INTERUNIVERSITY PH.D. PROGRAM BETWEEN

POLITECNICO DI BARI AND UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO

IN INDUSTRY 4.0

Nanostructured materials for functional textiles

PhD candidate

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Cycle

XXXVII Cycle (2021-2022)

Tutors

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Description of the research program

The research activity will be aimed at the development of nanostructured materials for their application as functional coatings, including antimicrobial, self-cleaning, thermally and optically responsive.
Specific focus will be devoted to antimicrobial coatings on textile surfaces to provide additional tools capable of addressing the enormous incidence of bacteria and viruses and also strengthen the ability to inactivate and destroy a wide range of microorganisms. In particular, the preparation of nano-structured materials through bottom-up approaches, allows to obtain nanoparticles as final products, in a range of compositions (metals, semiconductors, oxides and heterostructures) with controlled shape, crystalline structure and electronic properties, which can be combined with other materials to give rise to nanocomposites with characteristics going beyond the properties of the individual constituents. [1]
The integrability of nanostructures in matrices and/or systems is compatible with additive manufacturing processes, considered among the key aspects for the development of Industry 4.0 [2]. The combination of functional nanomaterials, such as photocatalytic ones, with compounds, such as other semiconductors, metals or graphene derivatives, have been shown to be effective in improving antimicrobial performance, both by increasing the photocatalytic performance of the resulting composite and conveying additional properties. [1,3]
In order to pursue the objectives of this project, preparative approaches will be carried out using synthetic, characterization and testing strategies for consolidated material properties, adapting them in a flexible way having in mind their scalability, sustainability and compatibility with environment.
In particular, the research will be divided into the following points:
• *Design and construction of hybrid nanostructured materials* formed by two or more components, each characterized by peculiar properties depending on dimensions, surface chemistry and morphology. Nanostructures will be designed and built by coupling *i. a metallic domain with a semiconductor oxide* (e.g TiO_2) which is able to increase the separation capacity of charge carriers in the semiconductor improving the photocatalytic efficiency, and to act as a sensitizer, extending the response of the photocatalyst to visible light. Indeed a significant improvement in the photocatalytic efficiency guided by visible light of composites obtained, for instance, by deposition of Ag on TiO_2 nanostructures has been demonstrated in the literature. [4] They will also be considered *ii. heterostructures consisting of coupled nanostructured semiconductors* (e.g. TiO_2 and Cu_xO) in which the electronic configuration of the two materials is able to improve the performance of the photocatalyst, also extending its response in the visible light spectrum. Systems will be studied *iii. nanocomposites based on semiconductors and graphene derivatives*, able to combine the action of photocatalytic oxides with the electronic and structural properties of graphene, to give rise to photocatalytic materials in which the response can be extended into the visible range, thanks to the characteristics of graphene, as it has been effectively demonstrated for other carbonaceous materials such as carbon nanotubes (CNTs) which coupled to TiO_2 have revealed a remarkable effectiveness in terms of degradation of organic molecules under irradiation with visible light [2, 4]. Furthermore, the 2D structure of graphene can interact with the external membrane of microorganisms, damaging it or even breaking it, and therefore inactivating them. [5]
• *Chemical, morphological and structural characterization* by means of electron microscopy spectroscopic techniques (TEM, SEM-EDS) and structural techniques such as for example XRD, BET). Their photocatalytic properties will be tested under both UV and Vis light irradiation, comparing them with commercial reference materials that will constitute the benchmarks for performance evaluation. Model molecules will be used, compounds representative of the structures of pathogenic microorganisms, whose degradation will be monitored with chemical investigation techniques such as UV-vis spectroscopy, FTIR and mass spectrometry (HPLC, GC-MS). The optimization of the preparatory approaches will be conducted on the basis of the investigation of the photocatalytic and antimicrobial properties of the developed nanostructured materials.
• *Deposition on a textile substrate:* formulations will be suitably designed in order to feature high dispersibility of the nanostructures in solvents or polymeric matrices for subsequent deposition on textiles. For this purpose, NPs functionalization procedures can also be applied to make them compatible with the dispersion medium or host matrix. In particular, the host matrix will be selected so as to sustain the subsequent deposition processes and resist the photocatalytic action of NPs. Different deposition techniques will be tested, including impregnation, spray coating, dip coating and plasma aerosol.
• *The characteristics of the coatings obtained will be extensively investigated* from the morphological point of view and in their mechanical properties (adhesion, durability, resistance to washing), chemical stability and antimicrobial efficiency. Tests to verify the antimicrobial capacity of the materials developed will be designed

and conducted in collaboration with groups with expertise in the biological field, using model systems or deactivated pathogens as well as in device engineering, designing optically and thermally responsive systems and device. The phenomena of release of NPs into the environment must be prevented to avoid harmful consequences for the environment and human health, by controlling the stability and effectiveness of the immobilization processes in the matrix or in any case on the substrate. Studies will also be conducted on the possible release of NPs into the environment, and on the toxicity of coatings in general, to assess their safety for humans and environment.

1. De Pasquale, I., et al., *TiO2-based nanomaterials assisted photocatalytic treatment for virus inactivation: perspectives and applications.* Current Opinion in Chemical Engineering, 2021. 34: p. 100716.
2. S. Murgolo, F. Petronella, R. Ciannarella, R. Comparelli, A. Agostiano, M. L. Curri, G. Mascolo "UV and solar-based photocatalytic degradation of organic pollutants by nano-sized TiO2 grown on carbon nanotubes" (2015) *Catalysis Today 240, 114-124.*
3. Pasquale, I., et al., *Photocatalytic TiO2-Based Nanostructured Materials for Microbial Inactivation.* 2020.
4. Basyigit, Z., *Application Technologies for Functional Finishing of Textile Materials*. 2021.
5. Habibi-Yangjeh, A., et al., *Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: Can we win against pathogenic viruses?* J Colloid Interface Sci, 2020. 580: p. 503-514.

Schedule of the research activities

Insert the research activities that you plan or you have completed for the three years, including any period abroad.

First academic year

	Description	**Period**	**Activity abroad**
Insert name of first research activity	Design, synthesis and characterization by means of chemical, morphological and structural characterization (UV-Vis spectroscopy, electron microscopy techniques (TEM,SEM-EDS)) of hybrid nanocomposites formed of Ag NPs and Reduced Graphene Oxide flakes, by using sustainable, scalable and environmentally friendly synthetic approaches. Chemical, morphological and structural characterization (by means of UV-Vis spectroscopy, electron microscopy techniques (TEM, SEM-EDS), XRD and BET).	11/2021-11/2022	NO
Insert name of second research activity	Test of the photocatalytic and antimicrobial properties of the synthesized materials under both UV and Vis light irradiation in solution and onto conventional substrates (i.e. glass) and comparison with commercial reference materials as benchmarks for performance evaluation.	11/2021-11/2022	NO

Second academic year

	Description	Period	Activity abroad
Insert name of first research activity	Test of the photocatalytic and antimicrobial properties of the materials synthesized in the first year, under both UV and Vis light irradiation, in solution and onto conventional substrates (i.e. glass) and comparison with commercial reference materials as benchmarks for performance evaluation.	11/2022-11/2023	NO
Insert name of the second research activity	Design, manufacturing and characterization by means of chemical, morphological and structural characterization (UV-Vis spectroscopy, electron microscopy techniques (TEM,SEM-EDS)) of hybrid nanocomposites formed of metal NPs or heterostructures based on metal/semiconductor oxides NPs, combined with Reduced Graphene Oxide flakes, by using sustainable, scalable and environmentally friendly synthetic approaches. Chemical, morphological and structural characterization (by means of UV-Vis spectroscopy, electron microscopy techniques (TEM, SEM-EDS), XRD and BET).	11/2022-11/2023	NO
Insert name of third research activity	Test of the photocatalytic and antimicrobial properties of the materials synthesized at the second year under both UV and Vis light irradiation in solution and onto conventional substrates (i.e. glass) and comparison with commercial reference materials as benchmarks for performance evaluation.	11/2022-11/2023	NO
Insert name of fourth research activity	Development of formulations with characteristics suitable for substrate deposition by using techniques such as dip coating, spray coating, impregnation and plasma aerosol and preliminary deposition tests on model substrates	11/2022-11/2023	NO

Third academic year

	Description	Period	Activity abroad
Insert name of first research activity	Development of formulations formed of the materials synthesized at the second year with characteristics suitable for substrate deposition by using techniques such as dip coating, spray coating, impregnation and plasma aerosol and preliminary deposition tests on model substrates	11/2023-11/2024	To be planned
Insert name of second research activity	Study and optimization of deposition and fabrication processes of coatings on suitable selected textiles, using different deposition techniques.	11/2023-11/2024	To be planned

Insert name of third research activity	Characterization of the coatings obtained for the verification of the suitability of the processes developed for application in the industrial field	11/2023-11/2024	To be planned

Provisional training and research activities plan

Specify with the related CFU (ECTS) the training activities that you plan to carry out or have completed in the three years (e.g., courses to attend, conferences, seminars, etc.). Please refer to the *Educational regulations of the Doctoral School of Politecnico di Bari*: http://www.poliba.it/sites/default/files/dottorati/regscudopoliba.pdf

Specify with the related CFU (ECTS) the research activities that you plan to carry out in the three years (e.g., individual research activity, supervision of students, integrative seminars to be given by the PhD student, activity of manuscript preparation for conferences or journals, activity of patents preparation, etc.).

First academic year

	Description	**Period**	**Duration**	**CFU**
PhD courses	Green photonics for a sustainable economy (SCuDo)	2021-2022	20 h	2
	Promozione della ricerca (Scienze Chimiche e Molecolari)	2022	10h	1
	The post-growth paradigm in planning research (Francesca Calace, SCuDo)	28/02/2022-31/03/2022	25h	2.5
	Watching nanomaterials with Xray-eyes: the power of X-ray diffraction with incoherent and coherent beams (C.Giannini, Scienze Chimiche e Molecolari)	2022	16h	1.6
	Advanced materials for sensing technologies (SCuDo, Rosaria Picca)	12/2021-1/2022	10h	1
	Flexible and stretchable electronics (SCuDo, Francesco Dell'Olio)	02/2022	20h	2
	Innovative materials for energy conservation technologies (SCuDo, Andrea Listorti)	03/2022-04/2022	10h	1
	Smart education for industry 4.0 (SCuDO, Veronica Rossano)	06/2022	20h	2
Master's degree courses	---	---	---	---
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Participation to seminars and international congresses or workshops	Participation in specialized seminars	2022	7h	2
	Workshop: "Chimica sotto l'albero-I giovani e la chimica: temi e sfide per le innovazioni del prossimo future" (SCI-Sez.Puglia)	20/12/2021	1day	1
Presentation of research products at international congresses or workshops	Presentation of research products at workshop: "Chimica sotto l'albero"	20/12/2021		2

	TOTAL OF CFU FOR TRAINING ACTIVITIES			**18**
Individual research activity	Design, synthesis and characterization of hybrid nanocomposites formed of metal NPs and derivatives of graphene by using sustainable, scalable and environmentally friendly synthetic approaches, test of the photocatalytic and antimicrobial properties of the materials obtained in solution and onto standard substrates and comparison with commercial reference materials as benchmarks for performance evaluation.	2021-2022	750 h	30
Students' supervision				
Integrative didactive activities				
Preparation of manuscripts for conferences or journals	Preparation of manuscripts for journals, as research products of individual research activity	2021-2022	300h	12
	TOTAL OF CFU FOR RESEARCH ACTIVITIES			**42**
	TOTAL OF CFU FOR YEAR I			**60**

Second academic year

	Description	**Period**	**Duration**	**CFU**
PhD courses	Laboratorio di inglese accademico (Scienze Chimiche e Molecolari)	2023	20h	2
	Sustainability in smart manufacturing: open research questions (SCuDo)	2022-2023	20h	2
	XPS as a powerful tools for surfaces and nanomaterials characterization (Scienze Chimiche e Molecolari, Ditaranto)	2022-2023	16h	1.6
	Multidisciplinary Research Applications of 3D Printing (SCuDo) Cenni di ecologia industrial (LCA, LCC) (Uni	2022-2023	20h	2
Master's degree courses	---	---	---	---
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Participation to seminars and international congresses or workshops	Participation in specialized seminars	2022	8h	2.4
Presentation of research products at international congresses or workshops	Presentation of research products at international congresses or workshops	2023		2

	TOTAL OF CFU FOR TRAINING ACTIVITIES			**12**
Individual research activity	Design, manufacturing and characterization by means of chemical, morphological and structural characterization of hybrid nanocomposites formed of metal NPs or heterostructures based on metal/semiconductor oxides NPs, combined with Reduced Graphene Oxide flakes and investigation of their photocatalytic and antimicrobial properties also compared with commercial reference materials as benchmarks for performance evaluation. Development of formulations with characteristics suitable for substrate deposition by using techniques such as dip coating, spray coating, impregnation and plasma aerosol.	2023	900h	36
Students' supervision				
Integrative didactive activities				
Preparation of manuscripts for conferences or journals	Preparation of abstract of report presented at conference. Articles concerning the research activity carried out for publication in scientific journals.	2023	300h	12
	TOTAL OF CFU FOR RESEARCH ACTIVITIES			**48**
	TOTAL OF CFU FOR YEAR II			**60**

Third academic year

	Description	**Period**	**Duration**	**CFU**
PhD courses	---	---	---	---
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Master's degree courses	---	---	---	---
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Participation to seminars and international congresses or workshops	---	---	---	---
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Presentation of research products at international congresses or workshops	Presentation of the results of the new experimental work at international congresses or conferences	2024		2
	TOTAL OF CFU FOR TRAINING ACTIVITIES			**2**

Individual research activity	Study and optimization of the deposition and fabrication processes of coatings on suitably selected textiles, using the mentioned deposition techniques. Characterization of the coatings obtained for the verification of the suitability of the processes developed for application in the industrial field	2023-2024	1000h	40
Students' supervision				
Integrative didactive activities				
Preparation of manuscripts for conferences or journals	Preparation of one or more manuscripts for a scientific journal, as a research product of the new experimental activity carried out and of the final paper of the research Thesis	2024	450h	18
	TOTAL OF CFU FOR RESEARCH ACTIVITIES			**58**
	TOTAL OF CFU FOR YEAR III			**60**
	TOTAL OF CFU FOR THE WHOLE PHD COURSE			**180**