂-rice and almost absent in the samples SiO₂@cur-rice [58, 59, 70, 71]. In the SiO₂@cur-rice ²⁹Si CPMAS NMR spectra, one additional peak are detected around -80 ppm which is associated to T³ silicon

environments, revealing the anchorage of curcuma, through 3-fold covalent grafting [58, 59, 70, 71].

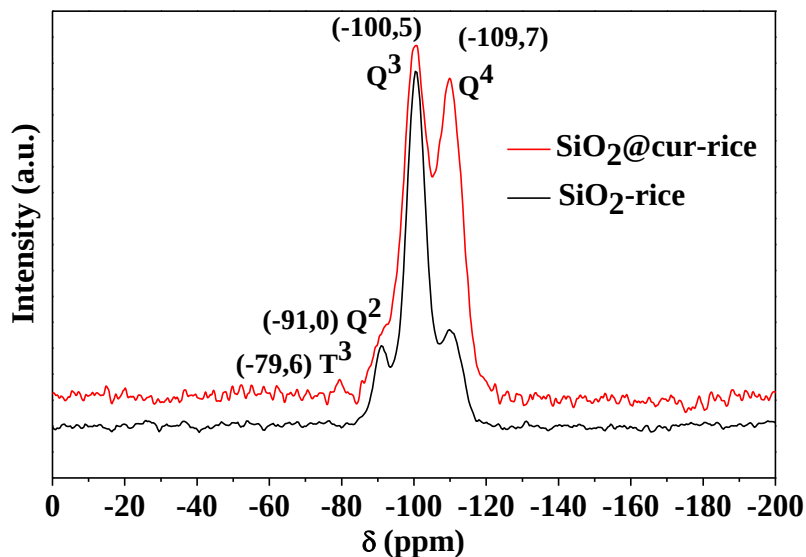


Figure 48 – ^{29}Si CPMAS NMR spectra of the samples: $\text{SiO}_2\text{-rice}$ (black spectrum) and $\text{SiO}_2\text{@cur-rice}$ (red spectrum) and the bands assignments.

4.4.4. TGA

The thermograms of the pristine ($\text{SiO}_2\text{-rice}$) and functionalized $\text{SiO}_2\text{-rice}$ ($\text{SiO}_2\text{@cur-rice}$) are shown in **Figure 49**. In the **Table 18** are summarized the total and partial weight loss for each degradation level of these samples.

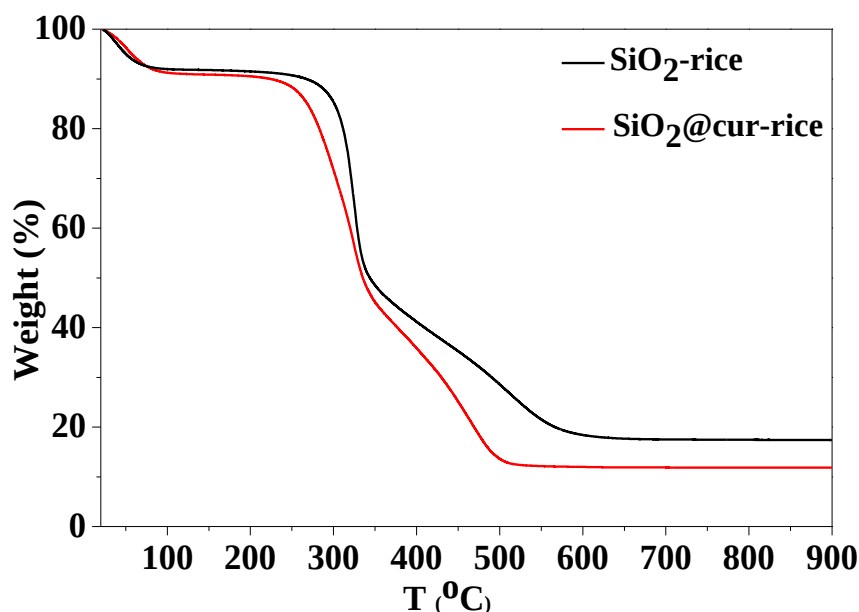


Figure 49 – Thermogravimetric curves of the samples: SiO₂-rice (black curve) and SiO₂@cur-rice (red curve), under O₂ atmosphere.

Table 18 – Weight loss for each degradation level obtained through the thermogravimetric curves.

Samples	1° weight loss (%)	2° weight loss (%)	Total (%)
SiO ₂ -rice	9.1 [21 – 175 °C]	74.4 [175 – 682 °C]	81.5
SiO ₂ @cur-rice	9.5 [21 – 168 °C]	83.5 [168 – 627 °C]	93.0

The thermogram of the SiO₂@cur-rice (red curve) present similar profile to the pristine (SiO₂-rice), being possible to identify the existence of two main steps of weight losses. The first, in the temperature range of ~ 21 to 168 °C (9.5%), is attributed to the removal physisorbed water, and the second one, which occurs in the range of ~ 168 to 627 °C (83.5%). This second weight loss in the SiO₂@cur-rice is higher than in corresponding pristine. In this way, we can associate this second weight loss not only the dehydroxylation of the silica surface and from the decomposition of ethoxy moieties, but

also the decomposition of the curcuma, confirming the results obtained by FTIR-ATR, and ^{29}Si CPMAS NMR. [69, 72].

4.5. Conclusions

The hydrothermal process was efficient in eliminating the metal oxides of the rice husk. This process allowed to obtain silica with high purity (99.7 % (wt/wt)), in a sustainable, environmentally friendly and economical way.

The silica obtained are composed of nearly spherical nanoparticles with heterogeneous particles size (20-40 nm) and exhibit mesoporous structure and high porous structure, as evidenced by TEM and N_2 adsorption-desorption isotherms at -196°C characterization.

The results obtained by EDS, N_2 adsorption-desorption isotherms at -196°C , FTIR-ATR, RMN, TGA, XPS and contact angle, indicate an efficient functionalization of the silica nanoparticles with organosilane F_{13}TES , by post-grafting methodology. The $\text{SiO}_2@\text{F}_{13}\text{TES}$ -rice present excellent easy-cleaning properties, displaying phobicity to water (threshold of superhydrophobicity), toluene, cyclohexane and artificial sweat, whereas the pristine silica nanoparticles (SiO_2 -rice) presented philicity to these liquids.

The curcuma was functionalized in the SiO_2 -riz successfully, presenting an identical coloring to that of curcuma (yellow-orange). The $\text{SiO}_2@\text{cur}$ -rice presented a good resistance to washing with high chemical stability.

CHAPTER 5

Anatase $\text{SiO}_2@ \text{TiO}_2$
Nanocomposites

5. Anatase SiO₂@TiO₂ nanocomposites

The prepared SiO₂@TiO₂ nanocomposites were characterized by SEM, TEM, DLS, EDS, FTIR-ATR, X-ray fluorescence and XRD. The results and respective discussion, by means of the characterization techniques used, are presented in this chapter.

5.1. SEM, TEM and DLS

Figure 50 and **Figure 51** show the SEM and TEM micrographs, respectively, of the SiO₂, TiO₂ and SiO₂@TiO₂ samples. In the SEM micrograph of the SiO₂@TiO₂ nanocomposite (**Figure 50**) is identified (red square) where the EDS analysis (**Figure 53**) was performed. In the **Figure 52** are illustrated the particles size distribution histograms, of the SiO₂ (**A**) and SiO₂@TiO₂ (**B**) samples, determined by SEM image analysis. Additionally, in the **Table 19**, are summarized the average particle size estimated by SEM and TEM images analysis and DLS as well as the polydispersion indexes (PDI) by DLS.

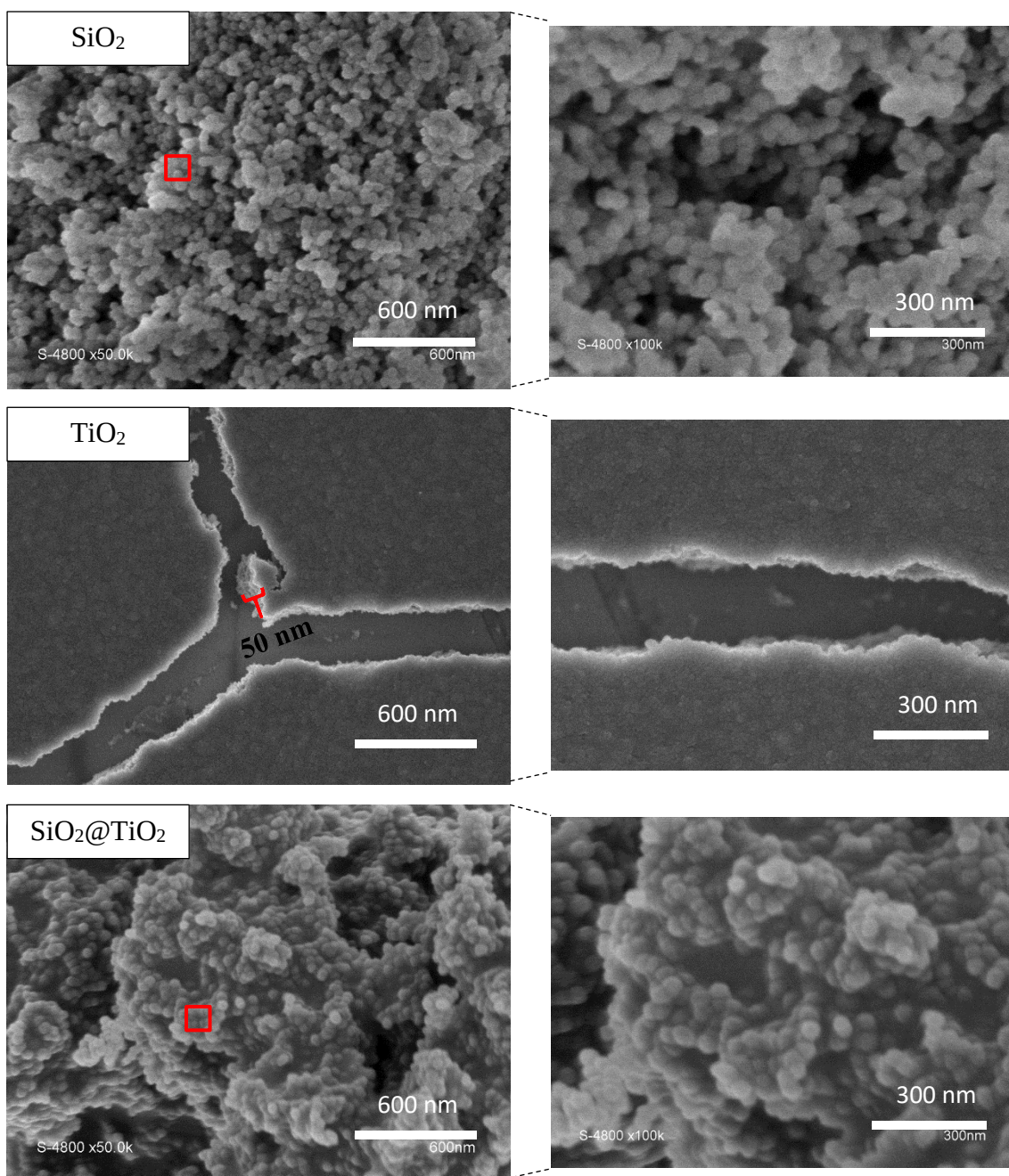


Figure 50 – SEM micrographs of SiO_2 , TiO_2 and $\text{SiO}_2@\text{TiO}_2$ samples.

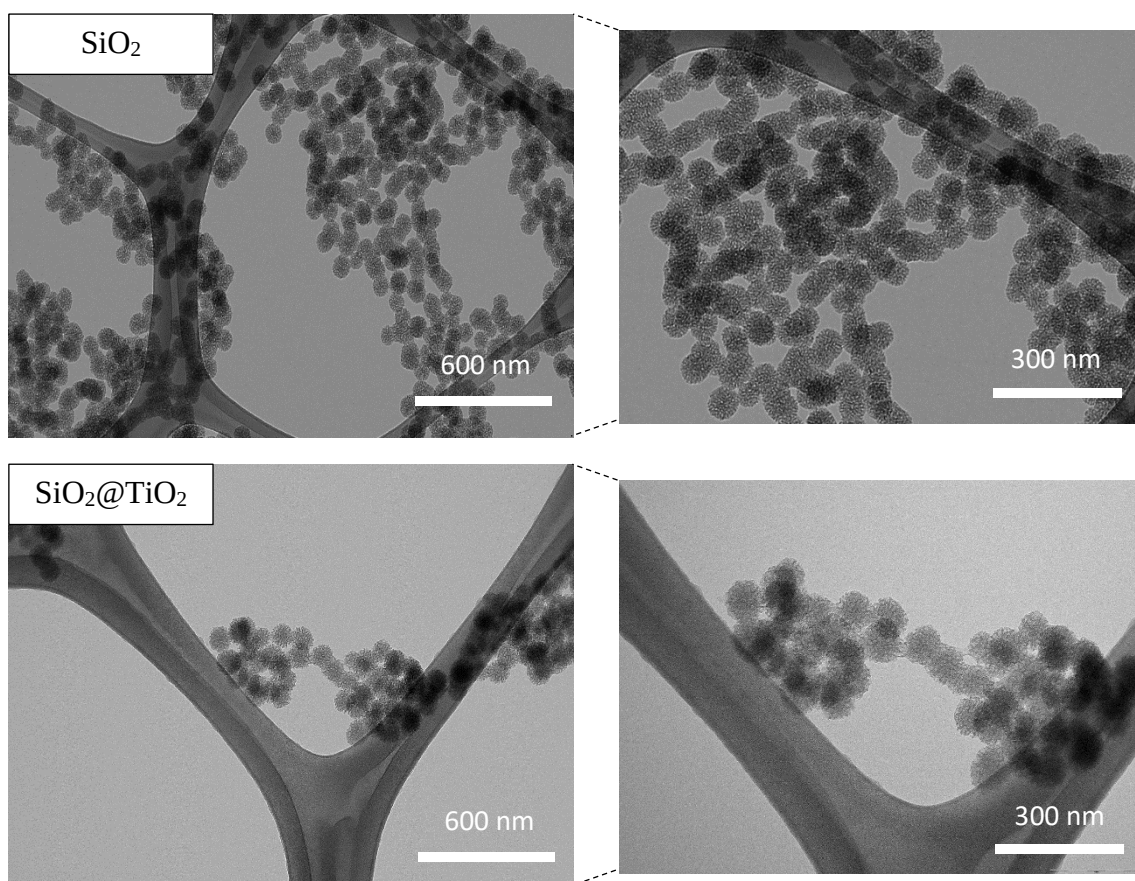


Figure 51 – TEM micrographs of SiO_2 and $\text{SiO}_2@\text{TiO}_2$ samples.

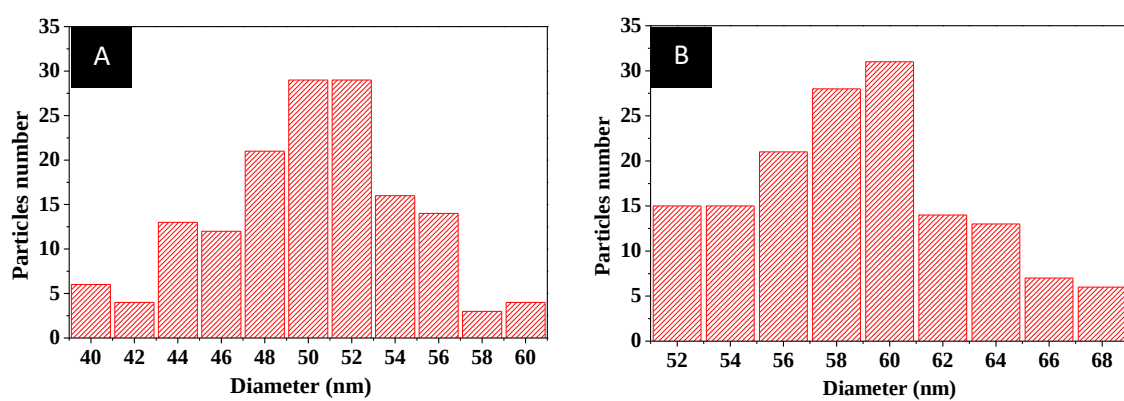


Figure 52 – Particles size distribution histograms of (A) SiO_2 and (B) $\text{SiO}_2@\text{TiO}_2$ nanomaterials, determined from SEM images analysis.

Table 19 – Average particle size estimated by SEM (d_{SEM}), TEM (d_{TEM}) and DLS (d_{DLS}) and polydispersion indexes (PDI) by DLS of the SiO₂ and SiO₂@TiO₂ samples.

Material	Particle size (nm)			
	d_{SEM}	d_{TEM}	DLS	
			d_{DLS}	PDI
SiO ₂	51 ± 4	52 ± 4	68 ± 2	0.15
SiO ₂ @TiO ₂	60 ± 5	56 ± 6	75 ± 9	0.18

The SEM and TEM images show that the SiO₂ sample is composed of nearly spherical nanoparticles with a wormhole-type mesoporous structure and particle size around 51 ± 4 nm (results analyzed aforementioned in **chapter 3, section 3.1**). A film of TiO₂ was formed on the silicon wafer (as show in **Figure 50**) with a thickness of 50 nm and with a very fine grain. In contrast to the near perfect spherical SiO₂ nanoparticles, the TiO₂ film deposited on SiO₂ nanoparticles (SiO₂@TiO₂ sample) show a rough surface and less than perfect spherical shape with the average diameter increasing to around 60 ± 5 nm. This is clearly attributed to the coating of a TiO₂ layer on the spherical SiO₂ nanoparticles. These results are in agreement with the results obtained by Bein *et al.* [42]. DLS analysis (**Table 19**) confirmed the particle size trend observed by SEM and TEM (**Table 19**). Nevertheless, the average hydrodynamic diameters are higher than the discrete particle sizes estimated by electron microscopy techniques [33, 58, 59]. A higher polydispersity index was observed in the SiO₂@TiO₂ sample due to possible loading effects of the formed nanocomposite [42].

5.2. EDS, STEM and X-ray maps

In the **Figure 53** are illustrated the EDS spectra (inset: atomic percentages of C, O, Si and Ti), of the SiO₂@TiO₂ sample, obtained during SEM experiment. In **Figure 50**, in the micrograph of the SiO₂@TiO₂ sample is identified (red square) where the EDS analysis was performed. The STEM micrographs and corresponding X-ray maps of the SiO₂@TiO₂ sample are illustrated in **Figure 54**.

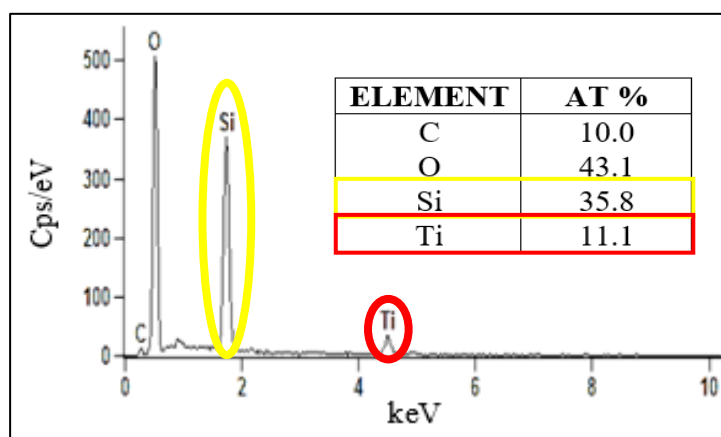


Figure 53 – EDS spectra of SiO₂@TiO₂ sample.

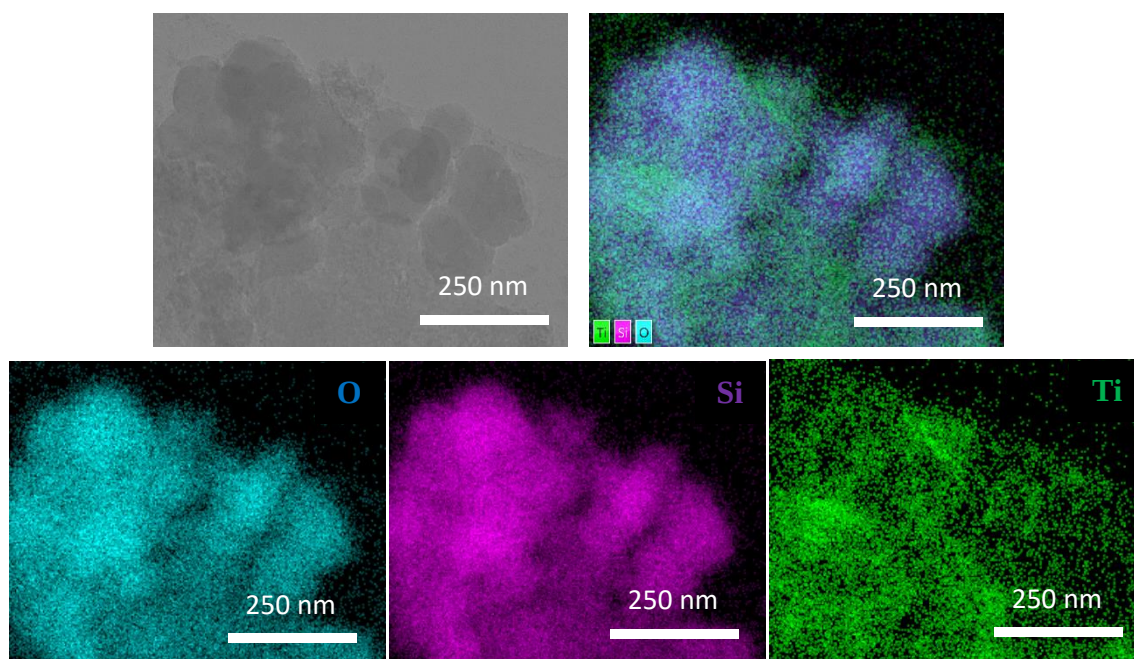


Figure 54 – STEM micrographs of SiO₂@TiO₂ sample and corresponding X-ray maps.

The EDS spectra and X-ray elemental maps by STEM reveal the presence of Ti in addition to the Si and O. A heterogeneous Ti mapping on the SiO₂ nanoparticles is observed, suggesting a thin layer of the TiO₂ on the SiO₂ nanoparticles (dark sides with

slight green spots) and between these, where the Ti concentration is higher (intense green parts).

5.3. FTIR-ATR

Figure 55 shows the vibrational spectroscopy FTIR-ATR of the SiO₂ (black spectrum) and SiO₂@TiO₂ (red spectrum) samples in the 4000-650 cm⁻¹ range.

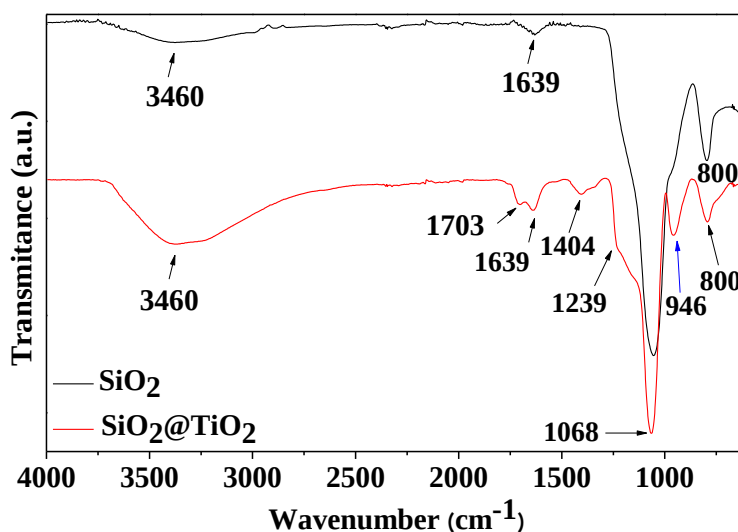


Figure 55 – FTIR-ATR spectra of SiO₂ (black spectrum) and SiO₂@TiO₂ (red spectrum) samples, in the 4000-400 cm⁻¹ range.

The interaction between TiO₂ and SiO₂ in the prepared SiO₂@TiO₂ nanocomposite (red spectrum in **Figure 55**) was clearly shown by the band at 946 cm⁻¹ assigned to symmetric Ti-O-Si stretching band, confirming that the SiO₂ reacted with TiO₂ to form Ti-O-Si structure [42]. Other two bands are observed: at 1404 cm⁻¹, corresponding to the Ti-O-Ti stretching vibration [72] and at 1703 cm⁻¹ assigned C=O vibration of the carboxylic group (-COOH) of the acetic acid, not involved in Ti chelation [71]. According to literature [42] the formation mechanism of SiO₂@TiO₂ nanocomposite is considered by electrostatic deposition. The isoelectric point of TiO₂ is 5.5 and that of the SiO₂ particles ranged from 1.8 to 2.7 [75, 76]. As the pH value was 3-5, the TiO₂ would have a positive surface charge density and the SiO₂ nanoparticles would have a

negative surface charge density. Thus, TiO_2 could be deposited on the surface of the SiO_2 nanoparticles driven by the electrostatic attraction between TiO_2 and SiO_2 .

5.4. X-ray fluorescence

SiO_2 (95.6 ± 0.2 wt/wt) and TiO_2 (4.3 ± 0.2 wt/wt) contents of the $\text{SiO}_2@\text{TiO}_2$ nanocomposites, determined by X-ray fluorescence, is summarized in **Table 20**.

Table 20 - Percentage by mass of the elements present in the sample $\text{SiO}_2@\text{TiO}_2$

Sample	% Elements (wt/wt)		
$\text{SiO}_2@\text{TiO}_2$	SiO_2 95.6 ± 0.2	CaO 0.1 ± 0.1	TiO_2 4.3 ± 0.2

5.5. XRD

Figure 56 show the X-ray diffractograms of $\text{SiO}_2@\text{TiO}_2$ nanocomposite.

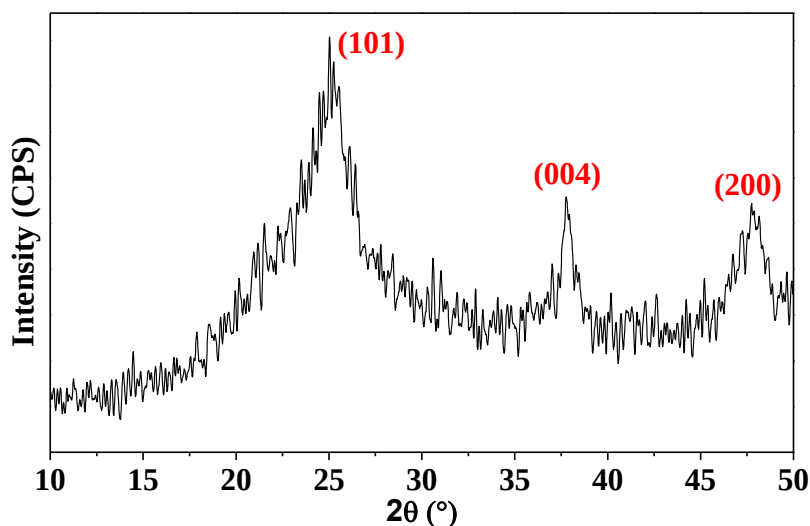


Figure 56 – X-ray diffractograms of powder extracted from colloid $\text{SiO}_2@\text{TiO}_2$ nanocomposites.

Anatase peaks at 25.3° , 38.1° and 48.2° , attributed to the (101), (004) and (200) Bragg reflection, respectively, and no traces of brookite or rutile were observed,

indicating that single-phase anatase nanocrystallites was formed. It is noteworthy that the phase anatase TiO_2 has the highest photoactivity among different crystal phases of TiO_2 [42, 53, 58].

5.6. Conclusions

A film of anatase TiO_2 was deposited on spherical SiO_2 nanoparticles with a mesoporous structure and particle size around 51 ± 4 nm. The results obtained indicated the efficient preparation of anatase $\text{SiO}_2@\text{TiO}_2$ nanocomposite with a rough surface and average diameter around 60 ± 5 nm.

In view of these results, this functional nanomaterial is potential candidate for the development of surfaces with self-cleaning properties. Consequently, in the second part of this work, we prepared functional BCM with this functional nanocomposite.

PART II

Characterization of Functional Bacterial Cellulose Organic-Inorganic Membranes

CHAPTER 6

Bacterial cellulose
membrane
functionalized with
silica nanoparticles
with easy-cleaning
properties

6. Bacterial cellulose membrane functionalized with silica nanoparticles with easy-cleaning properties

The BCM functionalized with silica nanoparticles with easy-cleaning properties were characterized by SEM, TEM, AFM, EDS, FTIR, XPS and TGA. These techniques allowed not only a morphological and chemical characterization of BCM, but also to evaluate the immobilization efficiency of the nanomaterials on BCM. Easy-cleaning properties were also evaluated (contact angle). The results and respective discussion are presented in this chapter. The photographs of the resulting samples are illustrated in Annex 1.

6.1. Morphological characterization

The morphological study of BCM functionalized with silica nanoparticles with easy-cleaning properties was performed by SEM, TEM and AFM (From **Figure 57** to **Figure 58**). The samples referenced in red and blue correspond to cellulose functionalized by in situ with functional nanomaterials synthesized and functionalized by sol-gel method (**Figure 60** – **Figure 62**) and with functional nanomaterials from rice husk and functionalized by post-grafting (**Figure 65**), respectively. The green samples correspond to cellulose functionalized by post-grafting (PG) with functional nanomaterials synthesized and functionalized by sol-gel method (**Figure 63** and **Figure 64**). In the SEM micrograph of the samples is identified (red square) where the EDS analysis was performed.

Average particle size of these functional nanomaterials incorporated into the BCM was estimated by SEM (d_{SEM}) and TEM (d_{TEM}) (**Figure 66** and **Table 21**).

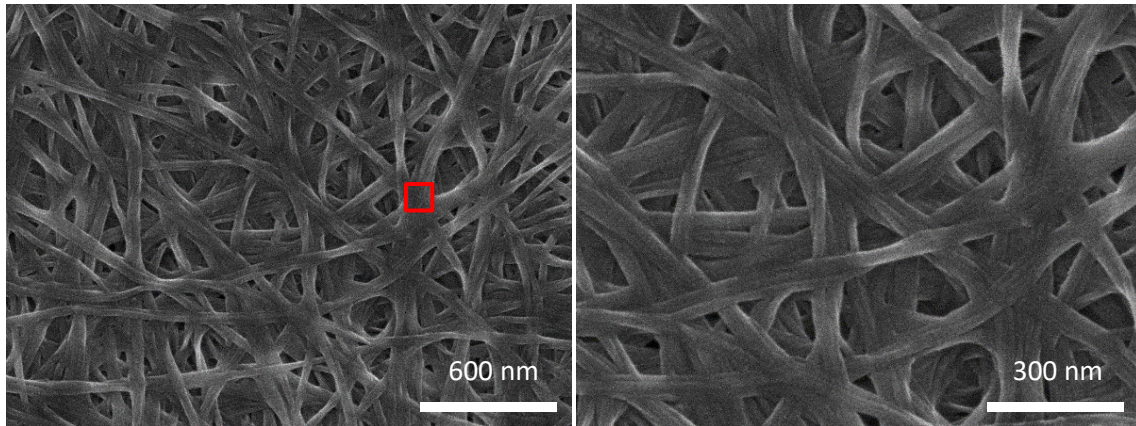


Figure 57 – SEM micrographs of BCM sample.

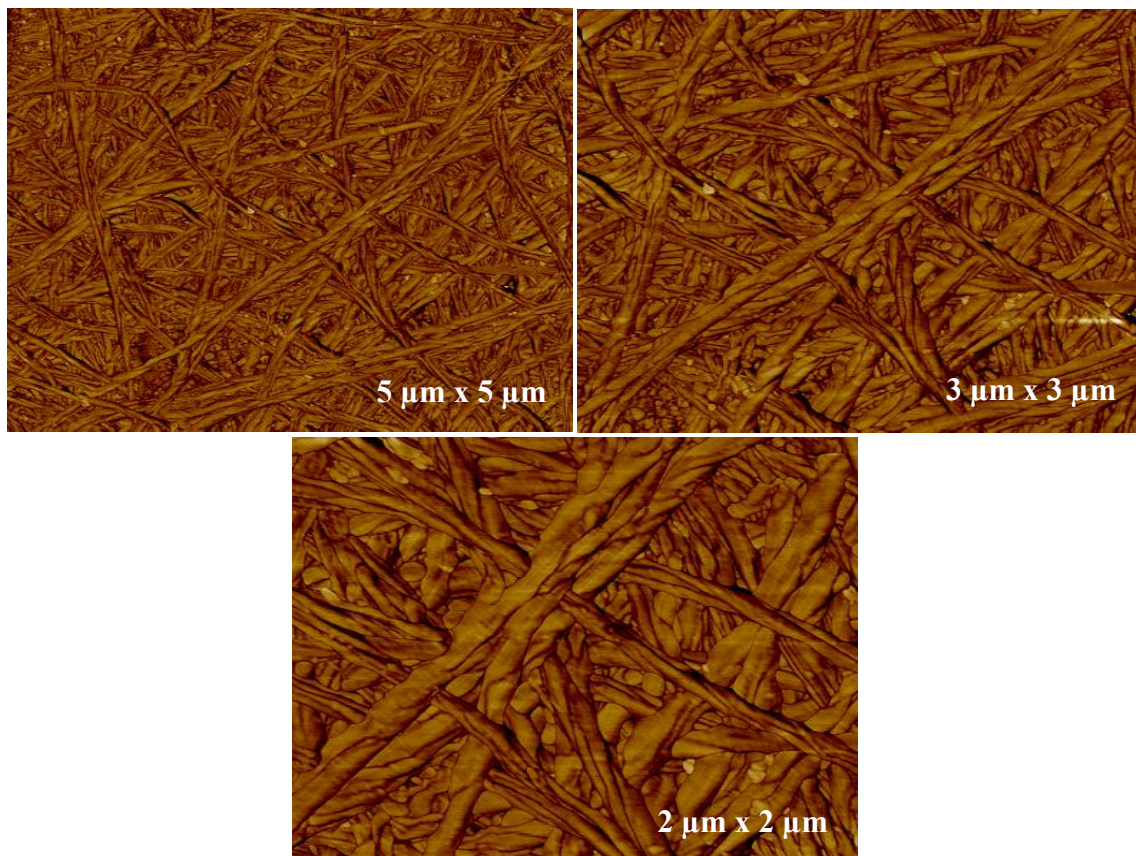


Figure 58 – AFM micrographs of BCM sample.

BCM@SiO₂

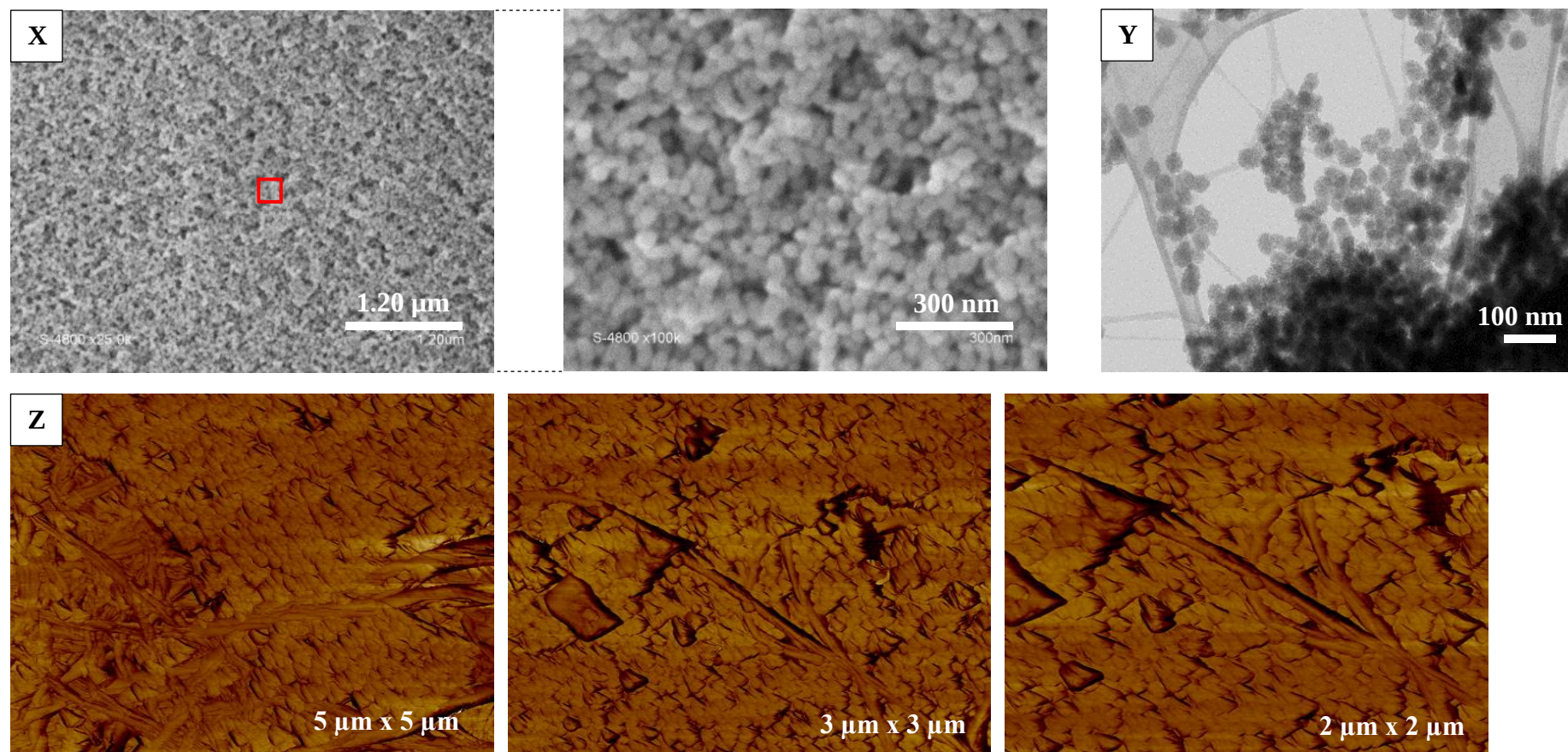


Figure 59 – (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@SiO₂ sample.

BCM@SiO₂@C₈TMS

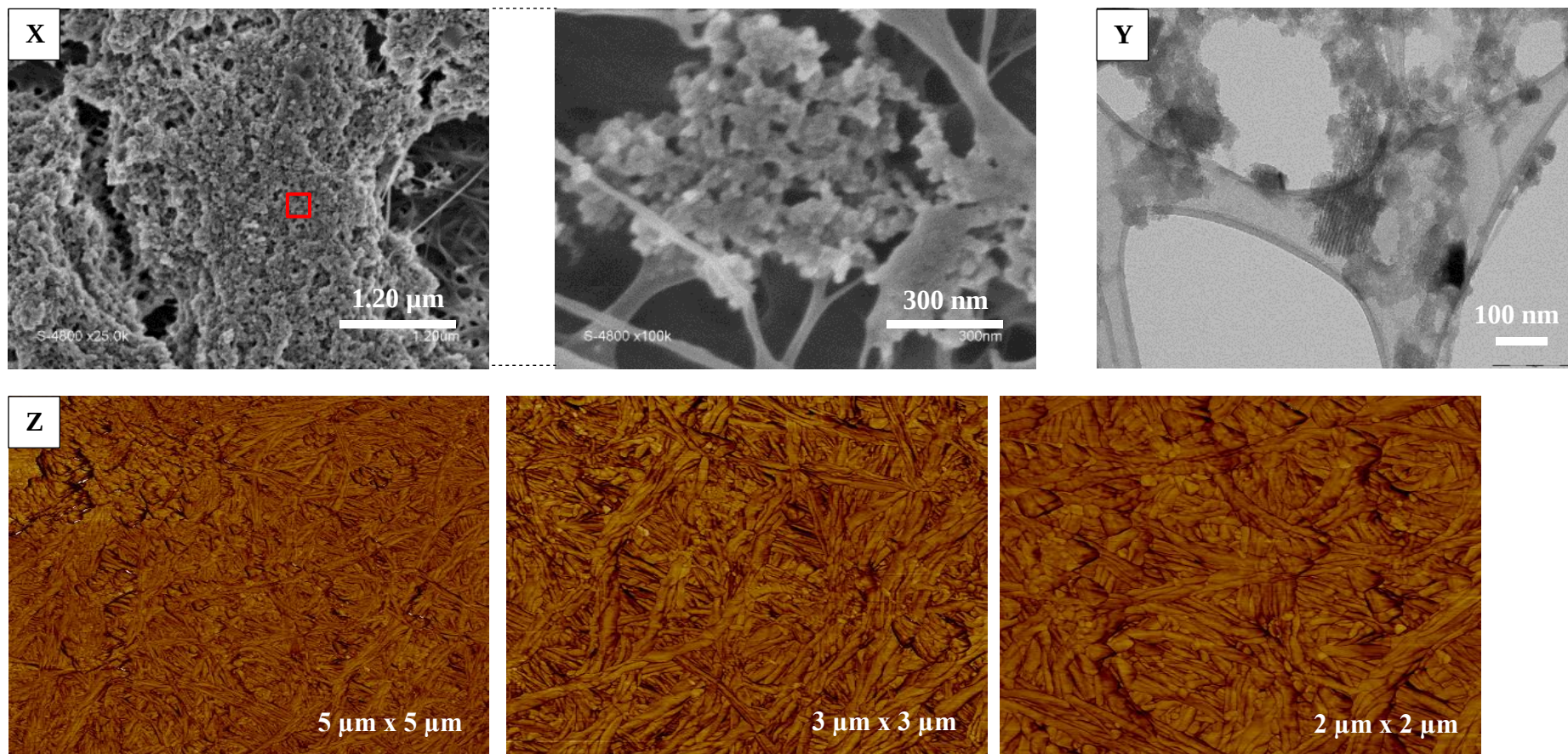


Figure 60 - (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@SiO₂@C₈TMS sample.

BCM@SiO₂@C₁₆TMS

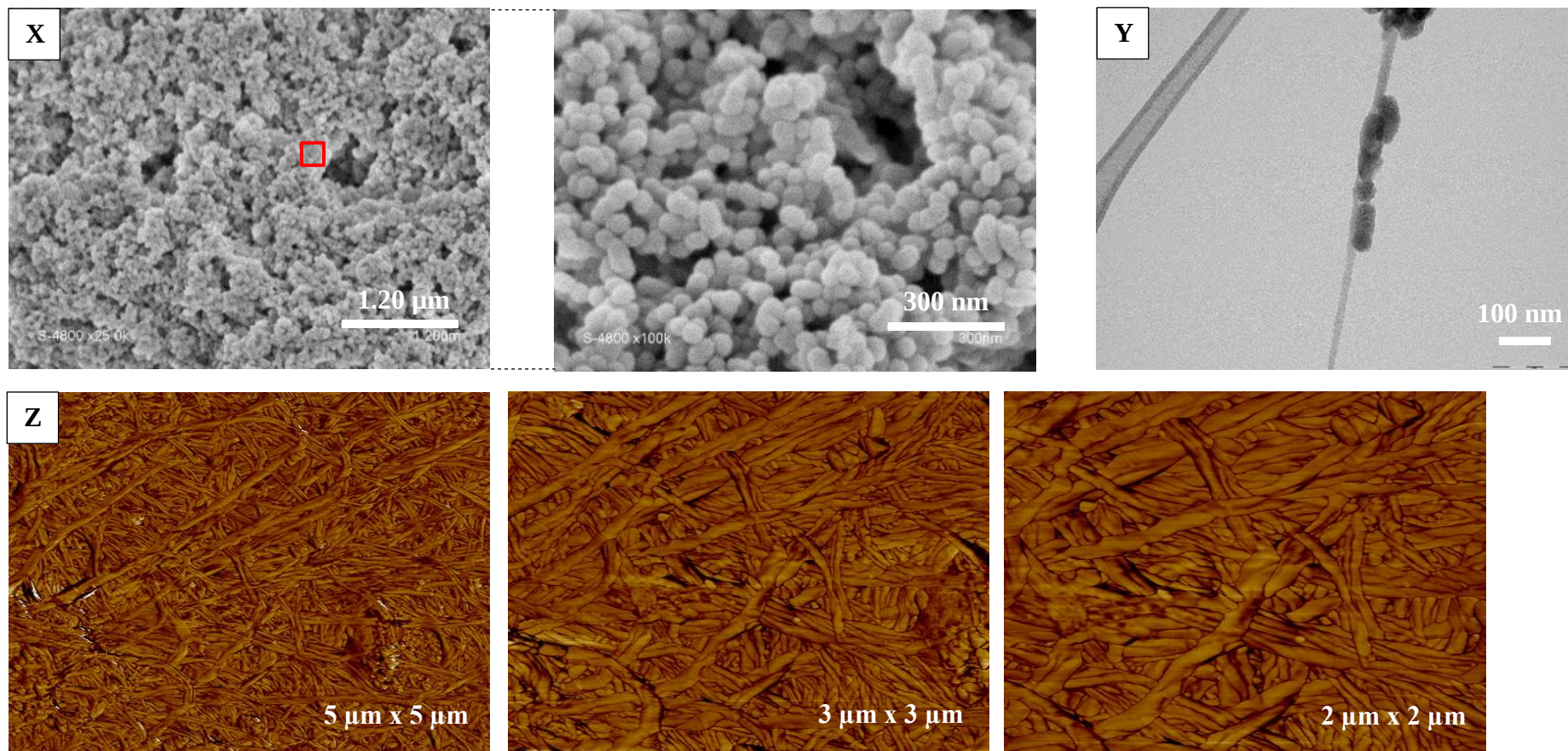


Figure 61 - (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@SiO₂@C₁₆TMS sample.

BCM@SiO₂@F₁₃TES

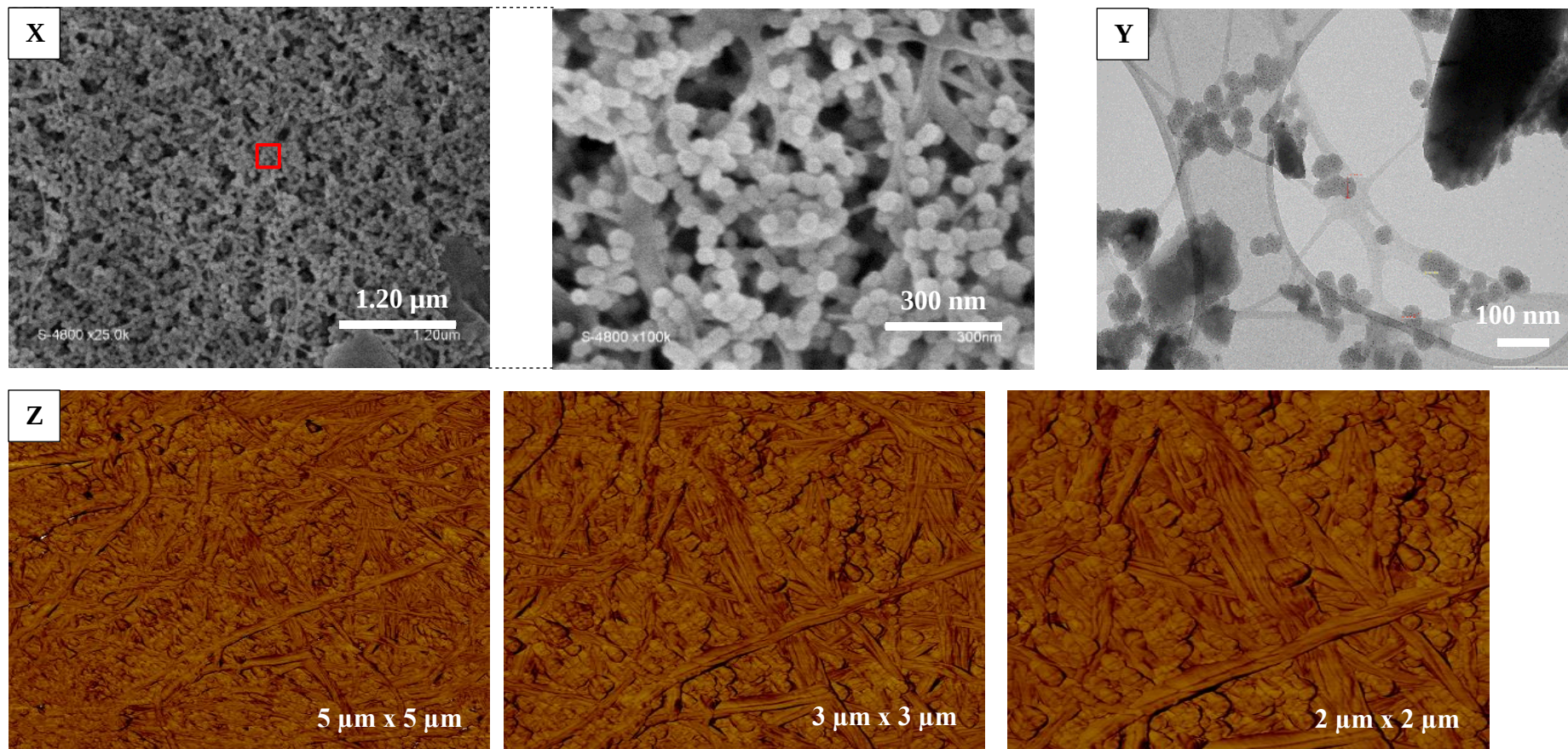
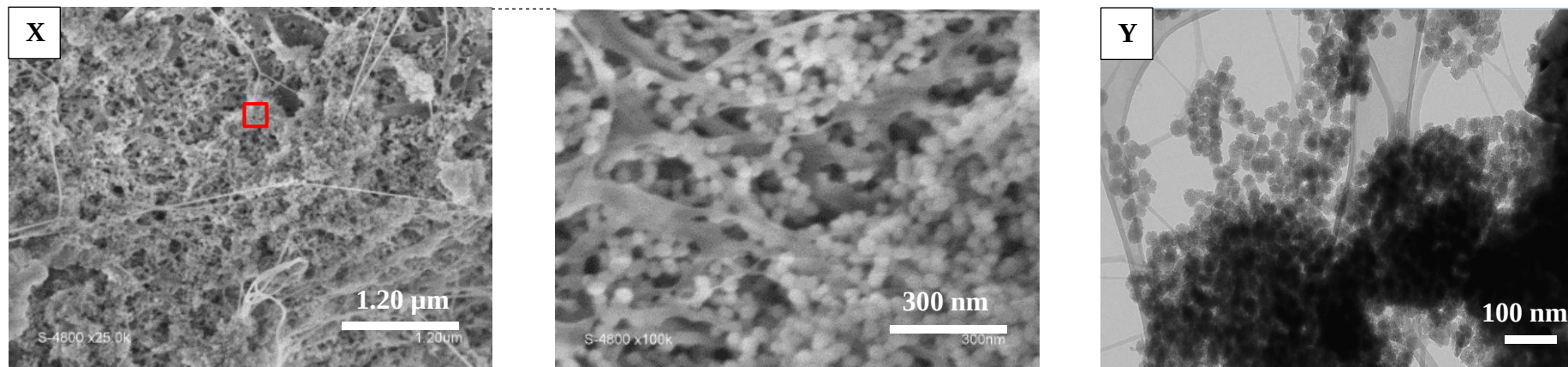


Figure 62 - (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@SiO₂@F₁₃TES sample.

BCM@SiO₂_PG



BCM@SiO₂@C₈TMS_PG

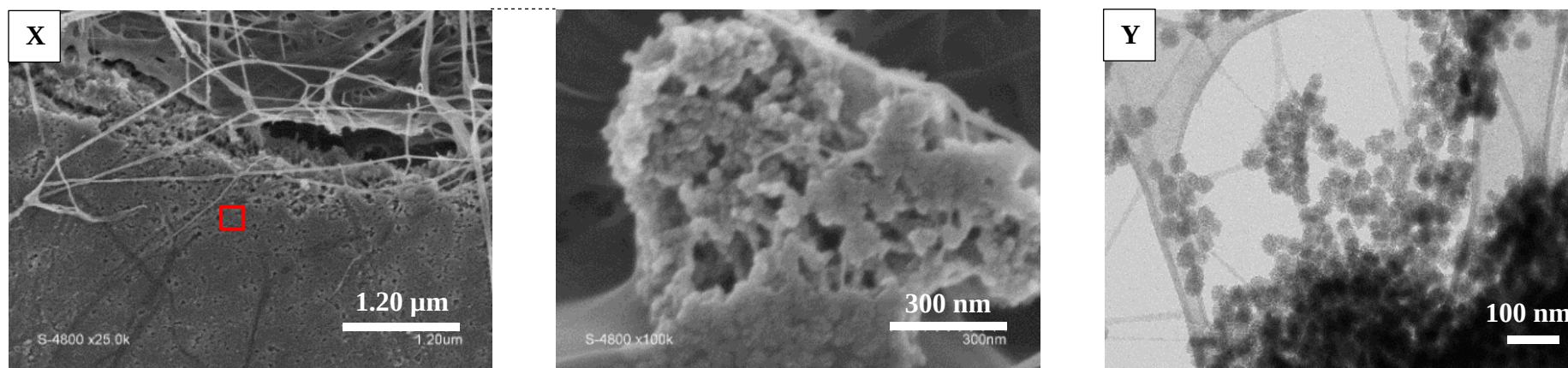
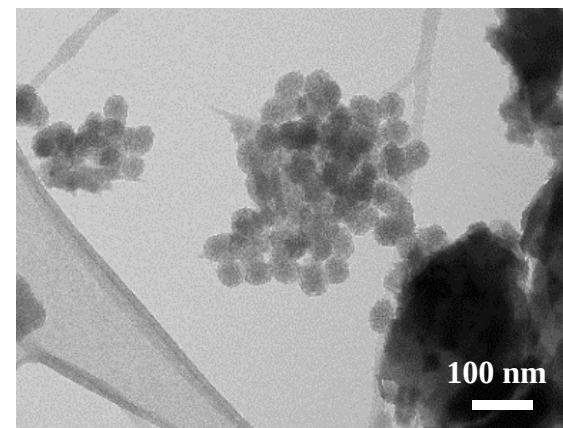
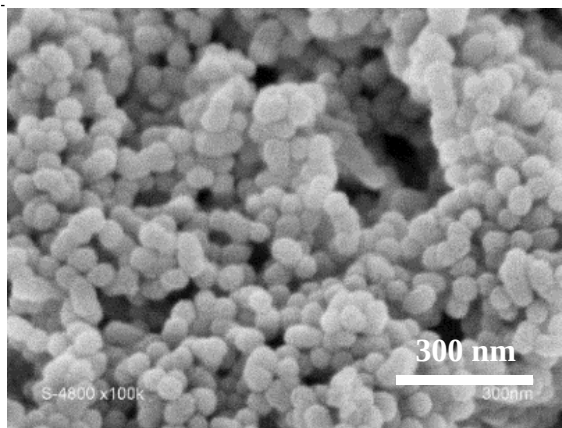
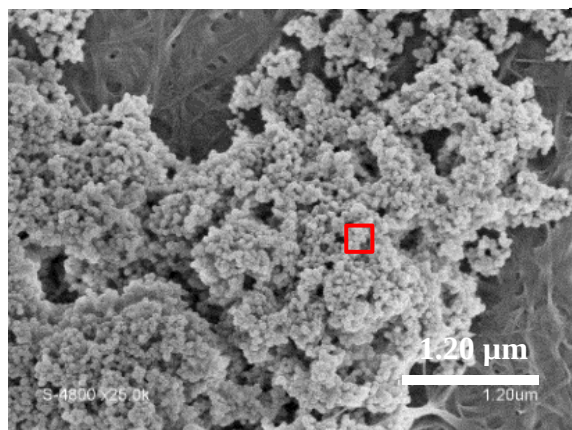


Figure 63 – (X) SEM and (Y) TEM micrographs of BCM@SiO₂_PG and BCM@SiO₂@C₈TMS_PG samples.

BCM@SiO₂@C₁₆TMS_PG



BCM@SiO₂@F₁₃TES_PG

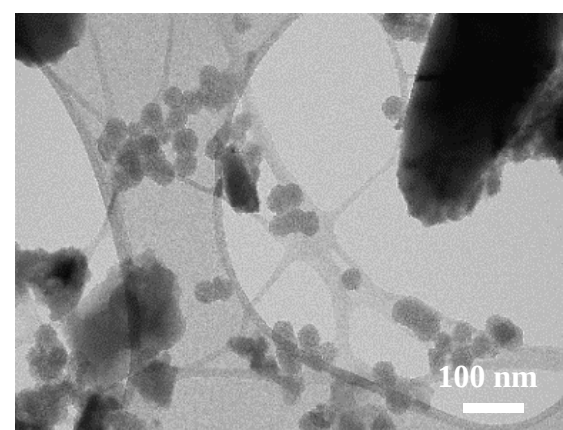
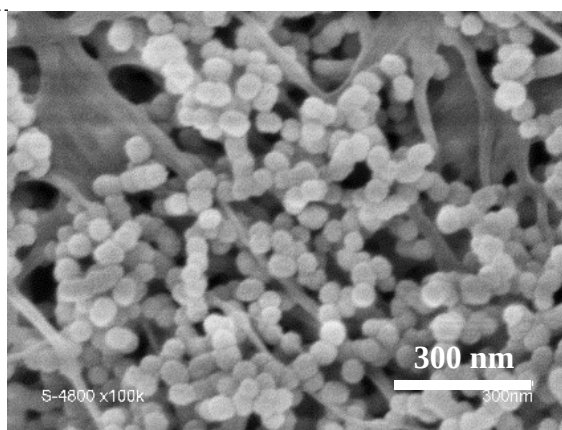
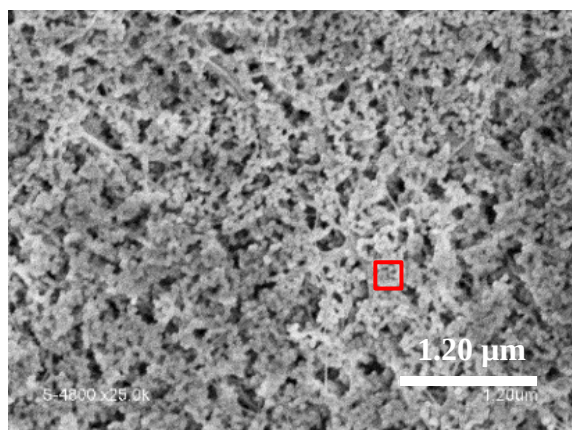
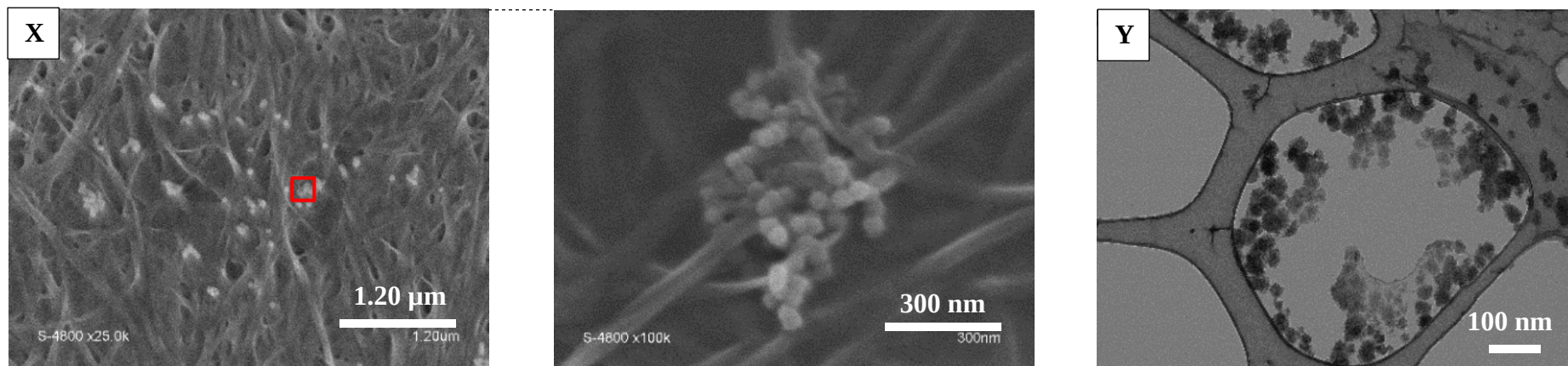


Figure 64 - (X) SEM and (Y) TEM micrographs of BCM@SiO₂@C₁₆TMS_PG and BCM@SiO₂@F₁₃TES_PG samples.

BCM@SiO₂-rice



BCM@SiO₂@F₁₃TES-rice

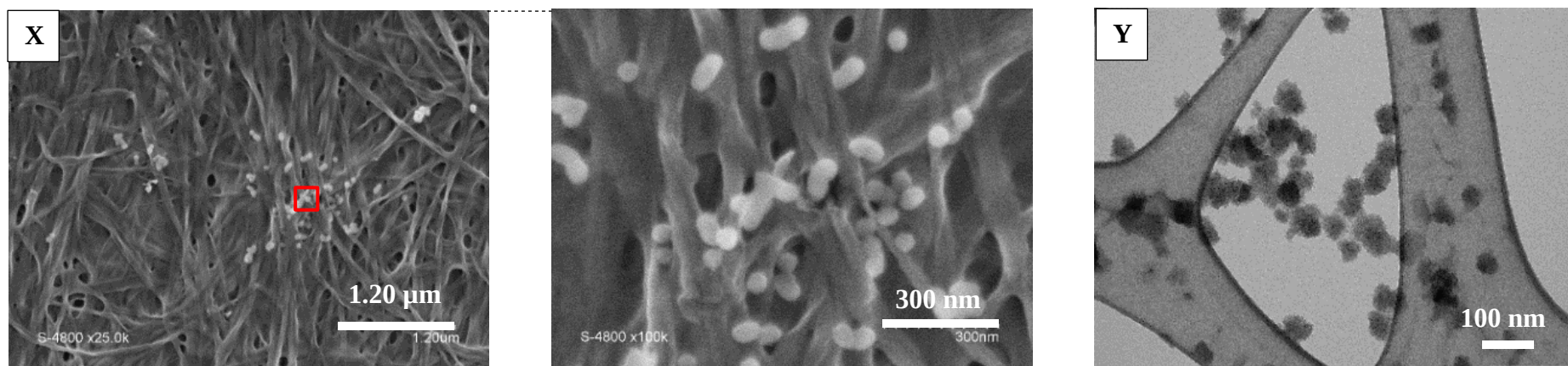


Figure 65 - (X) SEM and (Y) TEM micrographs of BCM@SiO₂-rice and BCM@SiO₂@F₁₃TES-rice samples.

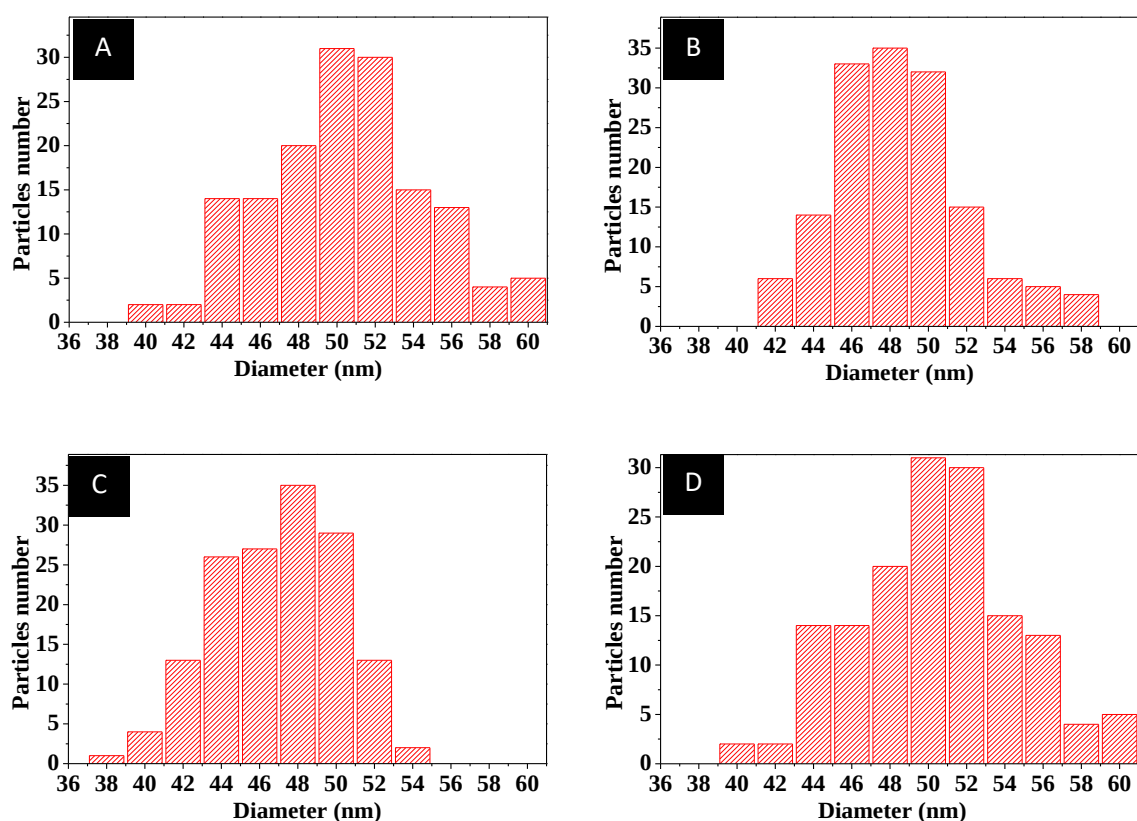


Figure 66 – Particles size distribution histograms of nanoparticles incorporated into the functionalized BCM: (A) BCM@SiO₂, (B) BCM@SiO₂@C₈TMS, (C) BCM@SiO₂@C₁₆TMS and (D) BCM@SiO₂@F₁₃TES, estimated from SEM images analysis.

Table 21 – Average particle size estimated by SEM (d_{SEM}) and TEM (d_{TEM}) of the functional nanomaterials (synthesized and functionalized by sol-gel method) incorporated into the BCM

Material	Particle size (nm)	
	d_{SEM}	d_{TEM}
BCM@SiO ₂	52 ± 3	54 ± 2
BCM@SiO ₂ @C ₈ TMS	49 ± 2	50 ± 2
BCM@SiO ₂ @C ₁₆ TMS	49 ± 4	50 ± 3
BCM@SiO ₂ @F ₁₃ TES	52 ± 4	51 ± 2

Micrographs of pristine BCM (**Figure 57** and **Figure 58**) exhibit smooth longitudinal fiber-like structures. After the immobilization of the functional silica nanoparticles on the BCM, the micrographs (**from Figure 59 to Figure 65**) reveal that the cellulose fibers are coated with particles with the same morphology (spherical) and average particle size as the bare functional silica nanoparticles (**Figure 20 - Figure 22** and **Table 7** in **chapter 3, section 3.1**), imparting nanoscale surface roughness.

In the case of BCM@SiO₂, BCM@SiO₂@C₈TMS, BCM@SiO₂@C₁₆TMS (**Figure 59 –Figure 61**) and BCM@SiO₂@C₈TMS_PG and BCM@SiO₂@C₁₆TMS_PG (**Figure 63** and **Figure 64**) samples, the surface of the BCM fibers is coated with these silica nanoparticles. In BCM@SiO₂@F₁₃TES (**Figure 62**), BCM@SiO₂-rice, BCM@SiO₂@F₁₃TES-rice (**Figure 65**), BCM@SiO₂_PG (**Figure 63**) and BCM@SiO₂@F₁₃TES_PG (**Figure 64**), the BCM fibers are fully covered with the silica nanomaterials.

6.2. Chemical characterization

The chemical characterization of functional BCM was performed by EDS, FTIR-ATR and XPS.

6.2.1. EDS and X-ray maps

From **Figure 67** to **Figure 71** are illustrated the EDS spectra (inset: atomic percentages of C, O, Si and F) and corresponding X-ray elemental maps of pristine BCM and functional BCM, obtained during SEM experiment.

In the micrograph of each sample (**Figure 58 – Figure 65**), is identified (red square) where the EDS analysis was performed.

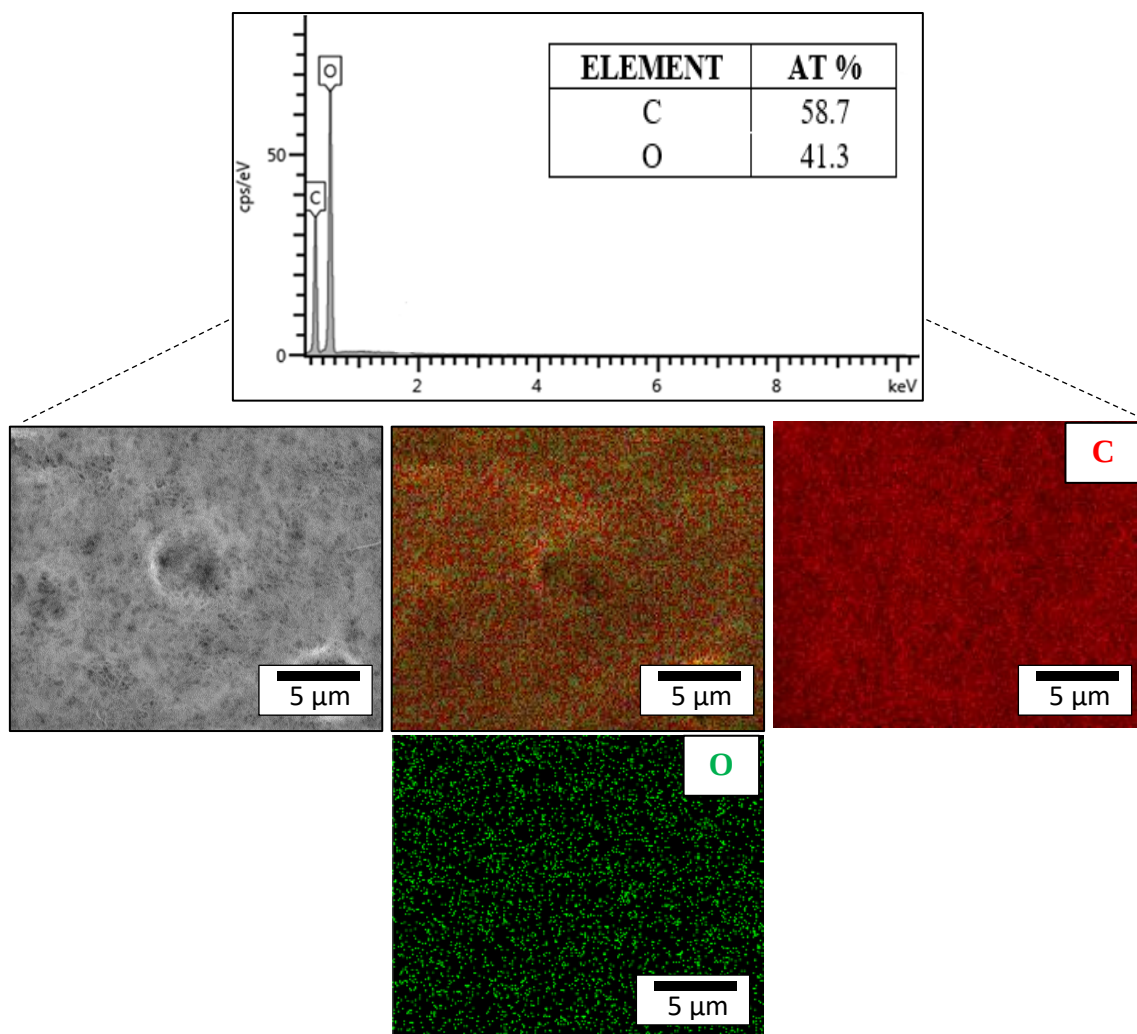
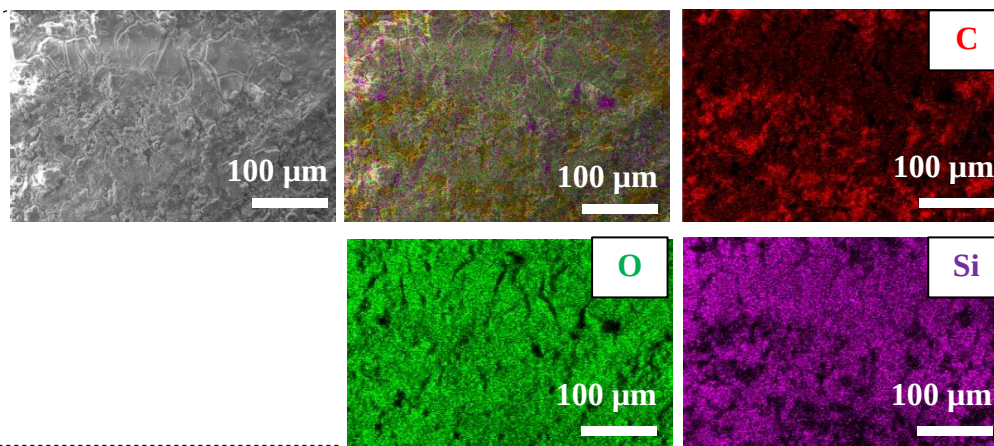
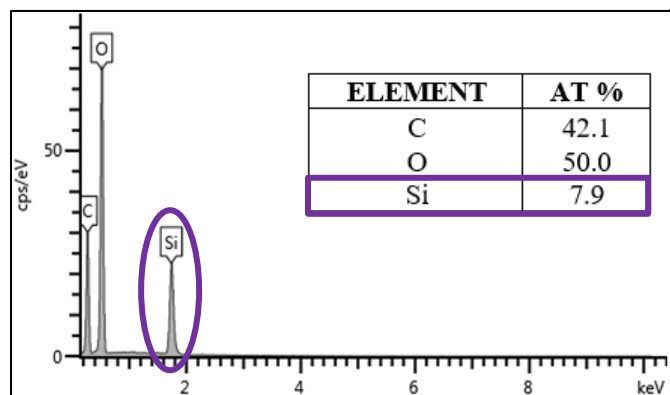


Figure 67 – EDS spectra and corresponding X-ray elemental maps of BCM sample.

BCM@SiO₂



BCM@SiO₂@C₈TMS

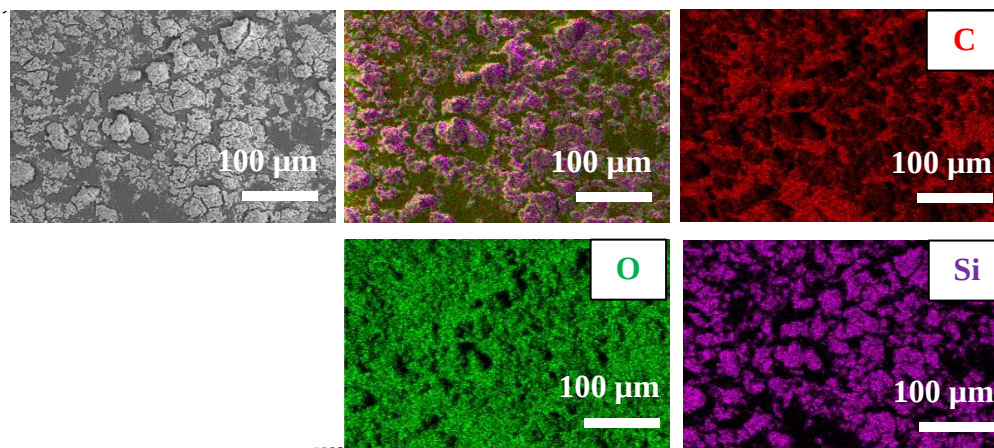
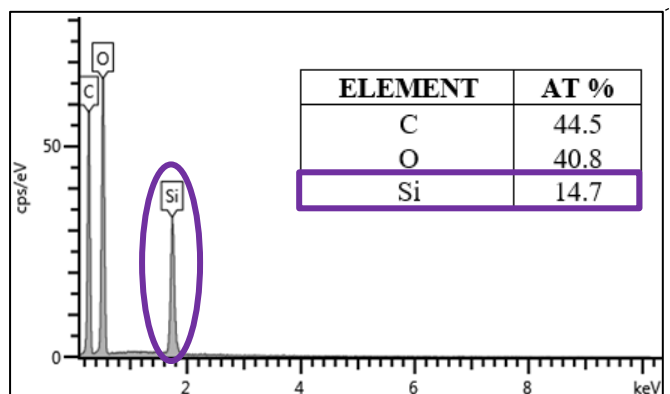
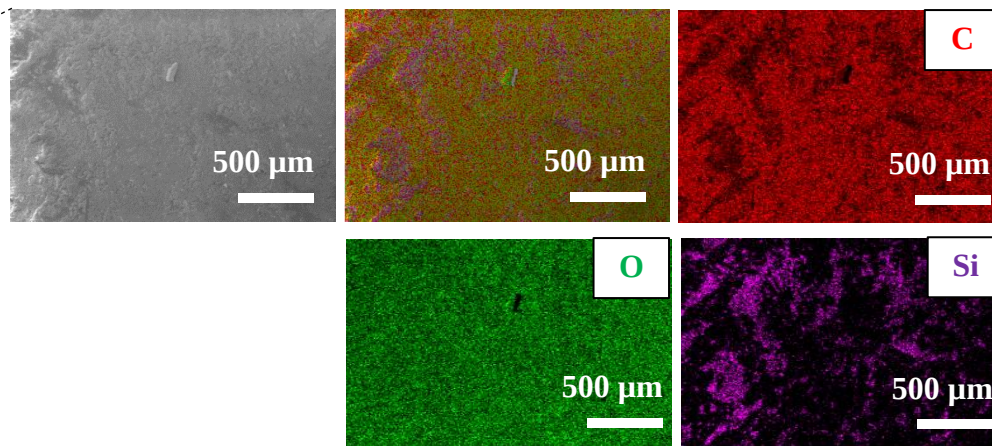
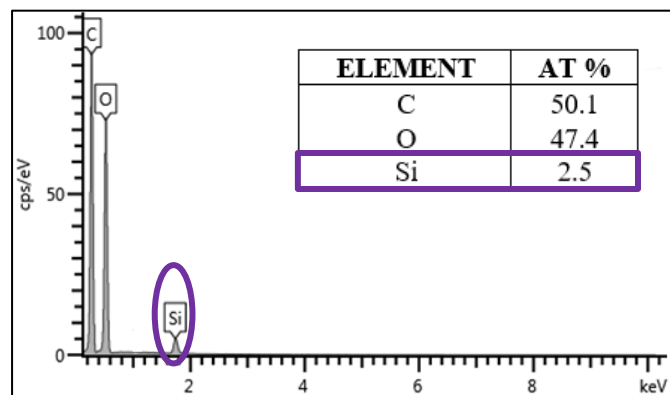


Figure 68 - EDS spectra and corresponding X-ray elemental maps of BCM@SiO₂ and BCM@SiO₂@C₈TMS samples.

BCM@SiO₂@C₁₆TMS



BCM@SiO₂@F₁₃TES

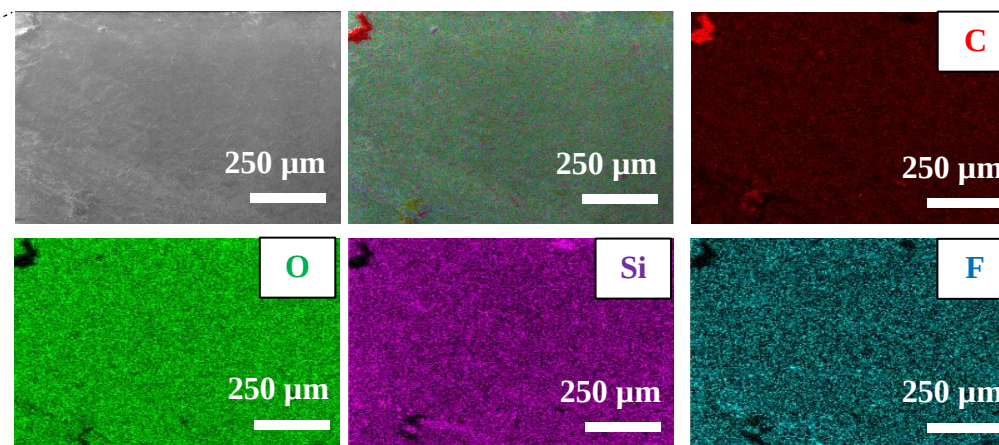
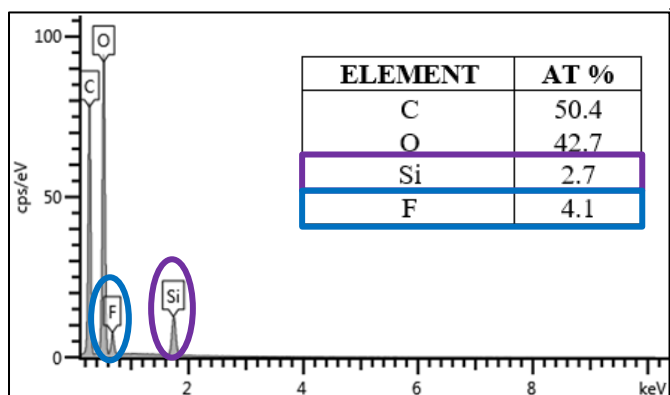
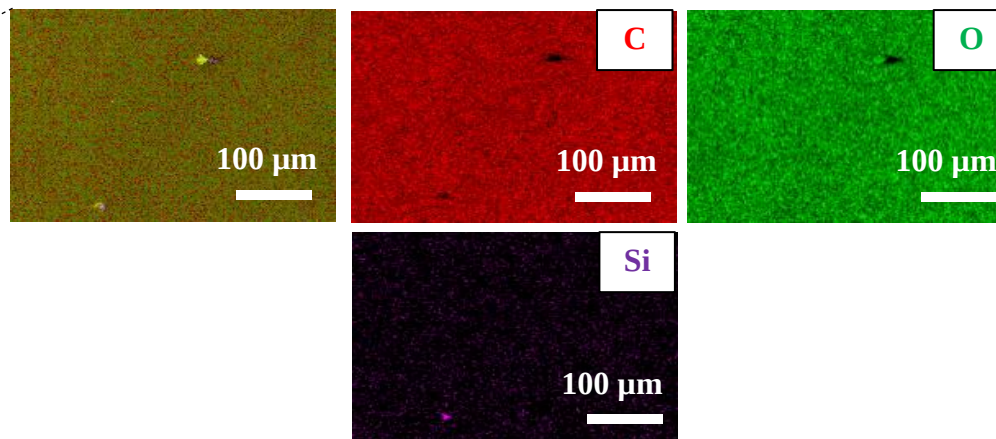
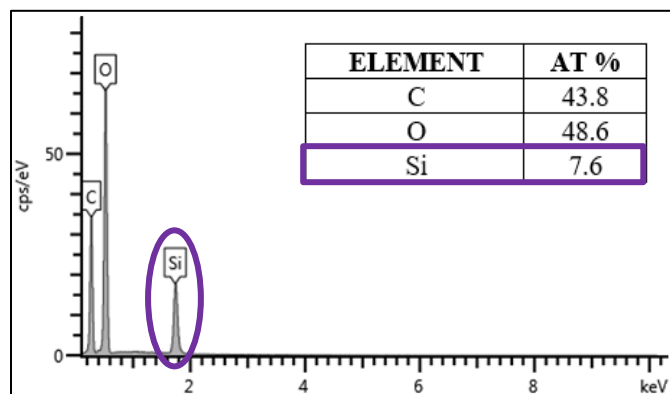


Figure 69 - EDS spectra and corresponding X-ray elemental maps of BCM@SiO₂@C₁₆TMS and BCM@SiO₂@F₁₃TES samples.

BCM@SiO₂-rice



BCM@SiO₂@F₁₃TES-rice

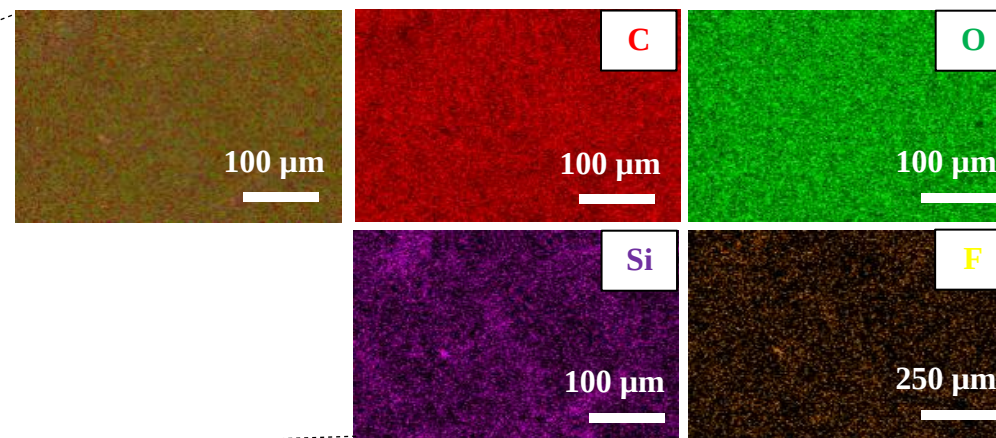
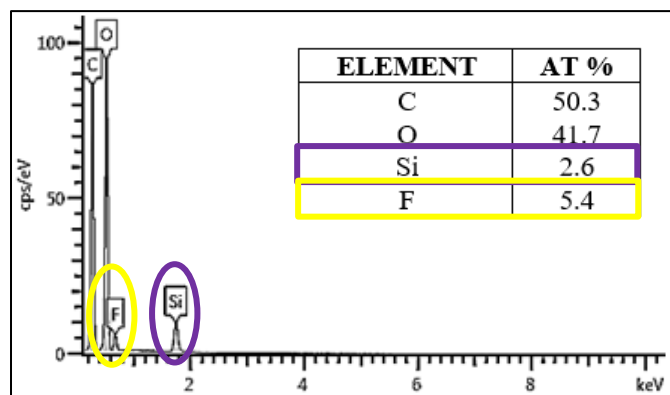


Figure 70 - EDS spectra and corresponding X-ray elemental maps of BCM@SiO₂-rice and BCM@SiO₂@F₁₃TES-rice samples.

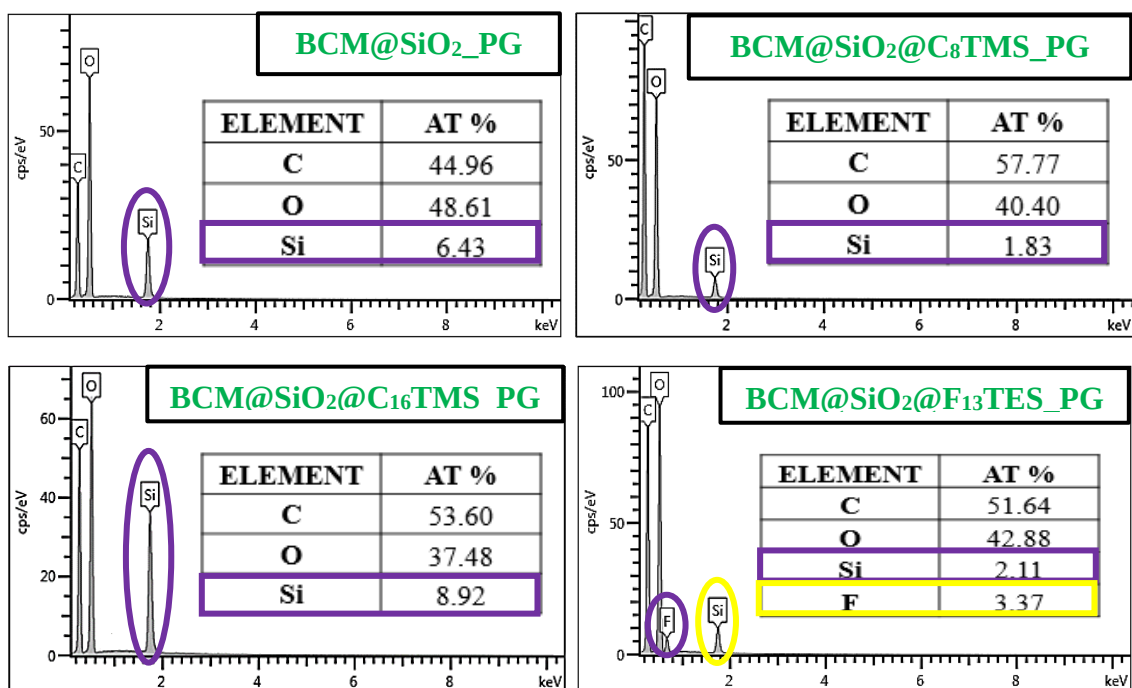


Figure 71 - EDS spectra of BCM@SiO₂_PG, BCM@SiO₂@C₈TMS_PG, BCM@SiO₂@C₁₆TMS_PG and BCM@SiO₂@F₁₃TES_PG samples.

The EDS spectra confirm the successful grafting of the silica nanoparticles by identifying of the elements Si (in all samples) and F (in the BCM@SiO₂@F₁₃TES, BCM@SiO₂@F₁₃TES-rice and BCM@SiO₂@F₁₃TES_PG samples) in the functional BCM. The X-ray elemental maps reveal that these elements are homogeneously distributed throughout the BCM surface.

6.2.2. FTIR-ATR

Figure 72 shows the vibrational spectroscopy FTIR-ATR of the BCM functionalized by in situ with silica-based nanomaterials, (A) BCM@SiO₂, (B) BCM@SiO₂@C₈TMS, (C) BCM@C₁₆TMS and (D) BCM@F₁₃TES (black spectrum) (nanomaterials obtained and functionalized by sol-gel method), in the 4000-1750 cm⁻¹ (left) and 1750-650 cm⁻¹ (right) range. The dotted lines highlight the characteristic peaks of silica-based nanomaterials (silica and organosilanes). In order to evaluate the chemical modification of the BCM, the vibrational spectra of the BCM (blue spectrum) and the respective functional silica-based nanomaterials (red spectrum), are presented together.

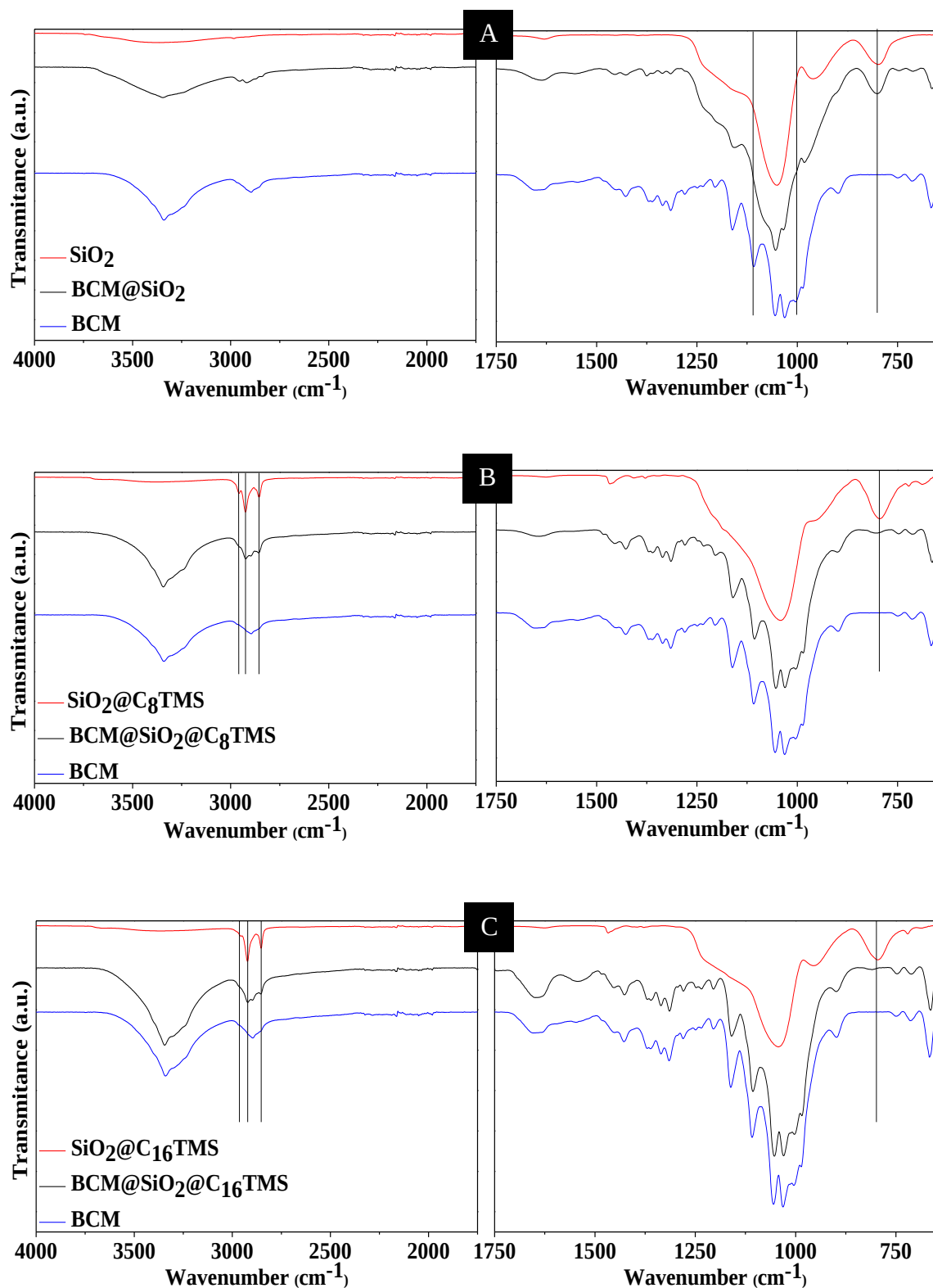


Figure 72 – FTIR-ATR spectra of (A) BCM@SiO₂, (B) BCM@SiO₂@C₈TMS and (C) BCM@SiO₂@C₁₆TMS samples, in the 4000-1750 cm⁻¹ (left) and 1750-650 cm⁻¹ (right) range. The dotted lines highlight the characteristic bands of silica-based nanomaterials (silica and organosilanes).

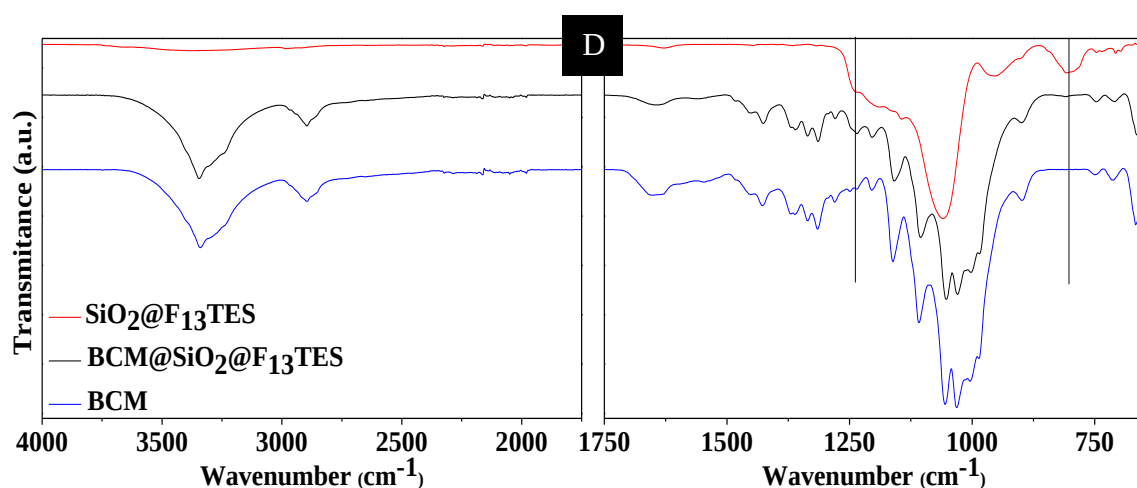


Figure 72 – cont – FTIR-ATR spectra of **(D)** BCM@SiO₂@F₁₃TES sample, in the 4000-1750 cm⁻¹ (left) and 1750-650 cm⁻¹ (right) range. The dotted lines highlight the characteristic bands of silica-based nanomaterials (silica and F₁₃TES).

The FTIR-ATR spectrum of the pristine BCM (blue spectrum) displays the characteristic bands of cellulose: stretching (3500-3300 cm⁻¹) and symmetric bending (1645 cm⁻¹) vibrations of H-bonded hydroxyl groups and adsorbed water; CH and CH₂ (CHOH; CH₂OH) stretching (3000-2870 cm⁻¹); C-OH and CH bending (1430-1330 cm⁻¹); C-O (-C-O-H) stretching (1200-1000 cm⁻¹); C-O (C-O-C) stretching (1150-1000 cm⁻¹); CH₂ asymmetric bending in plane (900-700 cm⁻¹) and OH bending out of the plane (700-650 cm⁻¹) vibrations [51, 69].

In the spectra of the BCM functionalized (black spectrum) with silica-based nanomaterials, new peaks are detected, sustaining the successful grafting of the functional silica-based nanomaterials (red spectrum) on the BCM (blue spectrum), namely: BCM@SiO₂ – Si-O-Si symmetric stretching vibrations (802 cm⁻¹) and furthermore, the disappearance of the bands at 1108 cm⁻¹ and 1004 cm⁻¹ by being masked by the silica band at 1050 cm⁻¹ (Si-O-Si asymmetric stretching vibrations); BCM@SiO₂@C₈TMS - C-H symmetric stretching of –CH₃ (2979 cm⁻¹), C-H antisymmetric stretching of –CH₂ (2925 and 2854 cm⁻¹) and Si-O-Si symmetric stretching vibrations (802 cm⁻¹) [37, 68]; BCM@SiO₂@C₁₆TMS - C-H symmetric stretching of –CH₃ (2961 cm⁻¹), C-H antisymmetric stretching of –CH₂ (2922 cm⁻¹) and Si-O-Si symmetric stretching

vibrations (802 cm^{-1}) [37, 68]; and BCM@SiO₂@F₁₃TES - C-H/C-C symmetric deformation ($1237\text{--}1144\text{ cm}^{-1}$) and Si-O-Si symmetric stretching vibrations (802 cm^{-1}) [68-70].

The FTIR-ATR of the BCM functionalized with the same nanomaterials but by post-grafting (BCM@SiO₂_PG, BCM@SiO₂@C₈TMS_PG, BCM@C₁₆TMS_PG and BCM@F₁₃TES_PG) and the FTIR-ATR of the BCM functionalized by in situ with silica nanoparticles from rice husk with easy-cleaning properties (BCM@SiO₂-rice and BCM@SiO₂@F₃TES-rice), are very similar to those presented and are presented in **Annex 2 (Figure 114 and Figure 115, respectively)**.

6.2.3 XPS

The chemical composition of BCM@SiO₂, BCM@SiO₂@C₈TMS, BCM@C₁₆TMS and BCM@F₁₃TES (BCM functionalized with nanomaterials obtained and functionalized by sol-gel method), was quantified through XPS analysis. The surface atomic percentages and core-level binding energies (BEs) of the different elements determined by XPS are summarized in **Table 22** and **Table 23**, respectively.

Table 22 – Surface atomic percentages for functionalized BCM with silica-based nanomaterials obtained by XPS^[a].

Sample	Atomic (%)			
	C 1s	O 1s	Si 2p	F 1s
BCM	60.3	39.7	-	-
BCM@SiO ₂	16.2	61.0	22.8	-
BCM@SiO ₂ @C ₈ TMS	48.6	40.2	11.2	-
BCM@SiO ₂ @C ₁₆ TMS	48.9	34.5	16.6	-
BCM@SiO ₂ @F ₁₃ TES	36.4	40.3	9.7	13.6

^[a] Determined by the areas of the respective peaks in the high-resolution XPS spectra.

Table 23 - Core-level binding energy and area of each component for silica nanomaterials obtained by curve fitting of XPS spectra.

Sample	C 1s		O 1s		Si 2p		F 1s	
	BE ^[a] (eV)	Area ^[b] (%)	BE ^[a] (eV)	Area ^[b] (%)	BE ^[a] (eV)	Area ^[b] (%)	BE ^[a] (eV)	Area ^[b] (%)
BCM	284.6 (1.2)	32.4	530.9 (1.5)	6.2	-	-	-	-
	286.2 (1.2)	50.8	532.6 (1.5)	93.8	-	-	-	-
	287.7 (1.2)	13.8	-	-	-	-	-	-
	288.7 (1.2)	3.0	-	-	-	-	-	-
BCM@SiO ₂	284.6 (1.4)	61.4	534.3 (1.6)	87.8	104.8 (1.7)	100	-	-
	286.2 (1.4)	33.9	536.2 (1.6)	12.2	-	-	-	-
	287.8 (1.4)	4.7	-	-	-	-	-	-
BCM@SiO ₂ @C ₈ TMS	284.6 (1.6)	68.6	533.9 (1.8)	93.1	104.4 (1.6)	60.1	-	-
	286.4 (1.6)	28.6	536.3 (1.8)	6.9	106.2 (1.6)	6.5	-	-
	288.2 (1.6)	2.8	-	-	-	-	-	-
BCM@SiO ₂ @C ₁₆ TMS	284.6 (1.6)	70.0	534.1 (1.8)	93.1	104.4 (1.6)	59.1	-	-
	286.4 (1.6)	24.6	536.5 (1.8)	6.9	106.4 (1.6)	7.5	-	-
	288.4 (1.6)	5.4	-	-	-	-	-	-
BCM@SiO ₂ @F ₁₃ TES	284.6 (1.4)	7.5	533.7 (1.8)	93.1	104.0 (1.8)	100	689.9 (2.2)	100
	286.3 (1.4)	48.3	536.5 (1.8)	6.9	-	-	-	-
	288.0 (1.4)	9.8	-	-	-	-	-	-
	291.8 (1.6)	27.0	-	-	-	-	-	-
	294.0 (1.4)	7.4	-	-	-	-	-	-

^[a] The values between brackets refer to the FWHM of the bands. ^[b] Relative area of each component in the different core-level region

The C 1s high-resolution spectrum of the pristine BCM exhibits three main components at 284.6, 286.2 and 287.7 eV attributed to C-H/C-C, C-O and O-C-O/C=O bonds of cellulose respectively, and a very weak band around 288.7 eV [33]. The main peak around 532.6 eV in the O 1s spectrum is assigned to the oxygen-based groups of the cellulose structure [33, 58].

In the functional BCM, besides carbon and oxygen, silicon and fluorine are also detected. Furthermore, there is a significant reduction of the carbon content (from 60.3 to 16.2%) and an increase of the oxygen loading (from 39.7 to 61.0 %), confirming the presence of silica nanoparticles. Moreover, the Bes of the main O 1s and Si 2p bands are higher than those of the corresponding bands of the SiO₂ samples, suggesting that the nanoparticles are covalently grafted to the BCM.

6.3. Thermal characterization

The thermograms of the pristine BCM (black thermogram) and functionalized BCM by in situ and post-grafting with SiO₂ (red thermogram), SiO₂@C₈TMS (blue thermogram), SiO₂@C₁₆TMS (green thermogram) and SiO₂@F₁₃TES (pink thermogram), obtained by sol-gel method, are show in **Figure 73** and **Figure 74**, respectively.

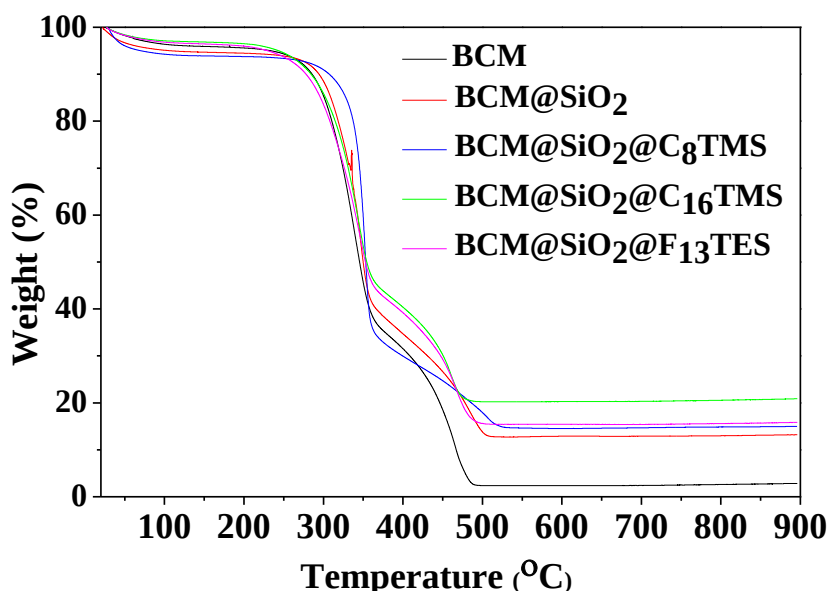


Figure 73 - Thermogravimetric curves of the samples: BCM (black thermogram), BCM@SiO₂ (red thermogram), BCM@SiO₂@C₈TMS (blue thermogram),

BCM@C₁₆TMS (green thermogram) and BCM@F₁₃TES (pink thermogram), under O₂ atmosphere.

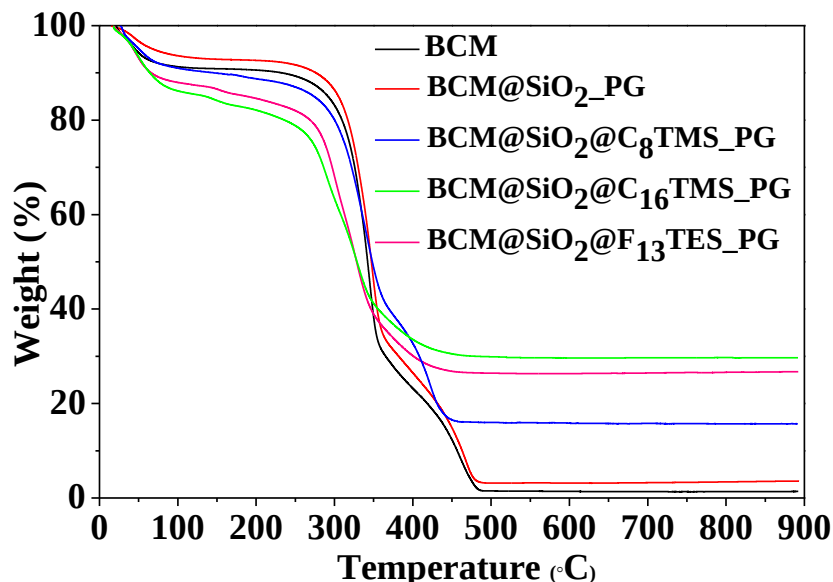


Figure 74 - Thermogravimetric curves of the samples: BCM (black thermogram), BCM@SiO₂_PG (red thermogram), BCM@SiO₂@C₈TMS_PG (blue thermogram), BCM@C₁₆TMS_PG (green thermogram) and BCM@F₁₃TES_PG (pink thermogram), under O₂ atmosphere.

The thermogravimetric curves of all samples exhibit two significant weight losses: from ambient temperature to 150 °C and from 150 °C to 500 °C.

The first weight loss is due to membrane dehydration. Physically adsorbed and hydrogen-bonded linked water molecules are removed at this first stage. The second weight loss is associated to the decomposition of the BCM [1]. From 500 °C, a variable residue is observed, according to the silica nanoparticles immobilized in the BCM. In the case of functionalized BCM by in situ (**Figure 73**), the residue loading increases in the order BCM@SiO₂ < BCM@SiO₂@C₈TMS < BCM@SiO₂@F₁₃TES < BCM@SiO₂@C₁₆TMS. These features confirm that BCM@SiO₂ and BCM@SiO₂@C₈TMS contain the highest fractions of inorganic component, whereas BCM@SiO₂@F₁₃TES and BCM@SiO₂@C₁₆TMS contain the highest loading of organosilane, in accordance with EDS results.

The TGA of the BCM functionalized by in situ with silica nanoparticles from rice husk (BCM@SiO₂-rice and BCM@SiO₂@F₁₃TES-rice), are not presented, but are very similar to those presented (BCM@SiO₂@F₁₃TES and BCM@SiO₂@F₁₃TES_PG).

Additionally, regardless of the method used to immobilize the nanomaterials in cellulose, the thermographic profile is the same.

6.4. Evaluation of easy-cleaning properties

The easy-cleaning properties of the BCM functionalized with silica-based nanomaterials with easy-cleaning properties were evaluated by measuring the contact angles. In **Figure 75** are illustrated representative photographs of deionized water, toluene, cyclohexane, artificial sweat droplets on the surface of the functional BCM and the corresponding contact angles (CA).

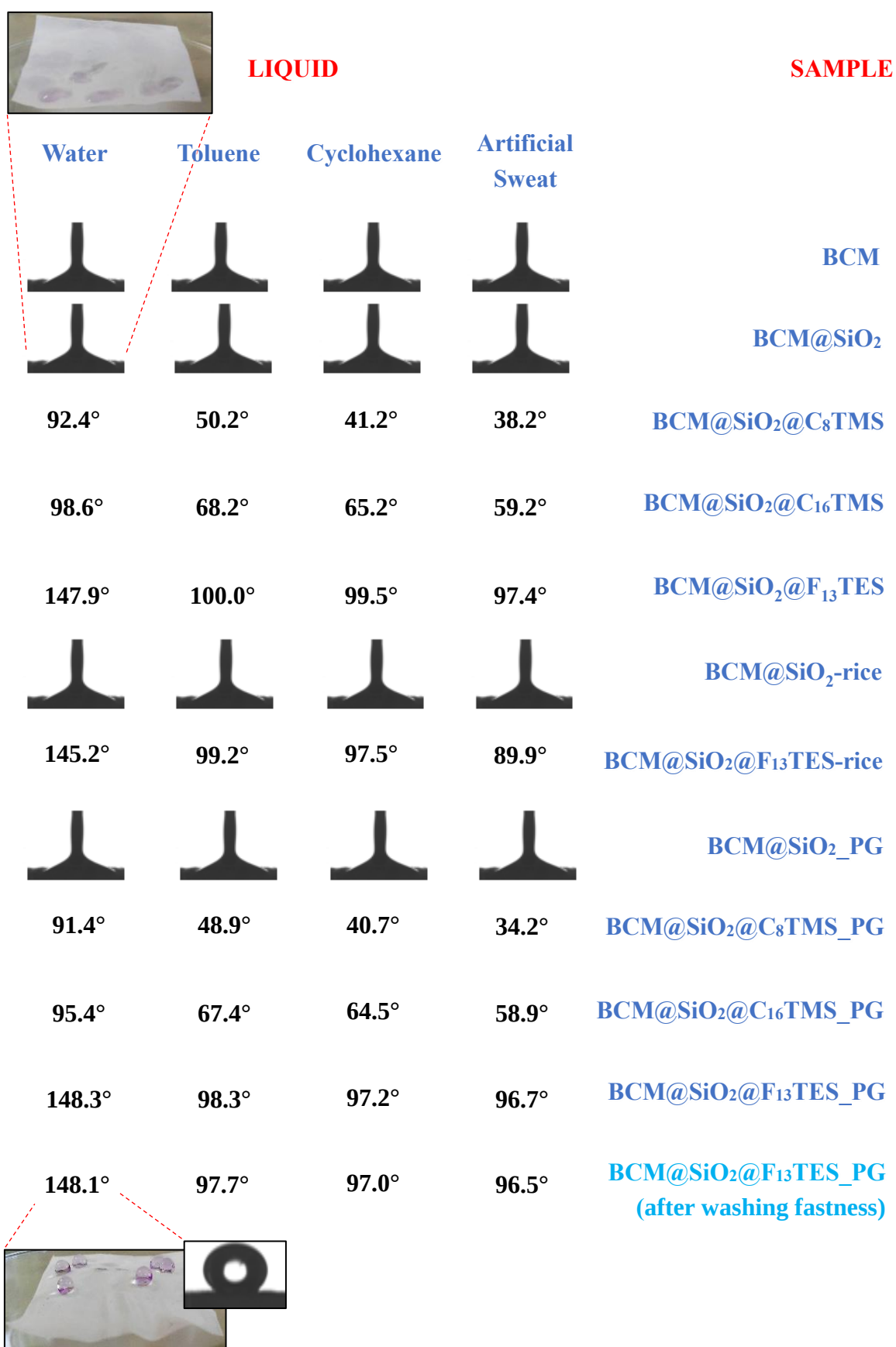


Figure 75 - Contact Angle between deionized water, toluene, cyclohexane, artificial sweat and the functional BCM.

The pristine BCM and BCM functionalized with SiO₂ (BCM@SiO₂, BCM@SiO₂-rice and BCM@SiO₂-PG) are amphiphilic resulting on the immediate absorption of all liquids droplets.

In contrast, the surface repellency of the functionalized BCM with silica nanoparticles containing functional groups is remarkably enhanced. Specifically, the BCM functionalized by in situ and post-grafting with SiO₂@F₁₃TES, displays a surface almost superhydrophobic ($> 150^\circ$). These properties are similar to those of others substrates (cotton fabrics by way of example) immobilized with silica nanoparticles functionalized with the organosilane F₁₃TES prepared by different methodologies [33, 73].

Independently of the immobilization method used (in situ and post-grafting), there are no significant differences in the values of the contact angle.

The repellency properties of functionalized BCM with silica-based nanomaterials reveals are better to those obtained by the respective immobilized nanoparticles (compare **Figure 75** and **Figure 28 (in chapter 3, section 3.8)**). This remarkable performance is a result of the synergy between two factors: a significant reduction of the surface free energy combined with an increase of the nanoscale surface roughness imparted by the nanometer size silica particles [33].

The sample with best efficiency easy-cleaning properties (BCM@SiO₂@F₁₃TES-PG, exhibited a good washing fastness, as evidenced by the constant performance of easy-cleaning properties.

6.5. Conclusions

Spherical silica nanoparticles with average particle size around 51 ± 4 nm, mesoporous structure and high porosity, synthesized and functionalized by sol-gel method and spherical silica nanoparticles with heterogeneous particles size (20-40 nm) with mesoporous structure and high porous structure obtained from rice husk with easy-cleaning properties, were successfully incorporated in BCM by in situ methodology and post-grafting methodology.

After immobilization of these silica nanoparticles on the cellulose, their size and morphology remained constant.

The surface repellency of the functionalized BCM with silica nanoparticles containing easy-cleaning properties was remarkably enhanced. Specifically, the BCM

functionalized by in situ and post-grafting with $\text{SiO}_2@\text{F}_{13}\text{TES}$, displayed a surface almost superhydrophobic ($> 150^\circ$).

The repellency properties of functional BCM reveals are better to those obtained by the respective immobilized nanoparticles. Furthermore, Contact angle values were similar regardless of the immobilization method used.

The functional BCM also presented a good resistance to washing with high chemical stability.

CHAPTER 7

Bacterial cellulose
membrane
functionalized with
anatase SiO_2 - TiO_2
nanocomposites

7. Bacterial cellulose membrane functionalized with anatase $\text{SiO}_2@\text{TiO}_2$ nanocomposites

The $\text{BCMD}@\text{SiO}_2@\text{TiO}_2\text{-PG}$ (BCM functionalized with $\text{SiO}_2@\text{TiO}_2$ in dry state) and $\text{BCMw}@\text{SiO}_2@\text{TiO}_2\text{-PG}$ (BCM functionalized with $\text{SiO}_2@\text{TiO}_2$ in wet state) samples were characterized by SEM, EDS, Raman and TGA and its photocatalytic activity was evaluated. The results and respective discussion are presented in this chapter.

7.1. SEM

In **Figure 76** is represented the SEM micrographs, of the samples $\text{BCMD}@\text{SiO}_2@\text{TiO}_2\text{-PG}$ and $\text{BCMw}@\text{SiO}_2@\text{TiO}_2\text{-PG}$, respectively. In the SEM micrograph of each sample is identified (red square) where the EDS analysis (**Figure 78**) was performed. The **Figure 77** are illustrated the particles size distribution histograms, of the $\text{SiO}_2@\text{TiO}_2$ (**A**) and $\text{SiO}_2@\text{TiO}_2$ in $\text{BCMw}@\text{SiO}_2@\text{TiO}_2\text{-PG}$ (**B**), estimated by SEM image analysis.

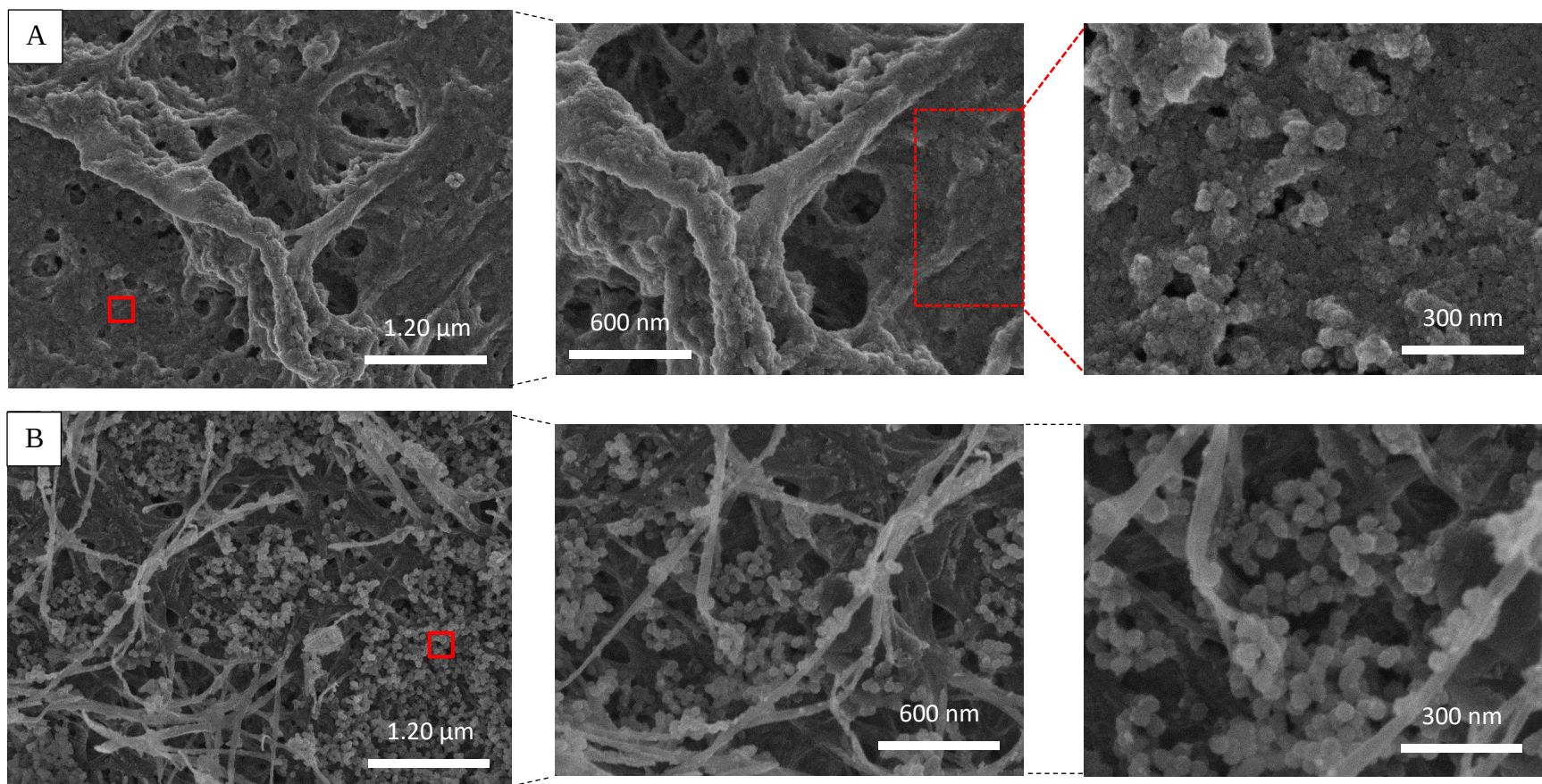


Figure 76 – SEM micrographs of (A) BCMD@SiO₂@TiO₂_PG and (B) BCMW@SiO₂@TiO₂_PG samples.

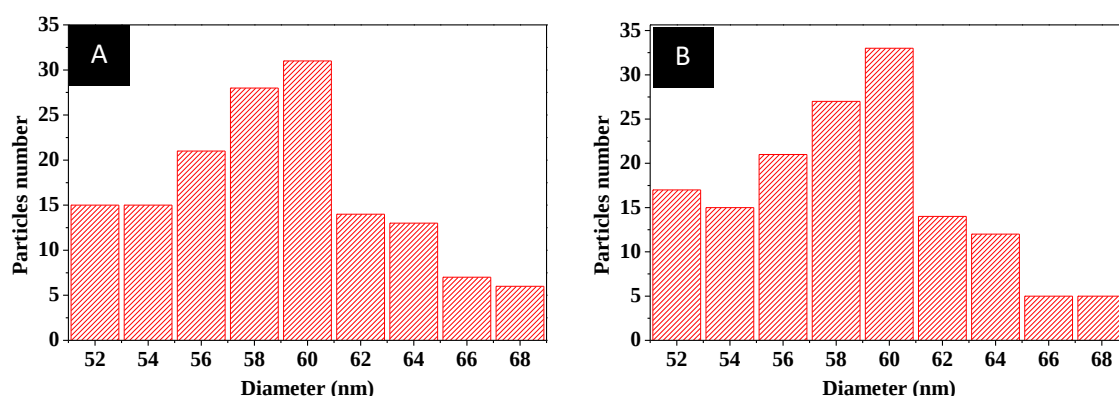


Figure 77 – Particles size distribution histograms of (A) SiO₂@TiO₂ and (B) SiO₂@TiO₂ in BCMW@SiO₂@TiO₂, estimated by SEM images analysis.

SEM micrographs of BCM exhibit smooth longitudinal fiber-like structures (**Figure 57 in chapter 6, section 6.1**), while BCM functionalized with SiO₂@TiO₂ nanocomposite reveal that the fibers are coated with particles. In the case of BCMW@SiO₂@TiO₂-dip (**Figure 76B**), the surface of fibers are coated with particles with the same morphology (spherical) and average particle size around 60 ± 2 nm (**Figure 76 and Figure 77**) as those of SiO₂@TiO₂ (**Figure 50 to Figure 52 in chapter 5, section 5.1**). In BCMD@SiO₂@TiO₂-dip (**Figure 76A**) the BCM fibers are fully covered with a film of an agglomerate of these nanoparticles.

7.2. EDS and X-ray maps

In **Figure 78** and **Figure 79** are illustrated the EDS spectra (inset: atomic percentages of C, O, Si and Ti) and corresponding X-ray elemental maps of BCMD@SiO₂@TiO₂_PG and BCMW@SiO₂@TiO₂_PG samples, respectively, obtained during SEM experiment.

In the micrograph of each sample (**Figure 76**), is identified (red square) where the EDS analysis was performed.

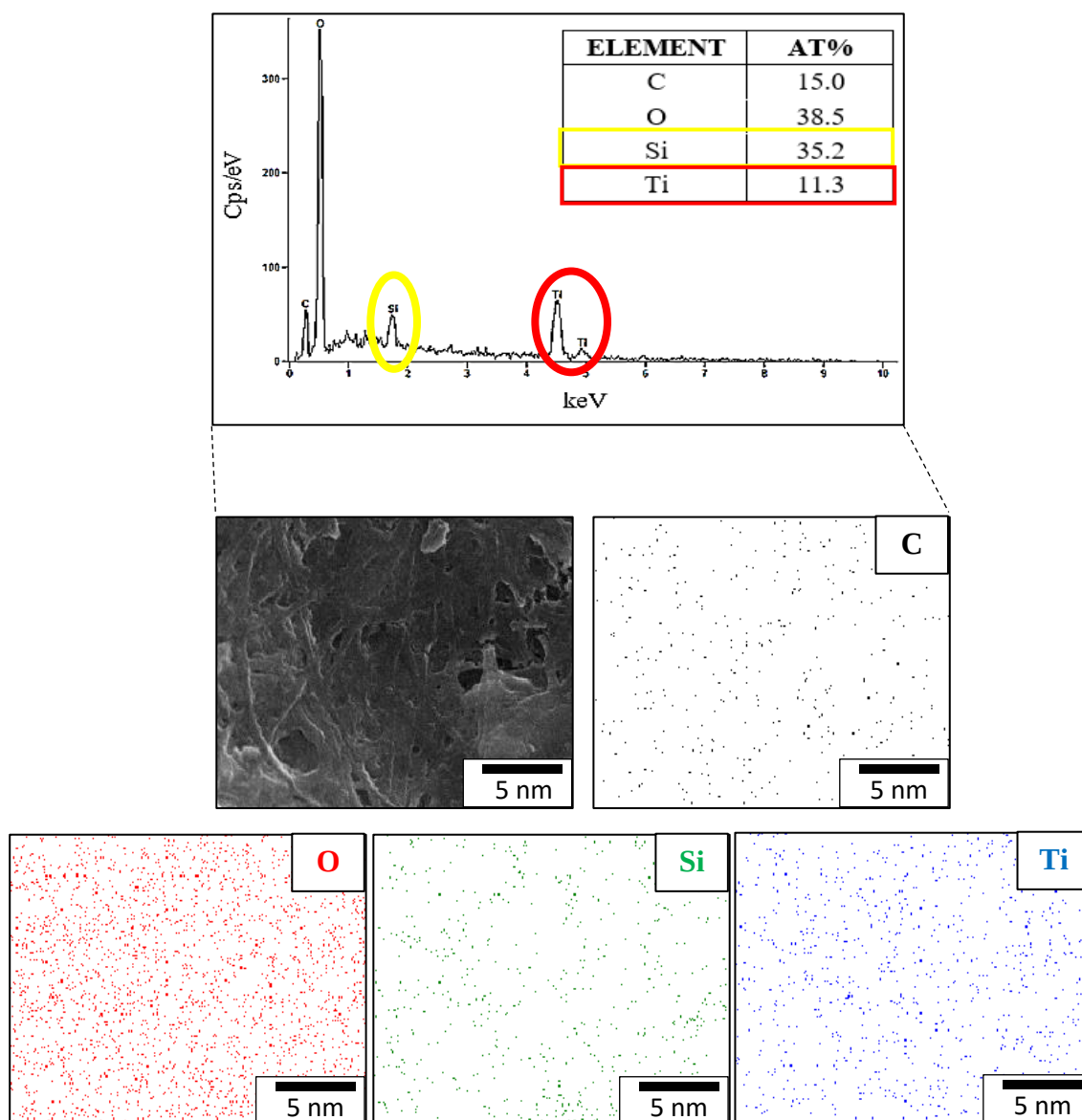


Figure 78 – EDS spectra and corresponding X-ray elemental maps of BCMD@SiO₂@TiO₂_PG sample.

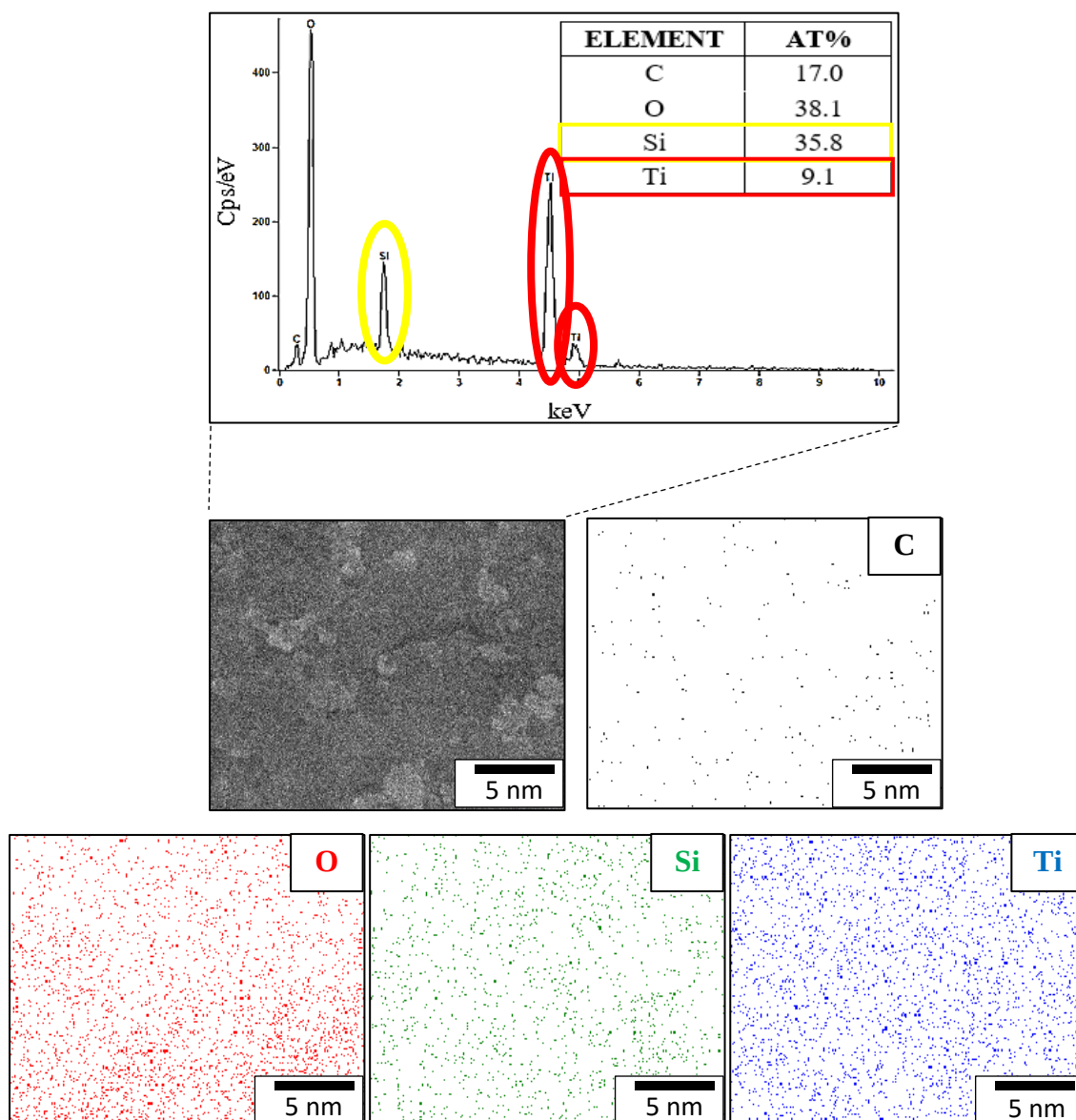


Figure 79 – EDS spectra and corresponding X-ray elemental maps of BCMW@SiO₂@TiO₂_PG sample.

The EDS spectra and X-ray elemental maps (**Figure 78** and **Figure 79**) confirm the existence of Si and Ti in the functionalized BCM, indicating the successful grafting of the SiO₂@TiO₂ nanocomposite in the BCM. The X-ray elemental maps confirm that these elements are homogeneously distributed throughout the BCM.

7.3. Raman

Figure 80 show the raman spectra of BCMW@SiO₂@TiO₂_PG (red spectrum) and BCMD@SiO₂@TiO₂_PG (blue spectrum) in the 100-900 cm⁻¹ range.

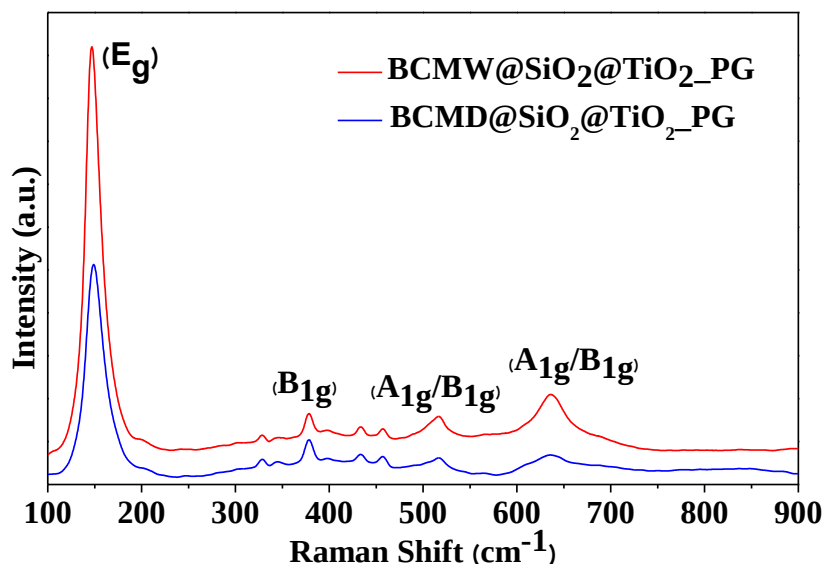


Figure 80 – Raman spectra of BCMW@SiO₂@TiO₂_PG (red spectrum) and BCMD@SiO₂@TiO₂_PG (blue spectrum) samples.

Raman spectra of BCM functionalized with SiO₂@TiO₂ nanocomposite show characteristic bands of anatase at 148 cm⁻¹ (E_g), 396 cm⁻¹ (B_{1g}), 513 cm⁻¹ (A_{1g}/B_{1g}), and 635 cm⁻¹ (A_{1g}/B_{1g}) [40, 68]. Therefore, anatase crystalline phase remains after immobilization of the SiO₂@TiO₂ nanocomposite in the BCM.

7.4. TGA

The immobilization efficiency of the nanocomposite was confirmed by TGA analysis. The TGA curves of the BCM (black thermogram), BCMD@SiO₂@TiO₂_PG (red thermogram) and BCMW@SiO₂@TiO₂_PG (green thermogram) are shown in **Figure 81**.

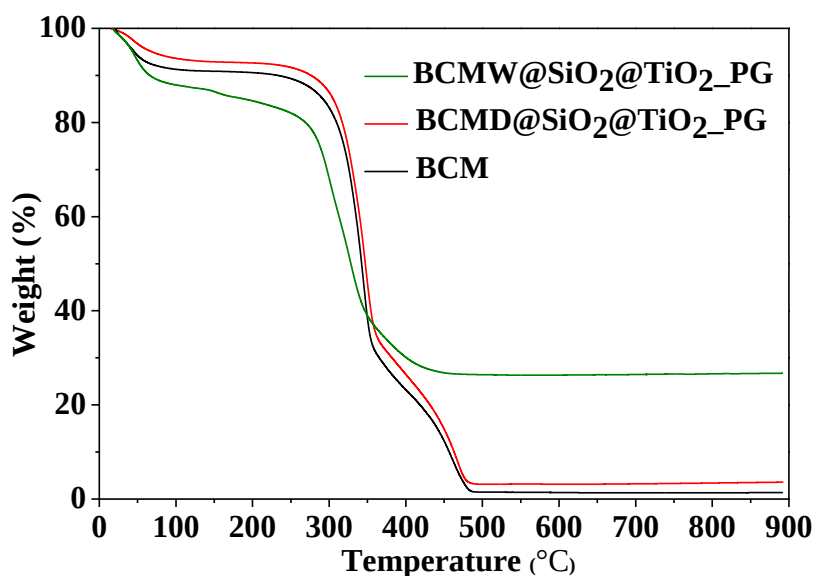


Figure 81 - TGA curves of the samples BCM (black thermogram), BCMD@SiO₂@TiO₂_PG (red thermogram) and BCMW@SiO₂@TiO₂_PG (green thermogram).

From 500 °C a gradual increase of residue is observed, confirming more or less efficient immobilization of the SiO₂@TiO₂ nanocomposite in the BCM according to the process employed. The residue loading, increase in the order BCMD@SiO₂@TiO₂_PG < BCW@SiO₂@TiO₂_PG, suggesting a higher immobilization efficiency of the SiO₂@TiO₂ nanocomposite in the BCM in wet state.

7.5. Photocatalytic activity

The self-cleaning properties of functional BCM were evaluated by measuring the area of the absorbance peak of MV dye in the visible region (450-700 nm) after each dosage of irradiation of UV light (5 min - 24 h) (**Figure 82**).

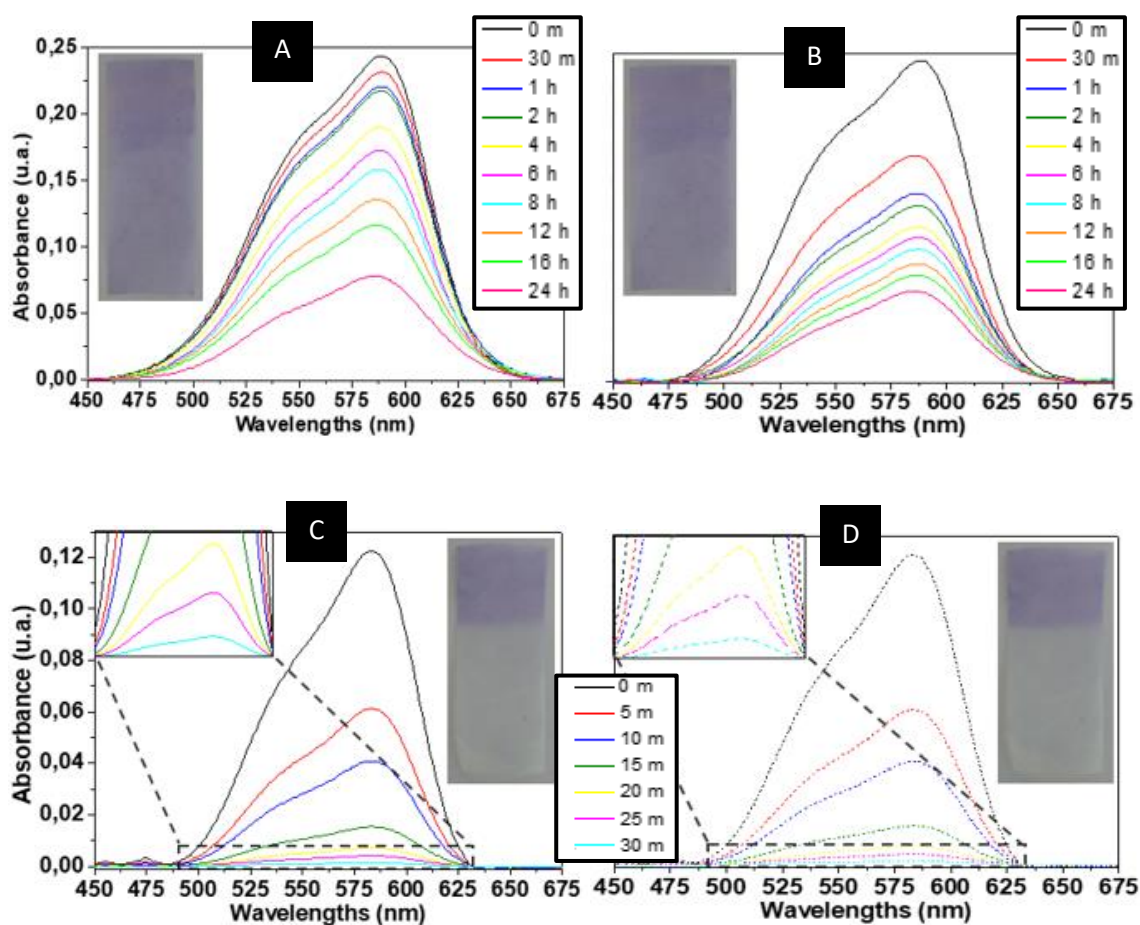


Figure 82 - Electronic absorption spectra of the samples: **(A)** pristine BCM, **(B)** BCMD@SiO₂@TiO₂_PG, **(C)** BCMW@SiO₂@TiO₂_PG and **(D)** BCMW@SiO₂@TiO₂_PG (after washing fastness).

The MV characteristic band decreases as a function of the irradiation time, being higher in the BCM which was functionalized in the wet state (BCMW@SiO₂@TiO₂_PG (**Figure 82C and 82D**)) occurring the completely decomposition of the MV dye after 30 minutes of irradiation. This sample, with best efficiency self-cleaning properties, exhibited a higher loading residue (**Figure 81**) and present good washing fastness (**Figure 82C vs. Figure 82D**), as evidenced by the constant performance of self-cleaning properties.

The enhanced photocatalytic activity of the functional BCM might be attributed to the unique physicochemical properties of SiO₂@TiO₂ nanocomposite which result from the strong interaction of TiO₂ filme and SiO₂ nanoparticles such as the increased

specific surface area of $\text{SiO}_2@\text{TiO}_2$ nanocomposite [42, 77] and the enhanced surface acidity of the nanocomposites [42, 78]. The increase in specific surface area facilitates more effective adsorption sites which might promote the photocatalytic activity by increasing the concentration of contaminants and reaction intermediates near the TiO_2 [42]. Additionally, mixed metal oxides often generate additional surface acidity over their individual members because of an increase in the polarizability of the hydroxide groups present in the mixed oxide [42]. In the $\text{SiO}_2@\text{TiO}_2$ nanocomposite, a complex oxide may form at the interface due to the existence of Ti-O-Si vibration in the FTIR spectrum (**Figure 55 in chapter 5, section 5.3**). These bonds enhance surface acidity of the $\text{TiO}_2@\text{SiO}_2$ nanocomposites and in turn improve the photocatalytic activity of the BC- $\text{SiO}_2@\text{TiO}_2$ membrane fabricated in this study [42].

7.6. Conclusions

BCM displaying self-cleaning properties have been prepared by incorporation of $\text{SiO}_2@\text{TiO}_2$ nanocomposite in BCM. TGA analyses demonstrate a higher loading for BCM functionalized in wet state possibly due to a better diffusion of the nanocomposite into the BCM during the process. This higher loading may correlate with the greater efficiency of the latter materials synthesized in the wet state compared to the other materials to degrade MV in much shorter time.

The functional BCM also presented a good resistance to washing with high chemical stability and the color and texture of the original features were maintained.

CHAPTER 8

Bacterial cellulose
membrane
functionalized with
silica nanoparticles
with natural-based
colored properties

8. Bacterial cellulose membrane functionalized with silica nanoparticles with natural-based colored properties

In **Figure 83** are illustrated representative photographs of **(A)** $\text{SiO}_2\text{@curc-rice}$, after the process of washing fastness, **(C)** BCM, **(D and E)** $\text{BCM@SiO}_2\text{@cur-rice}$ after the process of washing fastness and the resulting **(F)** $\text{BCM@SiO}_2\text{@cur-rice}$.

In order to evaluate the immobilization efficiency of $\text{SiO}_2\text{@cur-rice}$ on the BCM, the functionalized BCM with only **(B)** curcuma are presented together.

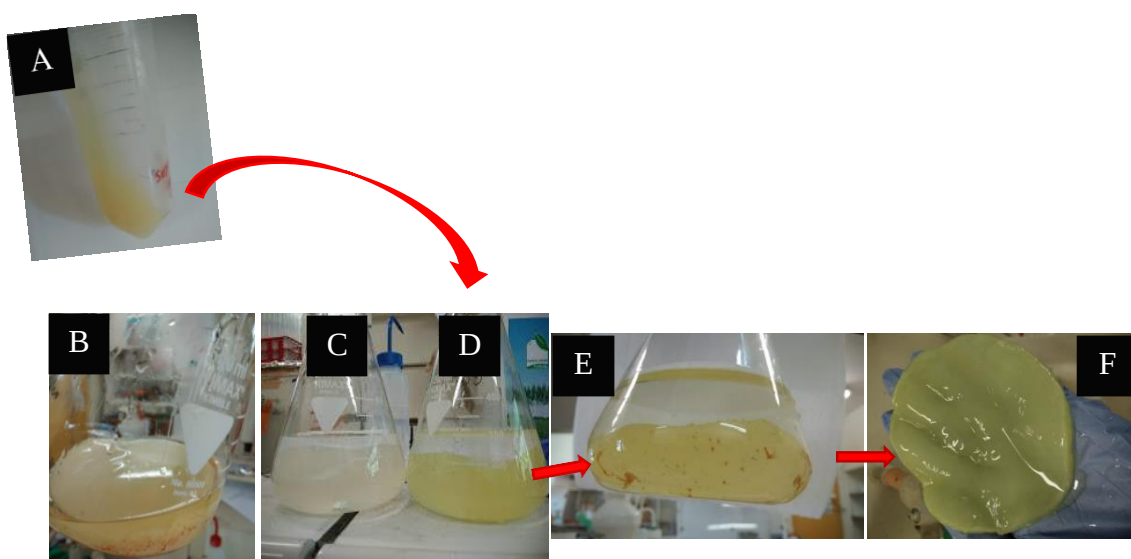


Figure 83 - Representative photographs of **(A)** $\text{SiO}_2\text{@cur-rice}$, after the process of washing fastness, **(B)** functionalized membrane with only curcuma, **(C)** BCM, **(D and E)** $\text{BCM@SiO}_2\text{@cur-rice}$ after the process of washing fastness and the resulting **(F)** $\text{BCM@SiO}_2\text{@cur-rice}$.

Through the analysis of **Figure 83**, it is possible to verify that the $\text{SiO}_2\text{@cur-rice}$ was immobilized in the BCM successfully presenting an identical coloring to that of $\text{SiO}_2\text{@cur-rice}$ (yellow) (**Figure 83A**). During the purification process of BCM, the resulting washing waters are clear, evidencing the immobilization efficiency of $\text{SiO}_2\text{@cur-rice}$ sample in the BCM (**Figure 83D** and **Figure 83E**). In contrast, the immobilization of only curcuma in the BCM, it wasn't efficient. After the BCM formation

process, the curcuma remained in the culture medium and the small part that was immobilized, exhibited no stability during the membrane purification process (**Figure 83B**). This fact demonstrates that the silica nanoparticles acts as linker between curcuma and the BCM structure.

The morphology, chemical composition and the immobilization efficiency of the BCM@SiO₂@cur-rice were characterized by SEM, TEM, EDS, FTIR-ATR and TGA. The results and respective discussion, are presented in this chapter.

8.1. SEM and TEM

In **Figure 84** is represented the SEM and TEM micrographs of the BCM@SiO₂@cur-rice sample. In the SEM micrograph of the sample BCM@SiO₂@cur-rice is identified (red square) where the EDS analysis (**Figure 86**) was performed. In the **Figure 85** are illustrated the particles size distribution histograms, of SiO₂@cur-rice (**A**) and SiO₂@cur-rice in BCM@SiO₂@cur-rice (**B**), estimated by SEM image analysis.

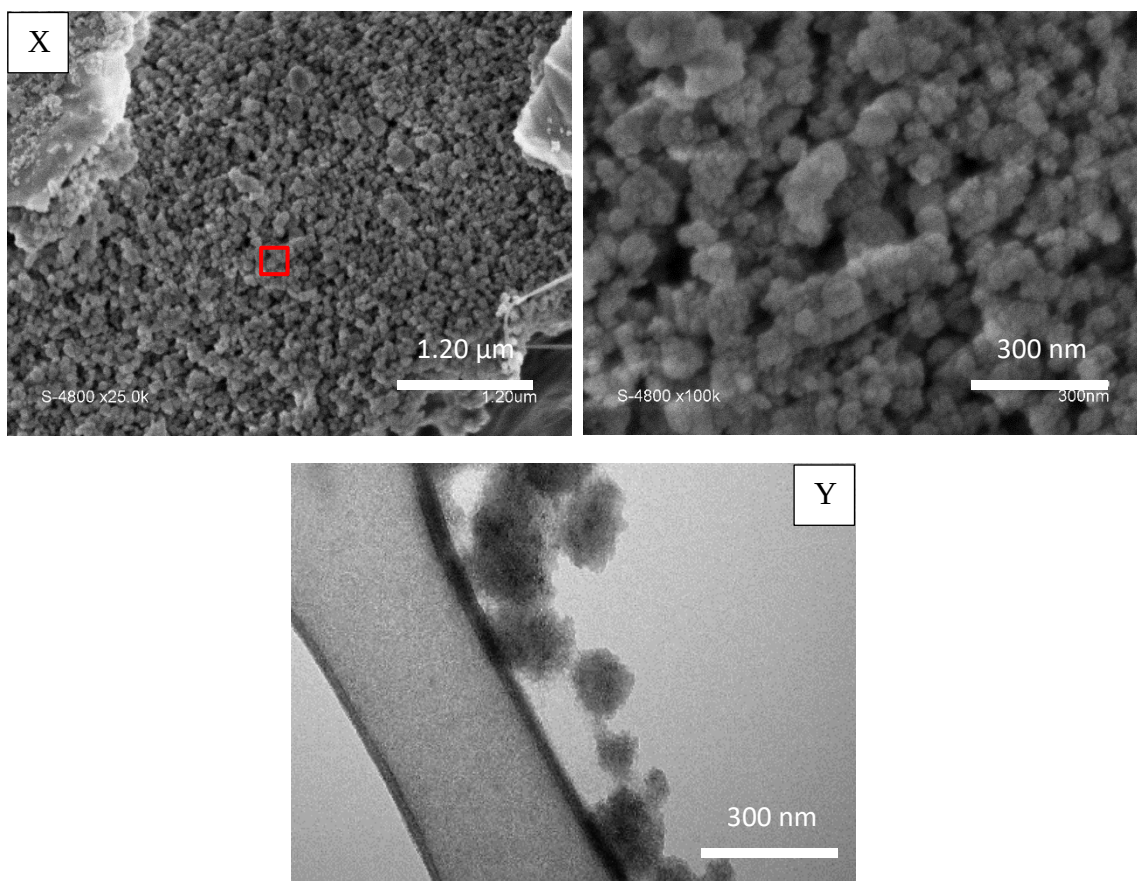


Figure 84 – (X) SEM and (Y) TEM micrographs of BCM@SiO₂@cur_rice samples.

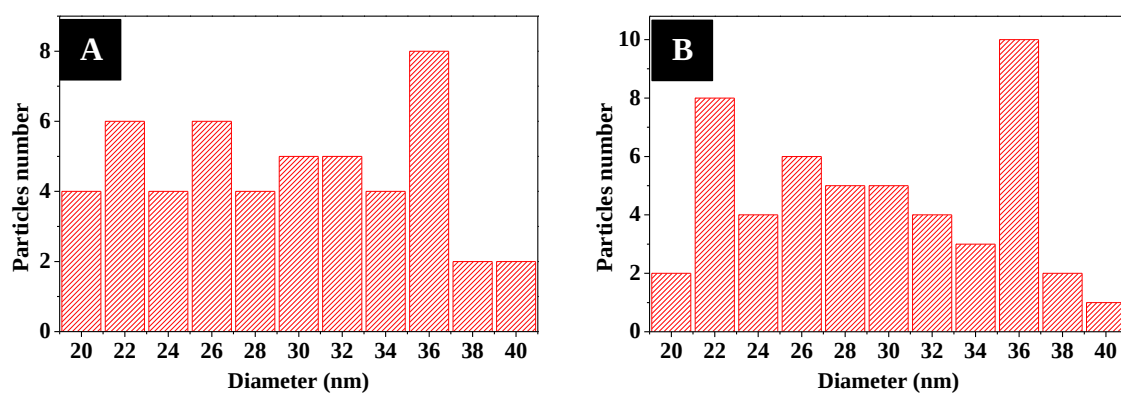


Figure 85 – Particles size distribution histograms of (A) SiO₂@cur-rice and (B) BCM@SiO₂@cur-rice samples, determined from TEM images analysis.

The SEM and TEM micrographs and EDS spectra (**Figure 84**) evidence the successful grafting of the SiO₂@cur-rice in the BCM (compare **Figure 84** with **Figure 57 (chapter 6, section 6.1)**). The SEM micrographs reveal that in the BCM@SiO₂@cur-rice sample, the fibers are totally coated with SiO₂@cur-rice; the SiO₂@cur-rice particles tend to form cluster coating the fiber surface.

After immobilization of SiO₂@cur-rice on BCM, the morphology and particle size of the silica nanoparticles remain unchanged (spherical with heterogeneous particle size (20-40 nm)).

8.2. EDS and X-ray maps

In **Figure 86** are illustrated the EDS spectra (inset: atomic percentages of C, O and Si) and corresponding X-ray elemental maps of BCM@SiO₂@cur-rice, obtained during SEM experiment.

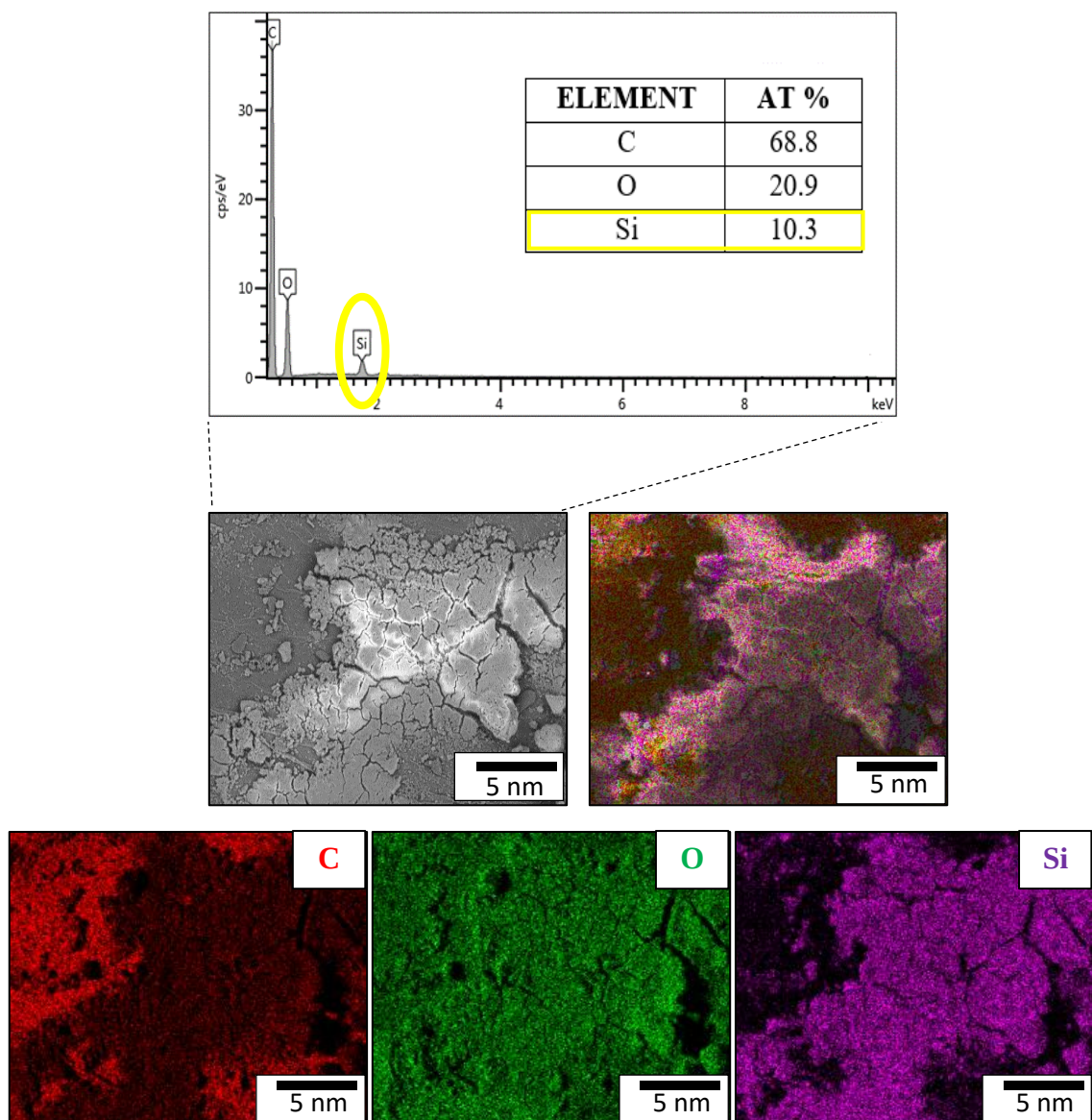


Figure 86 – EDS spectra and corresponding X-ray elemental maps of BCMD@SiO₂@cur-rice sample.

The EDS spectra and X-ray elemental maps confirm the existence of the characteristic elements of the SiO₂@cur-rice sample on the BCM surface, indicating their successful grafting. The X-ray elemental maps confirm the homogeneous distribution of these elements throughout the BCM.

8.3. FTIR-ATR

The vibrational spectroscopy FTIR-ATR of BCM@SiO₂@cur-rice sample (red spectrum), in the range 4000-650 cm⁻¹, are show in **Figure 87**. In order to evaluate the immobilization of SiO₂@cur-rice sample in the BCM, the vibrational spectra of the BCM (blue spectrum) and the SiO₂@cur-rice (black spectrum), are also presented together.

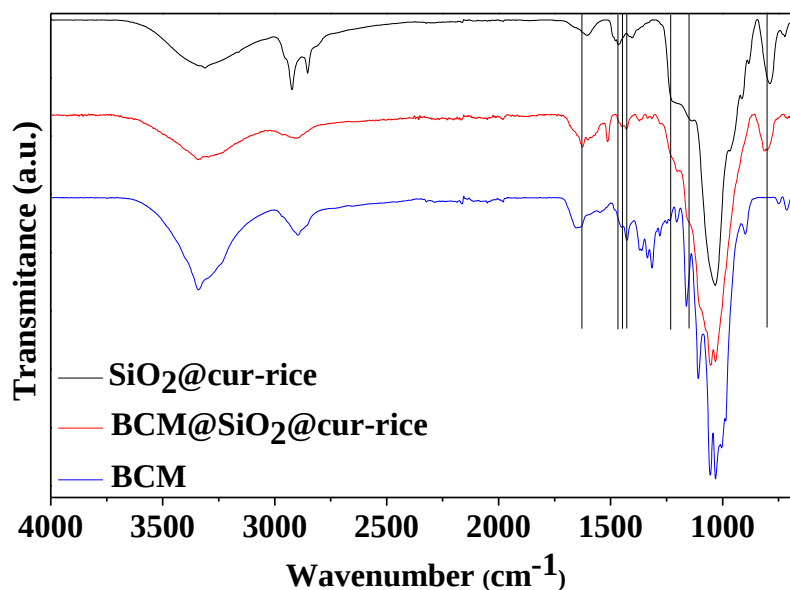


Figure 87 - FTIR-ATR spectra of BCM@SiO₂@cur-rice sample, in the 4000-650 cm⁻¹ range. The dotted lines highlight the characteristic peaks of SiO₂@cur-rice sample.

The FTIR-ATR spectra of the BCM@SiO₂@cur-rice (red spectrum) confirm the immobilization of SiO₂@cur-rice on the BCM successfully. The spectra displays the characteristic bands of cellulose (blue spectrum) (description of the characteristic bands of cellulose in **chapter 6, section 6.2.2**). However, new bands which match well the

fingerprint vibrational modes of the SiO₂@cur-rice (black spectrum) are identified, namely: C=C in plane stretching (1604 cm⁻¹), C-H antisymmetric deformation (1492 - 1463 cm⁻¹), C-H symmetric deformation (1373 cm⁻¹), Si-O-Si asymmetric stretching (1090 cm⁻¹ with a shoulder around 1228 cm⁻¹) and C=C symmetric stretching (925 - 815 cm⁻¹) vibrations [65].

8.4. TGA

The thermograms of the pristine BCM (black thermogram) and BCM@SiO₂@cur-rice (red thermogram) sample are shown in **Figure 88**.

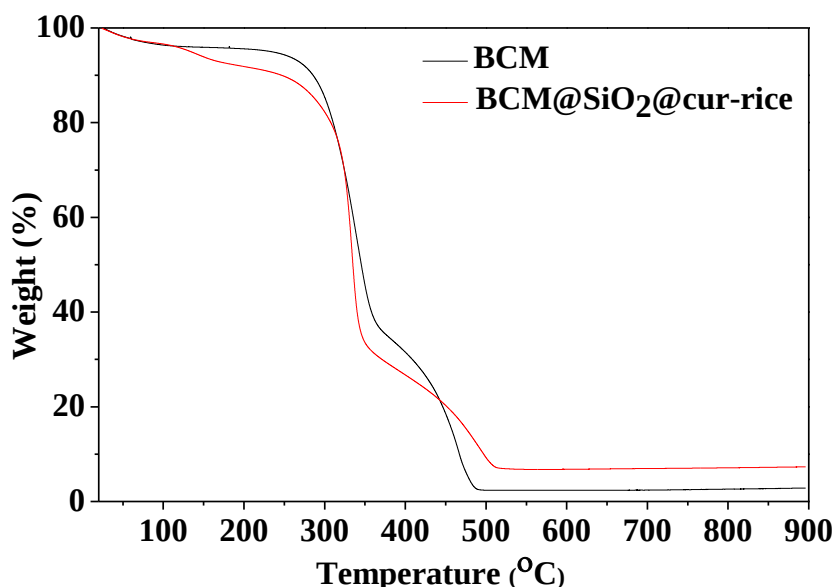


Figure 88 - Thermogravimetric curves of the samples: pristine BCM (black thermogram) and BCM@SiO₂@cur-rice (red thermogram), under O₂ atmosphere.

The TGA analysis confirms the grafting of the SiO₂@cur-rice on the BCM. In addition to the two weight losses associated to BCM dehydration (from ambient temperature to 150 °C) and decomposition of the BCM (from 150 °C to 500 °C), from 500 °C [1, 69], a variable residue is observed being major on the BCM@SiO₂@cur-rice sample (red thermogram).

8.5. Conclusions

Spherical silica nanoparticles with particles size between 20-40 nm obtained from rice husk and functionalized with curcuma, were successfully incorporated in BCM by in situ methodology, as evidenced by the results obtained by SEM, TEM, EDS, FTIR-ATR and TGA techniques. The SiO₂@cur-rice are homogeneously distributed throughout the BCM.

Silica nanoparticles provided a good chemical stability of curcuma in the BCM, having acted as a linker. In addition a good resistance to washing, the original features (namely the texture) of this functional biomaterial, were maintained.

CHAPTER 9

Bacterial cellulose
membrane
functionalized with
organic silicon
source

9. Bacterial cellulose membrane functionalized with organic silicon source

BCM also went prepared and functionalized in situ with different organic silicon source: BTEB (BCM@5%BTEB and BCM@BTEB), BTPD (BCM@BTPD) and BTSE (BCM@BTSE).

In **Figure 89** are illustrated representative photographs of pristine BCM (**A**) and BCM functionalized with 5% of BTEB (BCM@5% BTEB) (**B**) and 10% of BTEB (BCM@BTEB) (**C**). The photographs of the samples BCM@BTPD and BCM@BTSE are illustrated in **Annex 1**.

Through the analysis of **Figure 89**, it is possible to verify “white dots” in the functionalized BCM with BTEB with major concentration in BCM@BTEB sample (**C**). It is suggested that these white points are the result of an accumulation of BTEB at these sites on the BCM.

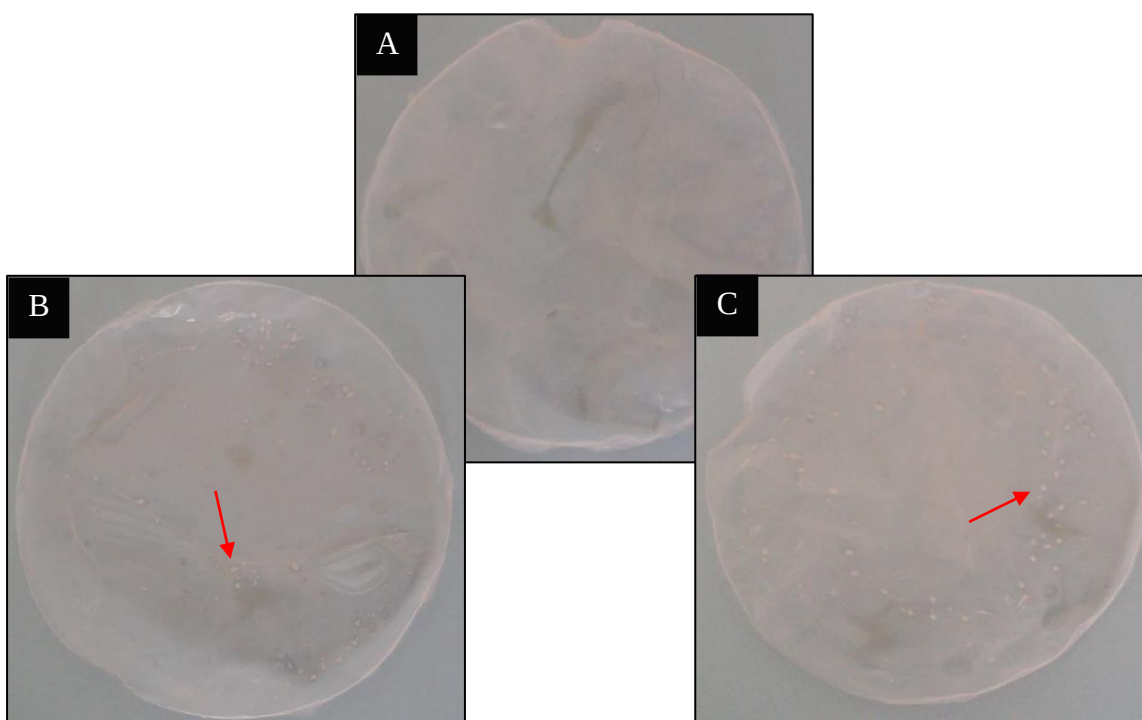


Figure 89 – Representative photographs of (A) BCM, (B) BCM@5%BTEB and (C) BCM@BTEB samples.

BCM@5% BTEB, BCM@BTEB, BCM@BTPD and BCM@BTSE, were characterized by SEM, TEM, AFM, EDS, FTIR-ATR, XPS, RMN and XRD, in order to

confirm the immobilization of the organic silicon source in the BCM. All samples were analyzed in different positions.

The results and respective discussion are presented in this chapter.

9.1. SEM, TEM and AFM

The morphological study of BCM@5%BTEB, BCM@BTEB, BCM@BTPD and BCM@BTSE, was performed by SEM, TEM and AFM (from **Figure 90** to **Figure 93**). In SEM micrograph of the samples is identified (red square) where the EDS analysis was performed. Average particle size of the nanomaterials in the BCM was estimated by TEM (d_{TEM}) (**Figure 94**).

The SEM and TEM micrographs of the BCM functionalized with organosilane BTEB, BTPD and BTSE, reveal the formation of spherical nanoparticles, with porous structure and heterogeneous particle size (30-100 nm in the case of BCM@5%BTEB and BCM@BTEB, 70-84 nm in the case of BCM@BTPD and 74-88 nm in the BCM@BTSE). The SEM micrographs show that in the samples BCM@5% BTEB, BCM@BTPD and BCM@BTSE (**Figure 90**, **Figure 92** and **Figure 93**), the surface of the fibers is coated with these nanoparticles. In the case of BCM@BTEB sample the BCM fibers are fully covered with a film of an agglomerate of the nanoparticles (**Figure 91**).

Surface roughness is evidenced in the AFM micrographs of the functionalized BCM compared with the pristine BCM (see **chapter 6, section 6.1**). This roughness is more evident in the BCM functionalized with BTEB (where the formation of white dots occurred), being higher in sample BCM@BTEB.

BCM@5%BTEB

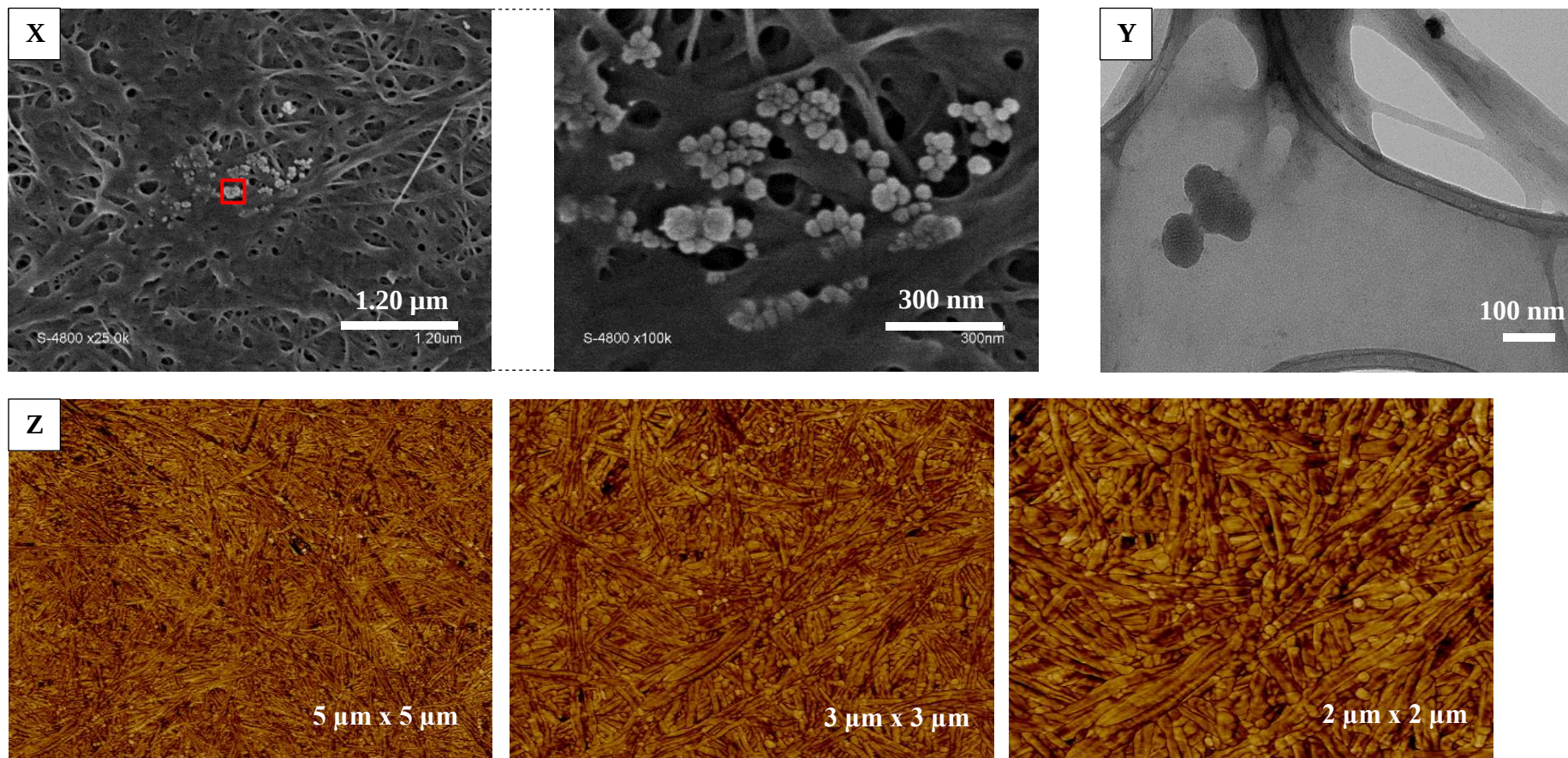


Figure 90 – (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@5%BTEB sample.

BCM@BTEB

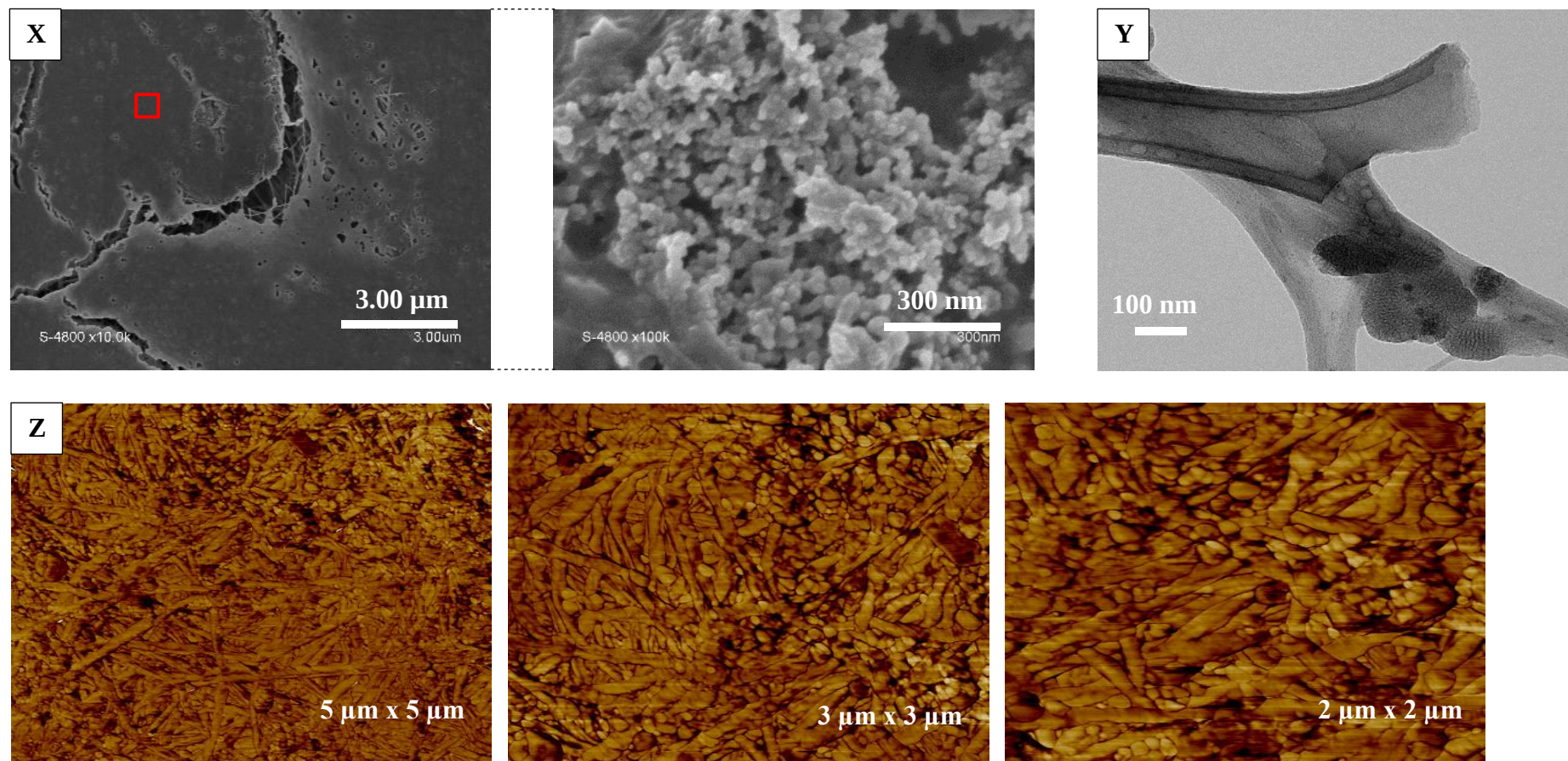


Figure 91 – (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@BTEB sample.

BCM@BTPD

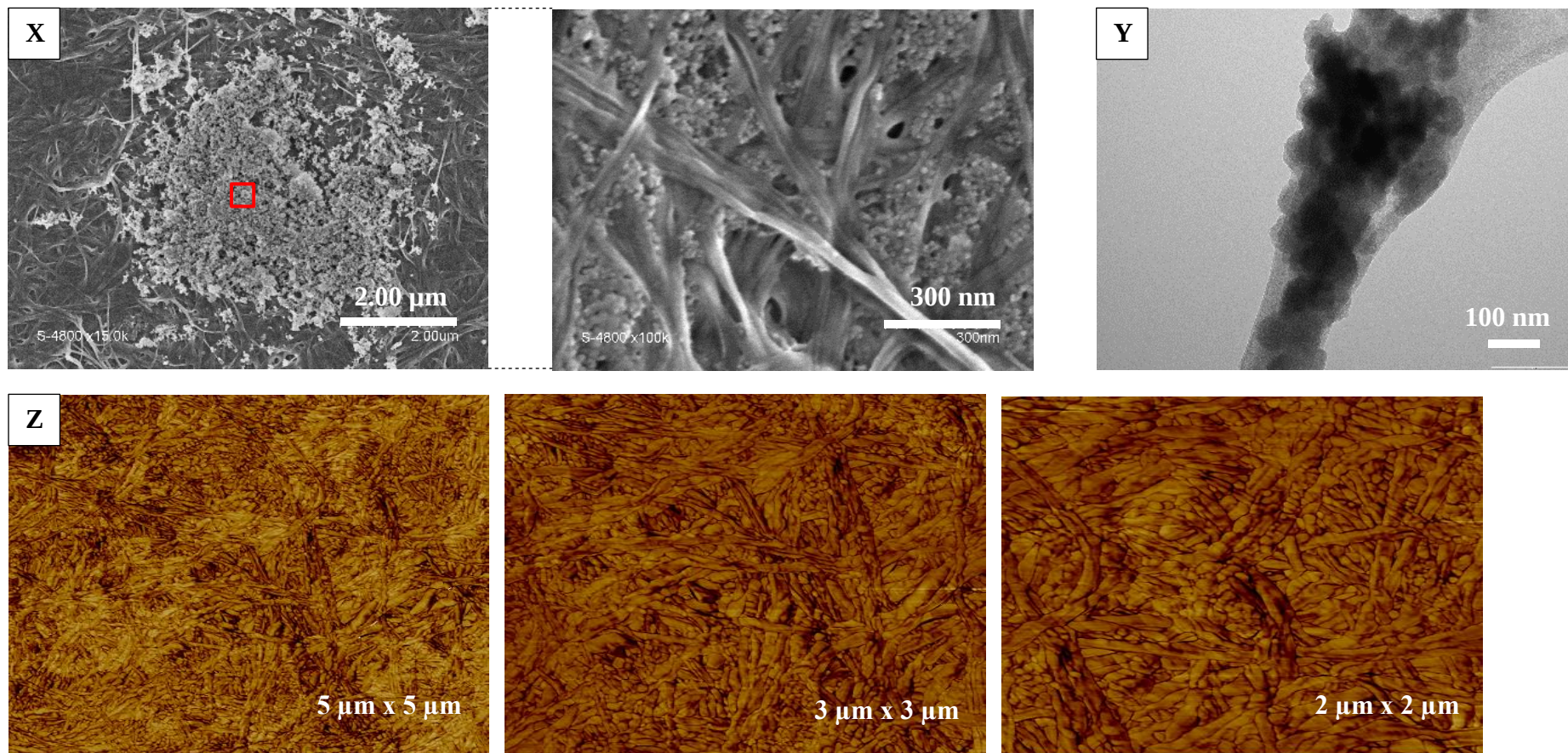


Figure 92 - SEM (X), TEM (Y) and (Z) AFM micrographs of BCM@BTPD sample.

BCM@BTSE

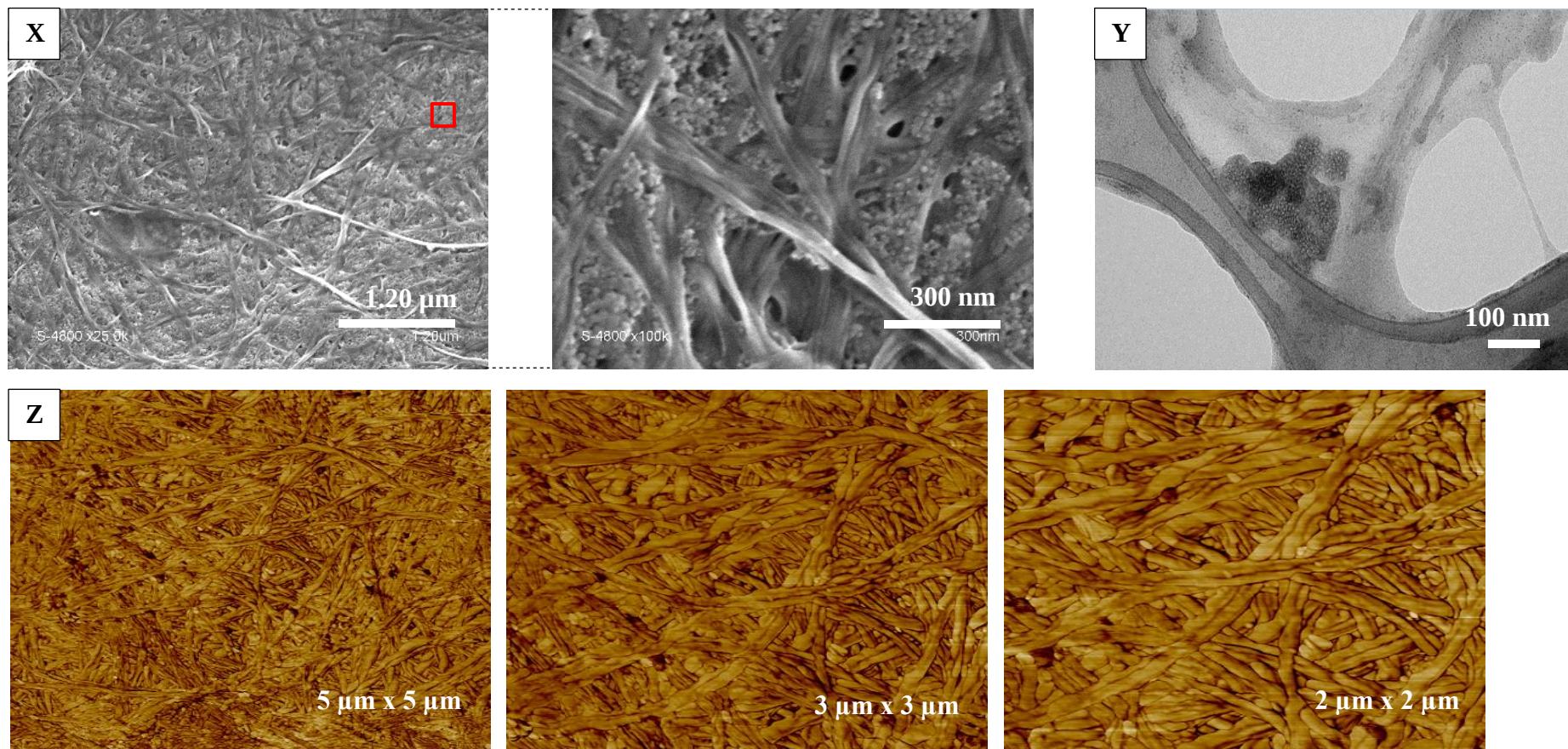


Figure 93 - (X) SEM, (Y) TEM and (Z) AFM micrographs of BCM@BTSE sample

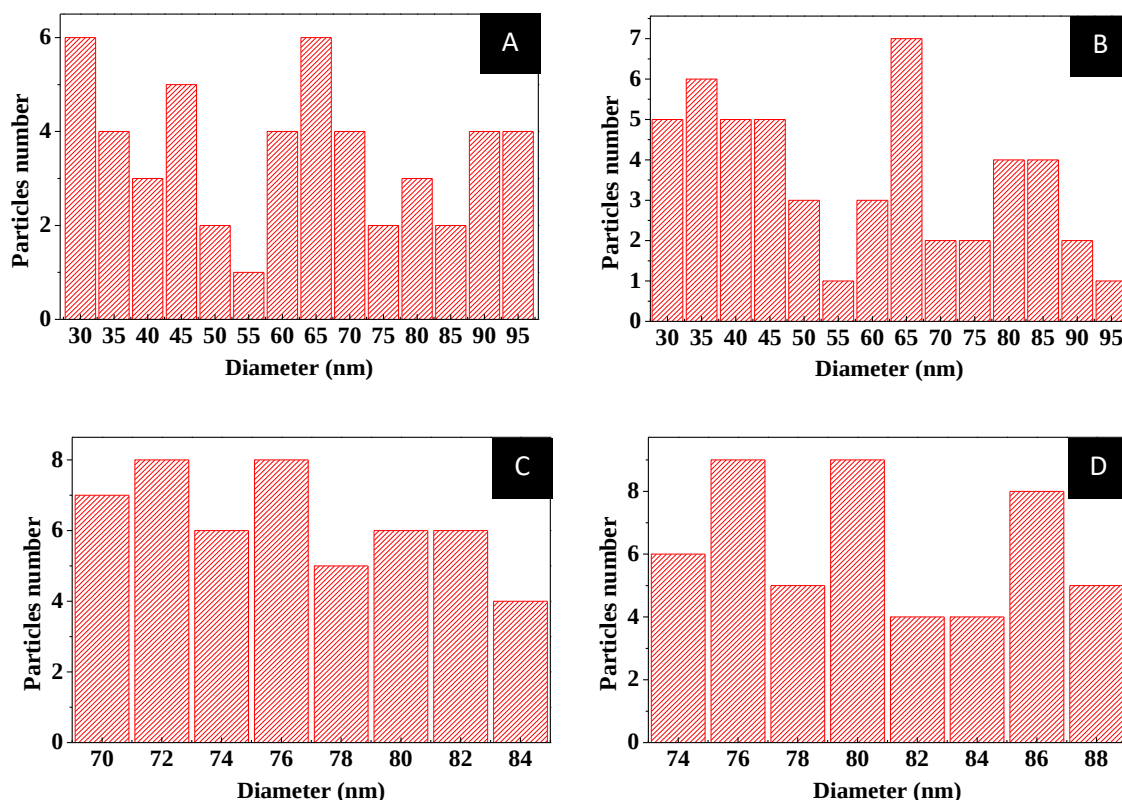


Figure 94 – Particles size distribution histograms of nanoparticles incorporated into the functionalized BCM: (A) BCM@5%BTEB, (B) BCM@BTEB, (C) BCM@BTPD and (D) BCM@BTSE, determined from TEM images analysis.

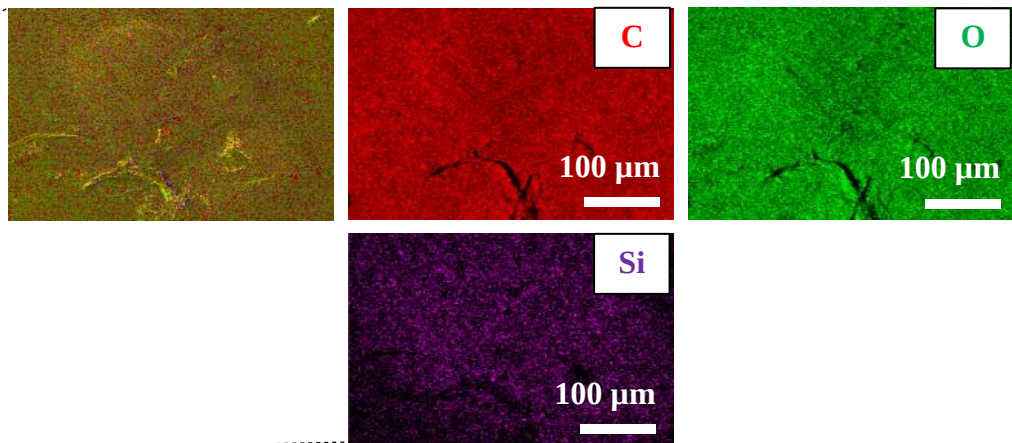
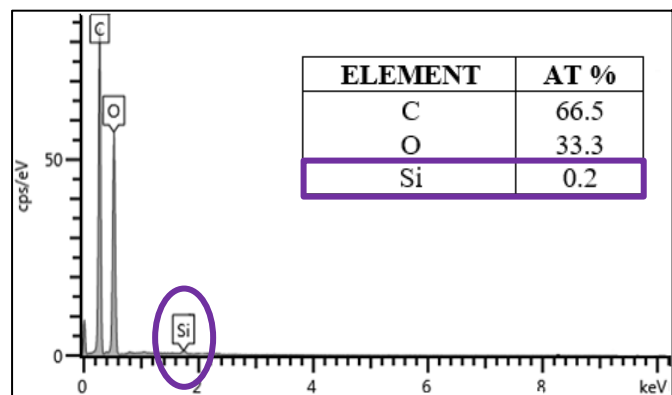
9.2. EDS, X-ray maps and XPS

From **Figure 95** and **Figure 96** are illustrated the EDS spectra (inset: atomic percentages of C, O, Si and S) and corresponding X-ray elemental maps of functionalized BCM, obtained during SEM experiment.

In the SEM micrograph of each sample (**Figure 90** – **Figure 93**), is identified (red square) where the EDS analysis was performed.

The EDS spectra evidence the successful grafting of the organosilanes on the BCM through the identification of elements Si (in all samples) and S (in the case of the sample BCM@BTPD). The X-ray elemental maps reveal that these elements are homogeneously distributed throughout the BCM surface.

BCM@5%BTEB



BCM@BTEB

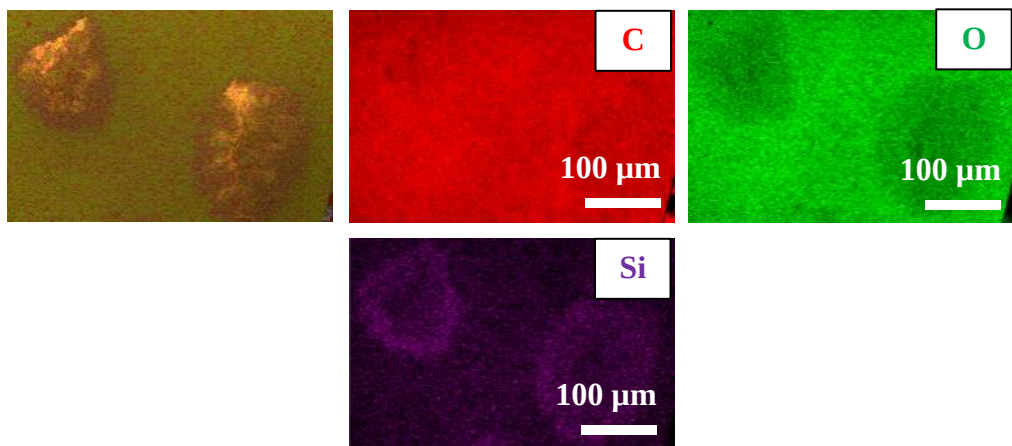
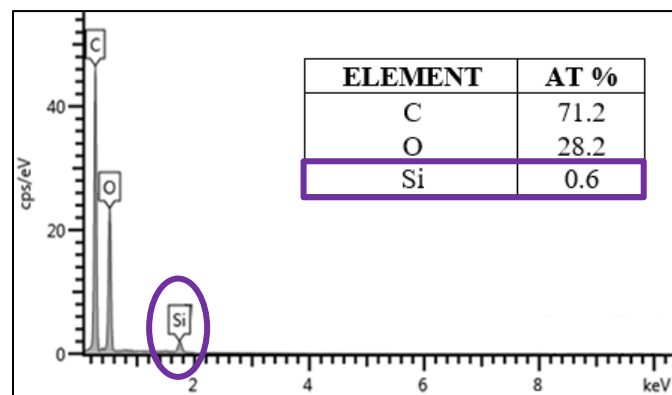
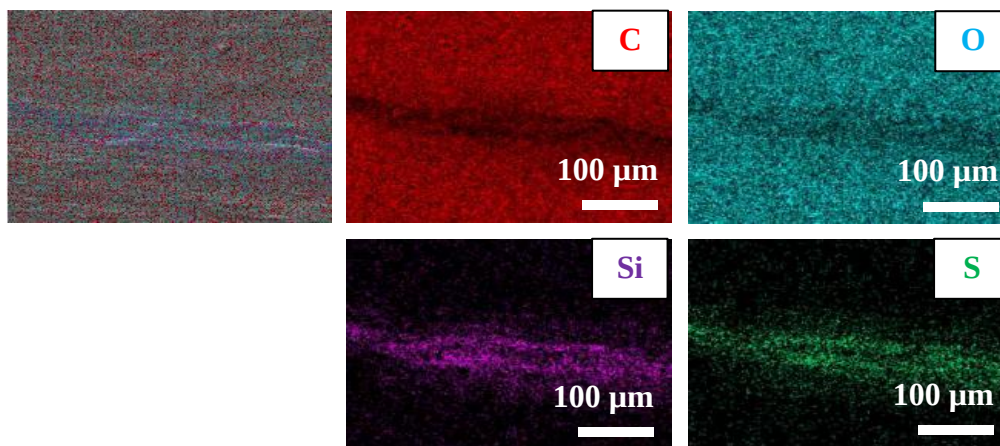
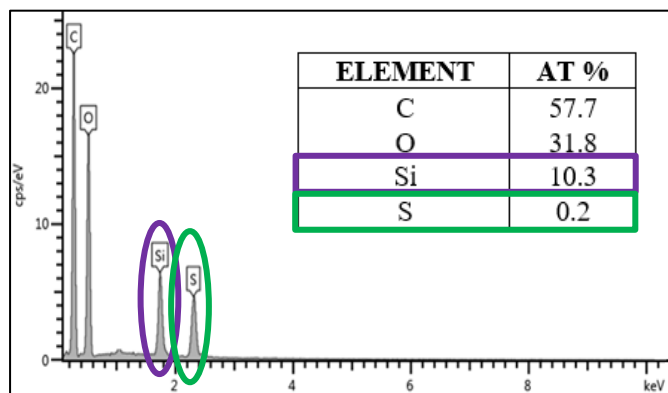


Figure 95 - EDS spectra and corresponding X-ray elemental maps of BCM@5%BTEB and BCM@BTEB samples.

BCM@BTPD



BCM@BTSE

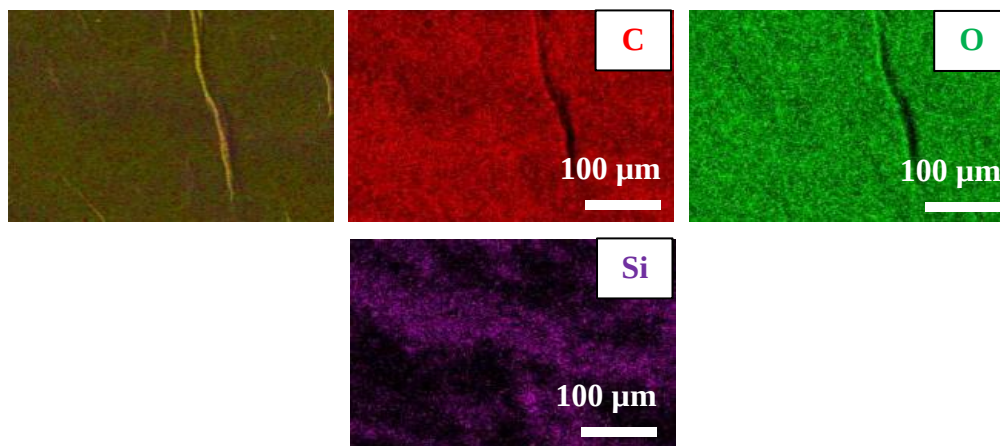
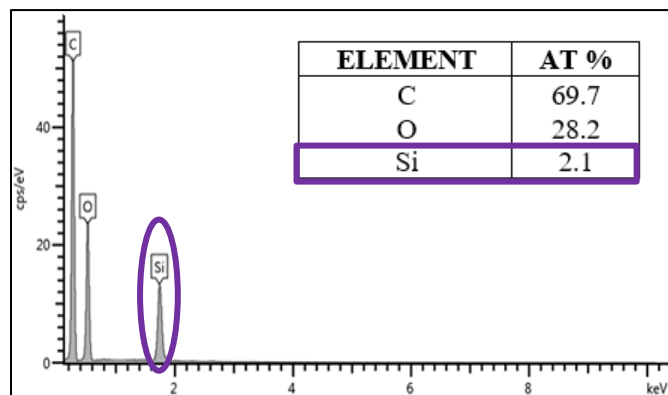


Figure 96 - EDS spectra and corresponding X-ray elemental maps of BCM@BTPD and BCM@BTSE samples.

The chemical composition of these samples was quantified by XPS analysis. The surface atomic percentages of the different elements are summarized in **Table 24**.

Table 24 – Surface atomic percentages for functionalized BCM with BTEB, BTPD and BTSE obtained by XPS^[a].

Sample	Atomic (%)			
	C 1s	O 1s	Si 2p	S 2p
BCM	60.3	39.7	-	-
BCM@BTEB	58.1	35.8	6.1	-
BCM@BTPD	57.3	34.9	4.0	3.8
BCM@BTSE	57.5	38.3	4.2	-

^[a] Determined by the areas of the respective peaks in the high-resolution XPS spectra.

9.3. FTIR-ATR

From **Figure 97** to **Figure 99** are illustrated the vibrational spectroscopy FTIR-ATR of the BCM@BTEB, BCM@BTPD and BCM@BTSE (red spectrum), respectively, in the 4000-1750 cm⁻¹ (left) and 1750-650 cm⁻¹ (right) range. The dotted lines highlight the characteristic bands of organosilanes. In order to evaluate the chemical modification of the BCM, the vibrational spectra of the BCM (blue spectrum) and the respective organosilane (black spectrum), are also presented together.

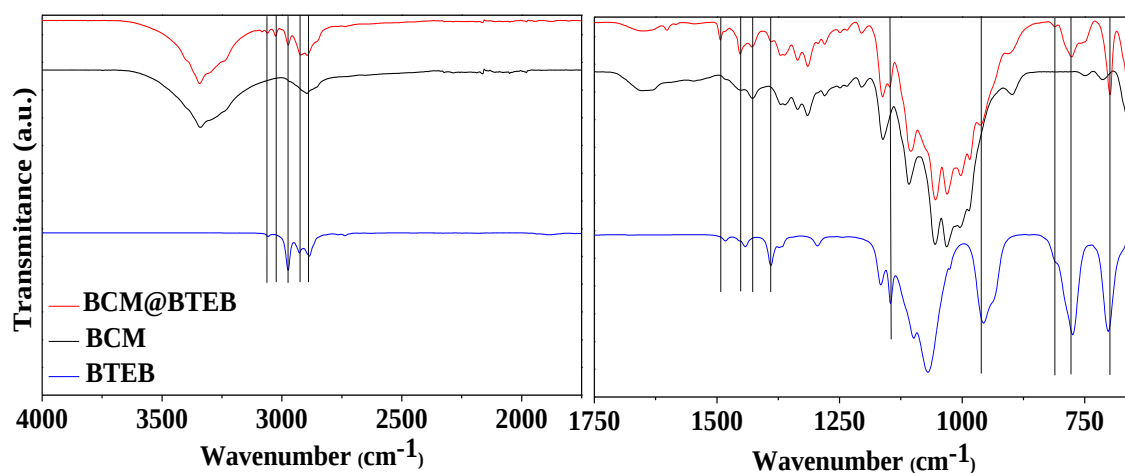


Figure 97 – FTIR-ATR spectra of BCM@BTEB in the 4000-1750 cm^{-1} (left) and 1750-650 cm^{-1} (right) range. The dotted lines highlight the characteristic peaks of BTEB.

The FTIR-ATR spectrum of BCM@BTEB show additional vibrational bands, when compared with pristine BCM, that are assigned to the grafted organically bridged silica sources BTEB: C-H symmetric stretching of $-\text{CH}_3$ (2974 cm^{-1}), C-H antisymmetric stretching of $-\text{CH}_2$ (2932 cm^{-1}), C=C stretching and C-H deformation in plane of Si-ph (1481 cm^{-1}), C=C stretching and C-H deformation in plane 2 stretching Si-C of Si-ph (1481 cm^{-1}), C-H symmetric deformation of $-\text{CH}_2$ (1390 cm^{-1}), antisymmetric stretching of Si-O-Si (1145 cm^{-1}), in-plane stretching Si-O of $\equiv\text{Si-O}$ (958 and 811 cm^{-1}) and C-H out-of-plane ring deformation of Si-ph (702 cm^{-1}) vibrations [68, 69, 79-81].

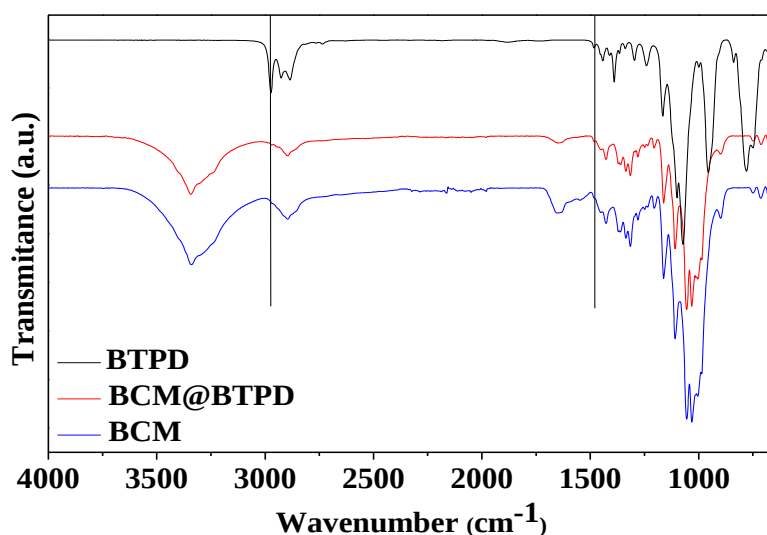


Figure 98 – FTIR-ATR spectra of BCM@BTPD in the 4000-650 cm^{-1} range. The dotted lines highlight the characteristic peaks of BTPD.

The presence of organosilane BTPD in the BCM@BTPD sample (red spectrum) is evidenced in the following vibrational bands: C-H symmetric stretching of $-\text{CH}_3$ (2974 cm^{-1}), C-H antisymmetric stretching of $-\text{CH}_2$ (2932 cm^{-1}) and antisymmetric stretching of Si-O-Si (1145 cm^{-1}) vibrations [65, 68].

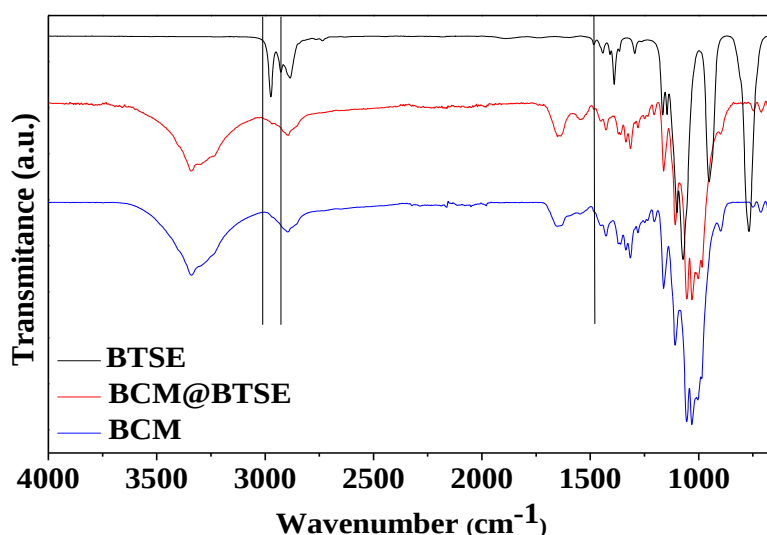


Figure 99 – FTIR-ATR spectra of BCM@BTSE in the 4000-650 cm^{-1} range. The dotted lines highlight the characteristic peaks of BTSE.

Comparing the FTIR-ATR spectrum of BCM@BTSE sample (red spectrum) with FTIR-ATR spectrum of pristine BCM (blue spectrum), the FTIR-ATR spectrum of functional BCM show additional vibrational bands that are assigned to the grafted BTSE: C-H symmetric stretching of $-\text{CH}_3$ (2974 cm^{-1}) and C-H antisymmetric stretching of $-\text{CH}_2$ (2926 cm^{-1}) vibrations, evidencing the successful grafting of the BTSE in the BCM [65, 68].

9.4. ^{29}Si CPMAS and ^{13}C CPMAS Solid-State NMR

Figure 101 present the ^{29}Si CPMAS (A) and ^{13}C CPMAS (B) NMR spectra of the BCM@BTEB and the bands assignments.

The ^{29}Si CPMAS NMR spectra of BCM@BTEB (**Figure 101A**), present peaks at -59, -70 and -78 ppm, which are respectively associated to T^1 [$\text{CSi}(\text{OR})_2(\text{OSi})$], T^2 [$\text{CSi}(\text{OR})(\text{OSi})_2$] and T^3 [$\text{CSi}(\text{OSi})_3$] silicon environments, revealing the anchorage of organosilane BTEB, through 1-, 2- and 3-fold covalent grafting [56, 57, 82, 83], indicating the incorporation of BTEB in the BCM successfully.

The presence of BTEB in BCM is confirmed in the ^{13}C CPMAS NMR spectra (**Figure 101B**): at 134 ppm which correspond to C-Phenyl and at 58 and 18 ppm, attributed to $\text{Si}-\text{OCH}_2\text{CH}_3$.

The organosilane BTEB is a crystalline organic-inorganic hybrid [84]. On the other hand, the BCM contain a large amount of highly crystalline cellulose polymer and are free of amorphous phases such as lignin and hemicellulose abundantly present in plant-derived cellulose. As a result, the BCM is basically constituted of a semi-crystalline polymer [28].

In the ^{13}C CPMAS NMR spectra, the peaks at 89 ppm and 65 ppm are assigned to the C4 carbon in ordered cellulose structure, and the peaks at 84 ppm and 63 ppm are assigned to the C4 carbon of disordered cellulose structure [85]. After immobilization of the BTEB on BCM a decrease in the intensity of the peaks responsible for the disordered cellulose structure and an increase in the intensity of the peaks relative to the ordered cellulose structure is observed. Thus, with the immobilization of organosilane BTEB in BCM, the crystallinity of BCM increases.

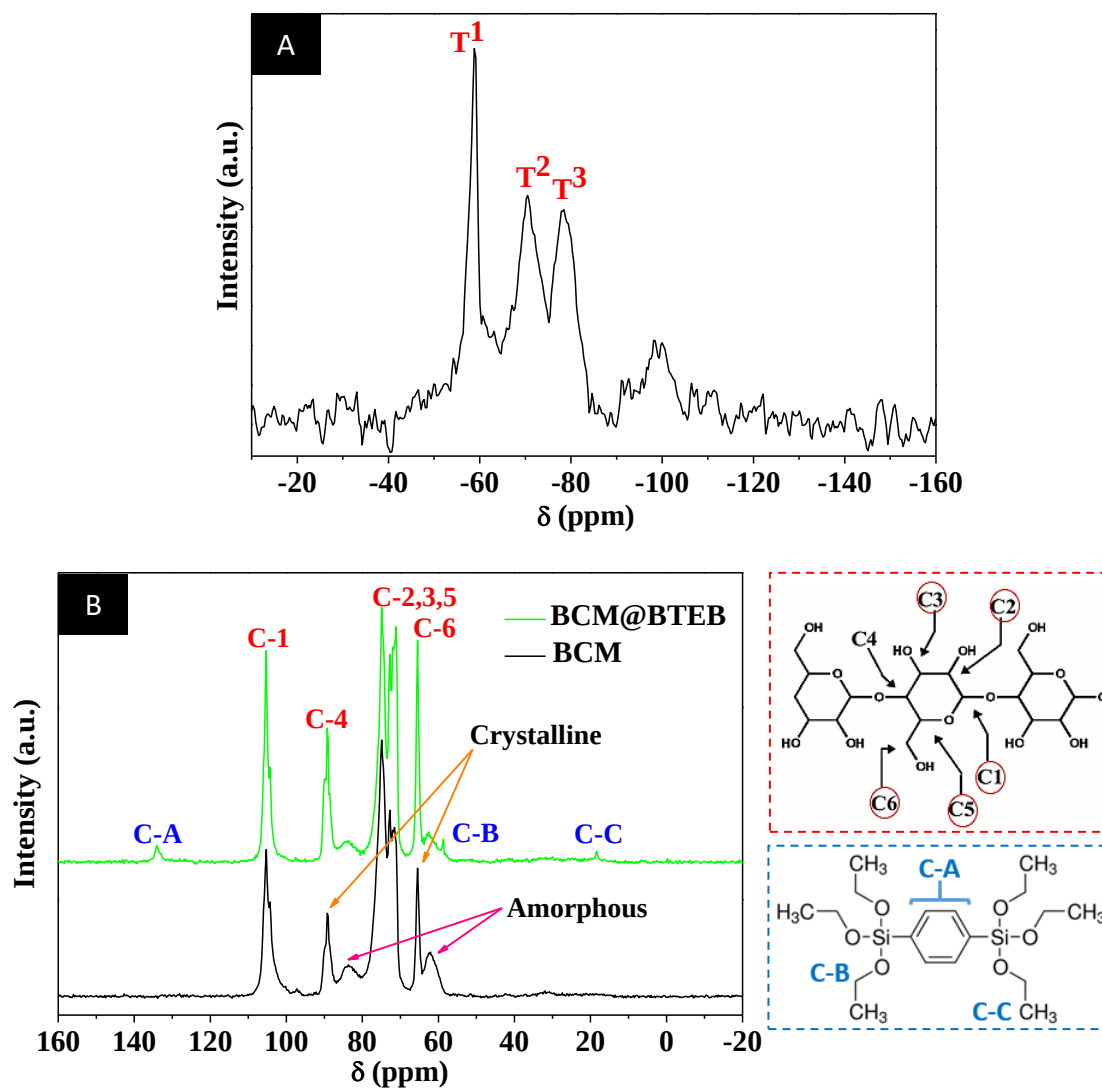


Figure 100 – (A) ^{29}Si CPMAS and (B) ^{13}C CPMAS NMR spectra of the BCM@BTEB and the bands assignments.

9.5. XRD

Figure 102 show the X-ray diffractogram of the pure BCM and BCM@BTEB samples.

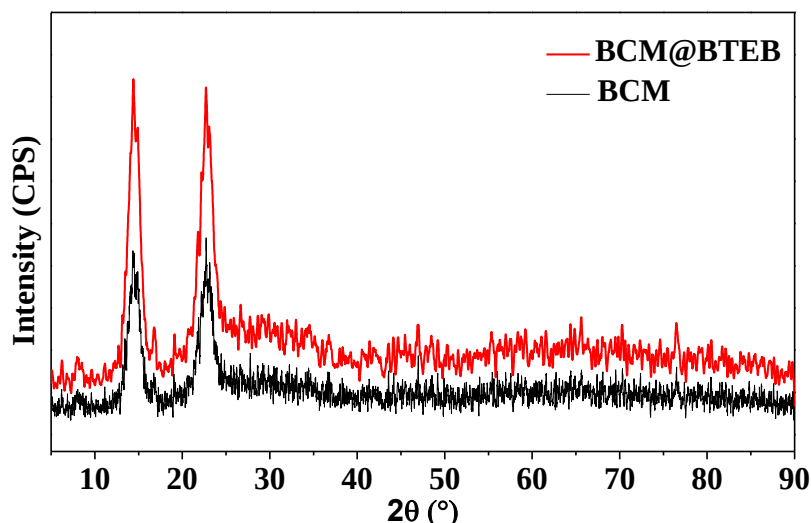


Figure 101 – X-ray diffractograms of BCM (black) and BCM@BTEB (red)

The X-ray diffractograms of BCM display two peaks localized at 14.4° and 22.7°, assigned to the 1 α phases of native cellulose (type I cellulose) and overlapped by amorphous haloes [51]. The peak at 14.4° is related to the contribution of the reflections from the monoclinic (110) and triclinic (100) planes. The peak at 22.5° corresponds to the contribution of the reflections from the monoclinic (002) and triclinic (110) planes [51, 85]. Nevertheless, the BCM@BTEB present similar diffraction pattern profiles, suggesting that a semi-crystalline structure was preserved during the immobilization of BTEB on BCM. However, the degree of crystallinity of these two samples was calculated from the *Segal equation* (eqn (1)) [51]:

$$\text{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

Where CrI corresponds the relative degree of crystallinity, I_{002} is the maximum intensity of the (002) plane diffraction and I_{am} is the intensity of the amorphous halo at $2\theta = 18.0^\circ$. According to this equation, the BCM show a CrI value equal to 75%. However an increase in crystallinity is observed in BCM@BTEB (CrI = 83%).

An increase in the amount of crystalline phase can lead to an improvement of the mechanical properties of BCM [51].

9.6. Conclusions

The results obtained indicate an efficient functionalization of the BCM by in situ, with the organosilanes BTEB, BTPD and BTSE.

After immobilization with these organosilanes, spherical silica nanoparticles porous structure and heterogeneous particle size, were formed in the cellulose fibers.

The results obtained by NMR and XRD indicate with the immobilization of organosilane BTEB in BCM, the crystallinity of BCM increases.

An increase in crystallinity and consequently an improvement in mechanical properties, open the way to obtain functional BCM which will find applications in several areas.

CHAPTER 10

General Conclusion

10. General conclusions

The objectives proposed for the project have been achieved and the execution of the activities proceeded as planned.

The spherical silica nanoparticles with average particle size around 51 ± 4 nm, narrow size distribution, wormhole-type mesoporous structure and high porosity were successfully synthesized and functionalized by in situ with organosilanes C_8TMS , $C_{16}TMS$ and $F_{13}TES$ by sol-gel method.

The hydrothermal process allowed to obtain silica with a higher purity (99.7 % (wt/wt)) than reported in the literature by conventional methods (90-95 % (wt/wt)). The silica obtained are composed of nearly spherical nanoparticles with heterogeneous particles size (20-40 nm) and exhibit mesoporous structure and high porous structure. The SiO_2 -rice were successfully functionalized with organosilane $F_{13}TES$ and curcuma.

The $SiO_2@F_{13}TES$ and $SiO_2@F_{13}TES$ -rice present excellent easy-cleaning properties, displaying phobicity to water (threshold of superhydrophobicity), toluene, cyclohexane and artificial sweat, whereas the pristine silica nanoparticles (SiO_2 and SiO_2 -rice) presented philicity to these liquids.

Regardless of the functionalization method (in situ vs post-grafting) and the method of obtaining silica nanoparticles (sol-gel method or from rice husk), the easy-cleaning properties obtained are very similar ($SiO_2@F_{13}TES$ and $SiO_2@F_{13}TES$ -rice). Anatase $TiO_2@SiO_2$ spherical nanocomposites, with average particle size around 60 ± 5 nm, prepared by a sol-gel method, have also been developed.

These hybrid nanomaterials were successfully incorporated into BCM by in situ and post-grafting. The size and morphology of these nanomaterials remained constant after immobilization on the BCM. BTEB, BTPD and BTSE were successfully incorporated into BCM by in situ. After immobilization of these different organosilanes on the cellulose, spherical silica nanoparticles with porous structure and heterogeneous particle size, were formed on the cellulose fibers.

The surface repellency of the functionalized BCM with silica nanoparticles containing easy-cleaning properties was remarkably enhanced. Specifically, the BCM functionalized by in situ and post-grafting with $SiO_2@F_{13}TES$, displayed a surface almost superhydrophobic ($> 150^\circ$). The repellency properties of functional BCM reveals are better to those obtained by the respective immobilized nanoparticles. Furthermore, regardless of the immobilization method used, the contact angle values were similar.

BCM displaying self-cleaning properties have been prepared by incorporation of $\text{SiO}_2@\text{TiO}_2$ nanocomposite in BCM. Methyl violet 2B dye decomposition measurements showed that the BCMW- $\text{SiO}_2@\text{TiO}_2$ (BCM functionalized in wet state) presented a good self-cleaning performance (fast Methyl violet 2B dye decomposition in 30 minutes).

The functional BCM also presented a good resistance to washing with high chemical stability and the original features, color and texture were maintained.

The good properties acquired in this versatile biomaterial open the way to obtain functional BCM which will find applications in several areas. The results obtained in this project, will open new avenues for the design of smart and innovative cellulose membrane.

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Annex

Annex 1 – Photographs of the BCM samples

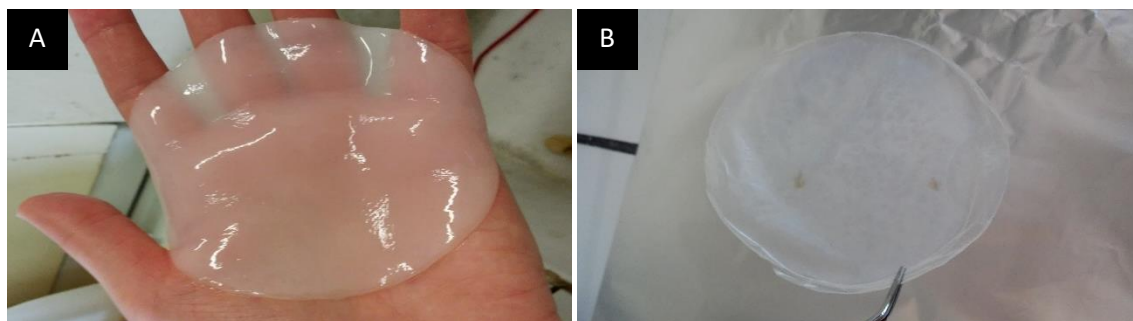


Figure 102 – Photographs of the pristine BCM in wet (**A**) and dry (**B**) state.

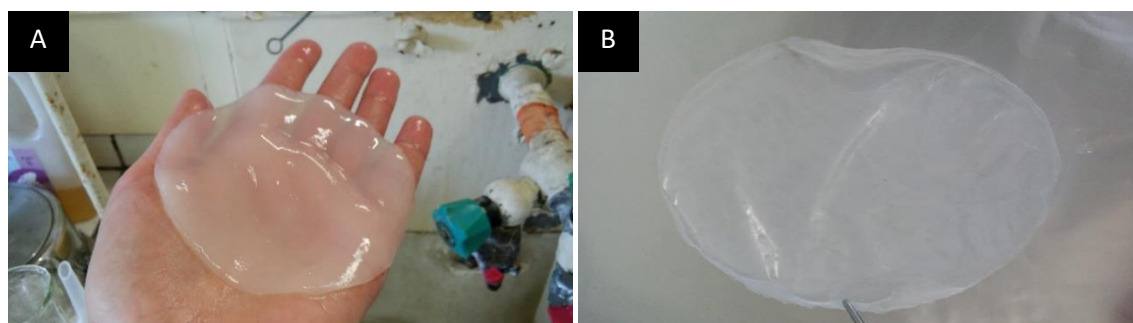


Figure 103 – Photographs of the BCM@SiO₂ in wet (**A**) and dry (**B**) state.

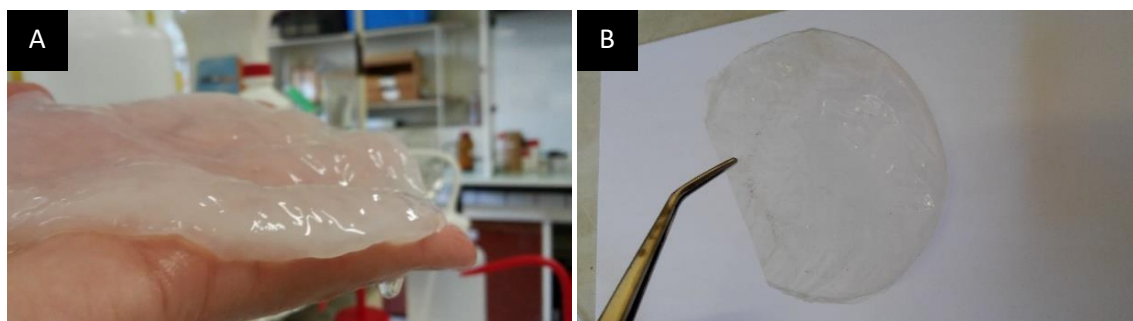


Figure 104 – Photographs of the BCM@SiO₂@C₈TMS in wet (**A**) and dry (**B**) state.

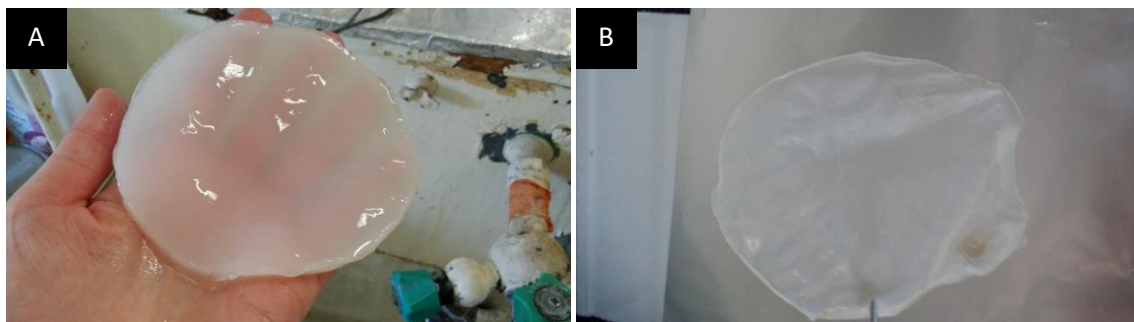


Figure 105 – Photographs of the BCM@SiO₂@C₁₆TMS in wet (**A**) and dry (**B**) state.



Figure 106 – Photographs of the BCM@SiO₂@F₁₃TES in wet (**A**) and dry (**B**) state.

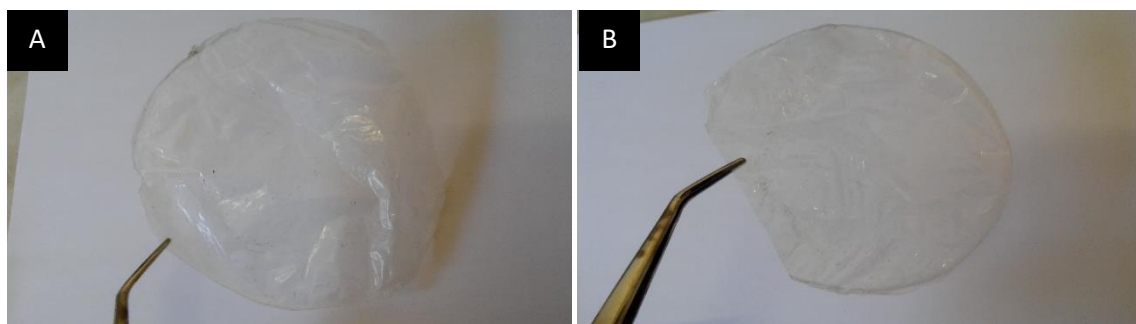


Figure 107 – Photographs of the BCM@SiO₂_PG (**A**) and BCM@SiO₂@C₈TMS_PG (**B**) samples.

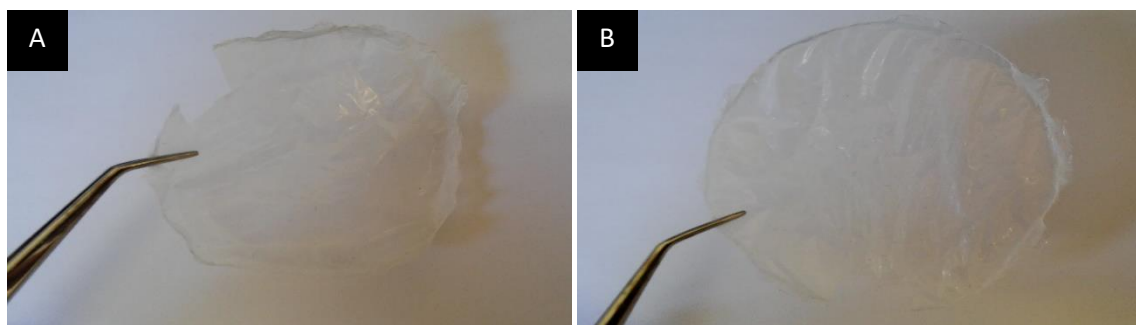


Figure 108 – Photographs of the BCM@SiO₂@C₁₆TMS_PG (**A**) and BCM@SiO₂@F₁₃TES_PG (**B**) samples.

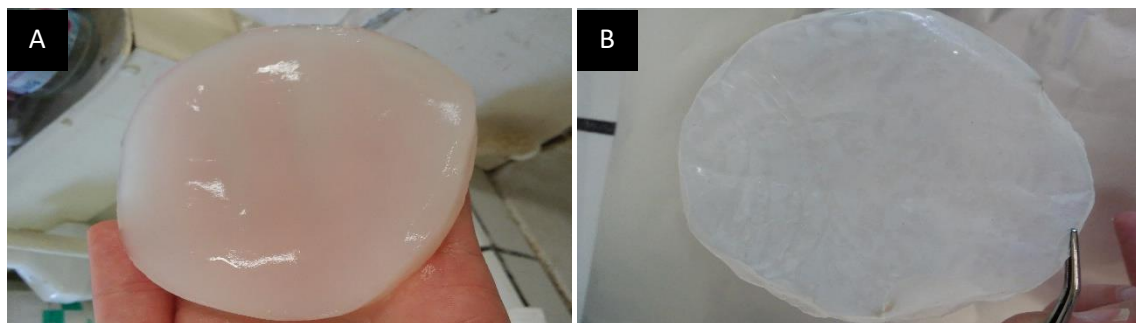


Figure 109 – Photographs of the BCM@SiO₂-rice in wet (**A**) and dry (**B**) state.

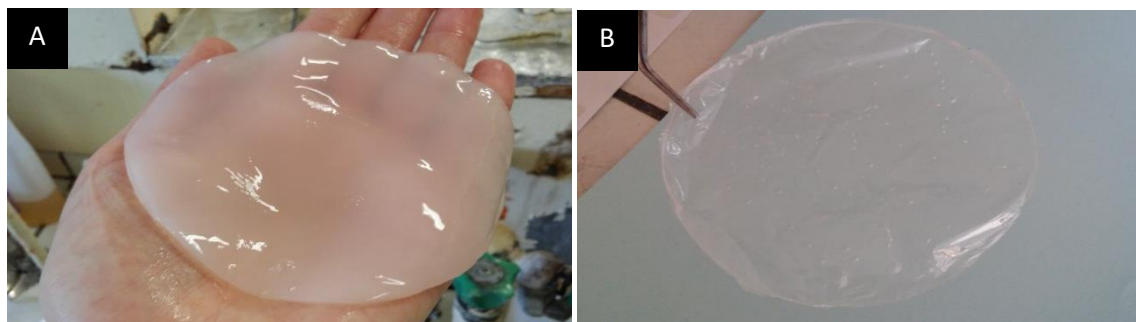


Figure 110 – Photographs of the BCM@SiO₂@F₁₃TES-rice in wet (**A**) and dry (**B**) state.

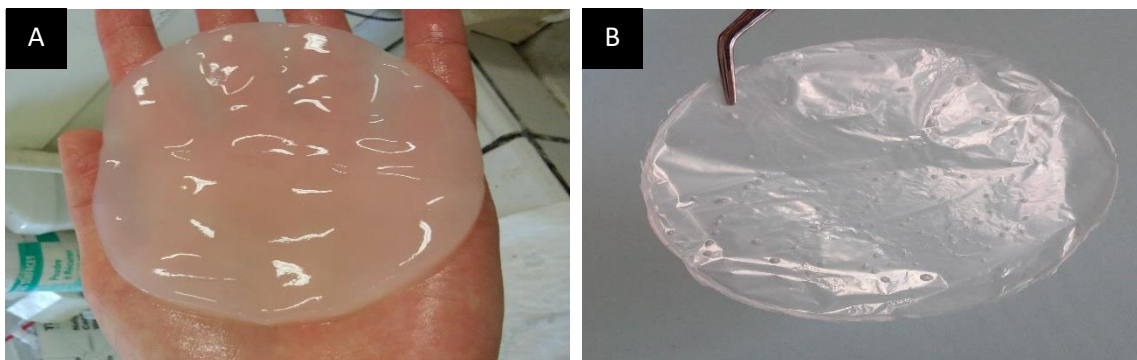


Figure 111 – Photographs of the BCM@SiO₂@BTPD in wet (**A**) and dry (**B**) state.

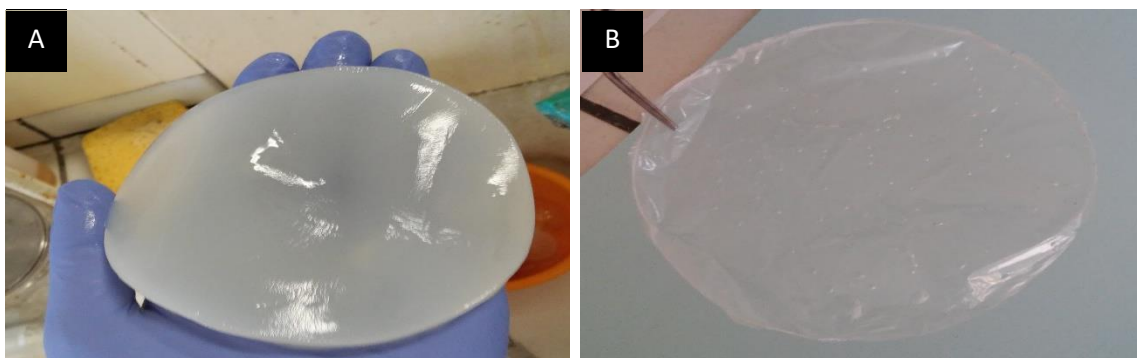


Figure 112 – Photographs of the BCM@SiO₂@BTSE in wet (**A**) and dry (**B**) state.

Annex 2

FTIR-ATR of BCM functionalized with silica-based nanomaterials obtained by sol-gel method and functionalized by post-grafting.

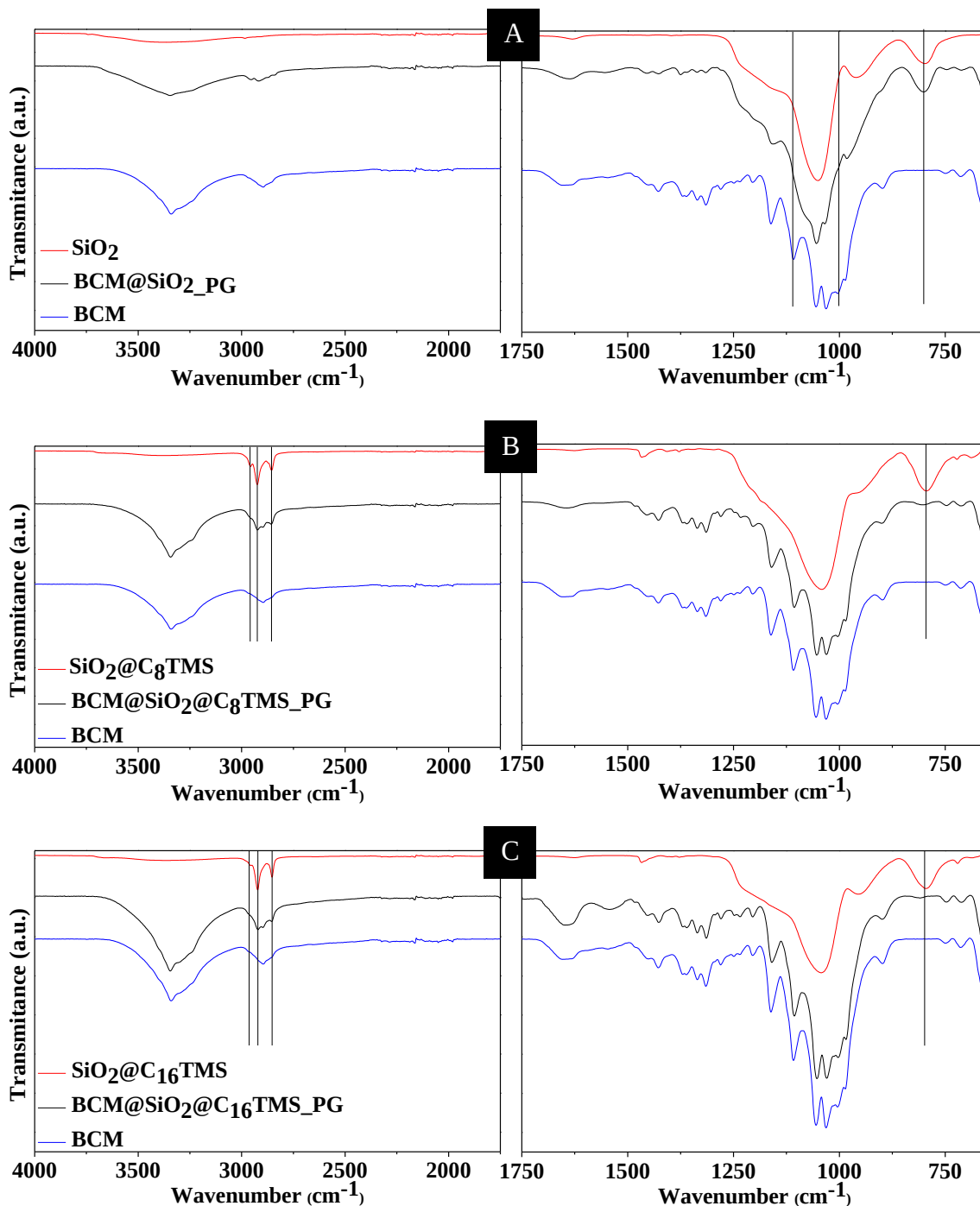


Figure 113 – FTIR-ATR spectra of (A) BCM@SiO₂, (B) BCM@SiO₂@C₈TMS and (C) BCM@SiO₂@C₁₆TMS samples, in the 4000-1750 cm^{-1} (left) and 1750-650 cm^{-1} (right) range.

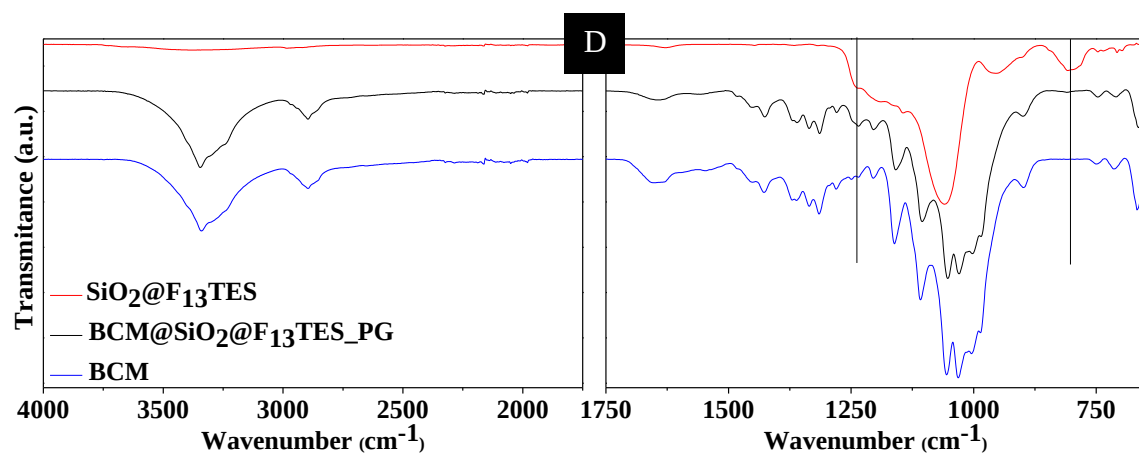


Figure 113 – cont – FTIR-ATR spectra of **(D)** BCM@SiO₂@F₁₃TES sample, in the 4000-1750 cm⁻¹ (left) and 1750-650 cm⁻¹ (right) range.

FTIR-ATR of BCM functionalized with silica-based nanomaterials obtained by rice husk and functionalized by post-grafting.

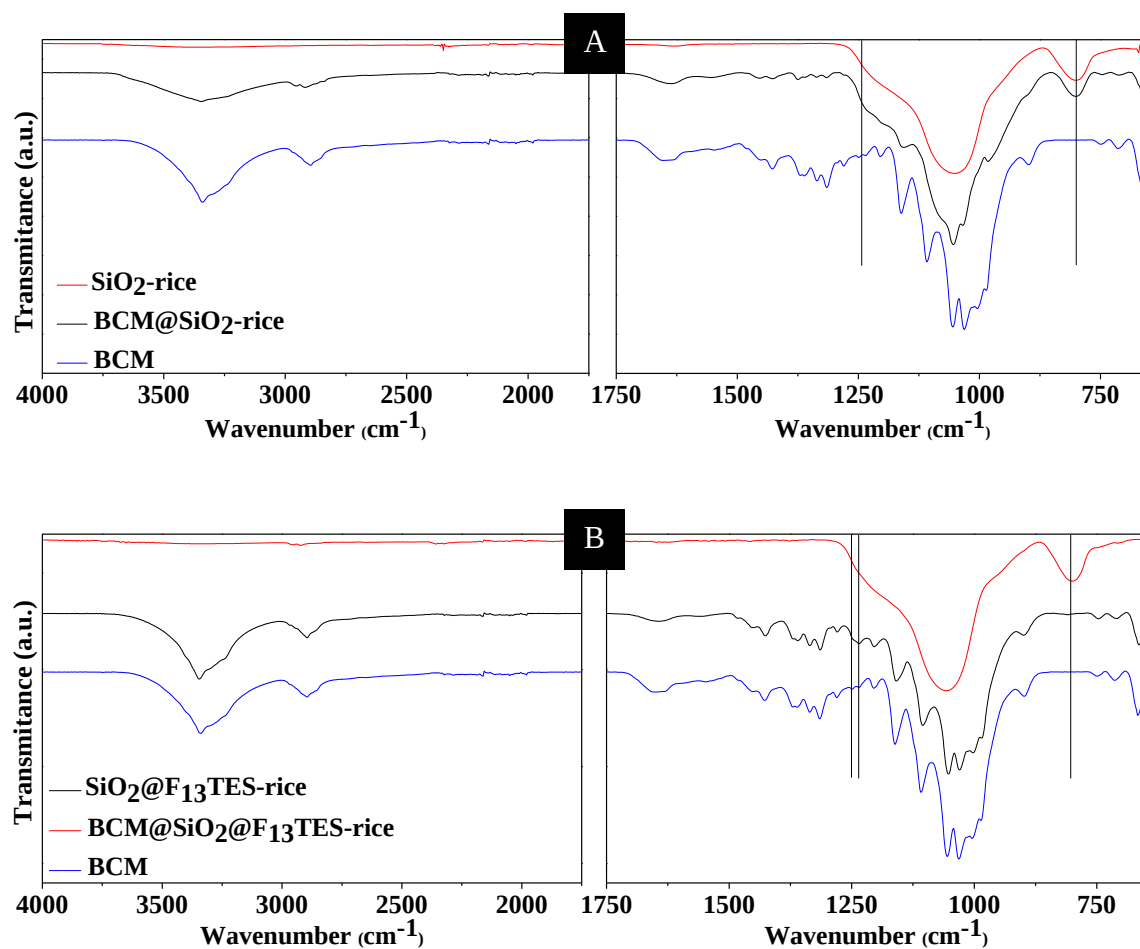


Figure 114 – FTIR-ATR spectra of (A) BCM@SiO₂-rice and (B) BCM@SiO₂@F₁₃TES-rice samples, in the 4000-650 cm⁻¹ (left) and 1600-650 cm⁻¹ (right) range.