Scuola di Dottorato "Vito Volterra" in Scienze Astronomiche, Chimiche, Fisiche e Matematiche e della Terra
PhD in Earth Science c.v. Environment and Cultural Heritage (XXXIX cycle)

PhD Research Proposal

NAIADE:
Nanoparticles for **A**nalysis and **I**dentification of polluting **A**gents and **D**yes in both indoor and outdoor **E**nvironment

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Introduction and state of the art

Cultural heritage conservation is a complex issue that requires interdisciplinary efforts with the final aim of preserving works of art. Indeed, the deterioration of materials is often caused by physical and chemical factors and biological agents. In order to assess the morphological changes, and the physical-chemical, biological, visual variations in each art object, a large number of physical parameters (e.g.: Temperature, RH) is typically monitored. The monitoring of cultural heritage is a highly specialized and critically important task, providing conservators with early warnings of potential damage and facilitating the creation of optimal conditions to minimize the infiltration of both indoor and outdoor pollutants. In recent years, the preservation of cultural heritage from air pollutants has gathered significant scientific attention, emphasizing the importance of preventive conservation[1]. Besides, some recent studies show the importance of the detection of volatile organic compounds (VOCs) derived from the deterioration of artifacts themselves and from those materials, which compose museum display cases, since they could become an additional risk for conservation.[2]

Gas sensing is a crucial tool for assessing environmental pollution and monitoring in museums. In cultural heritage conservation, it needs to be sensitive and both time- and cost-effective. Traditional quantitative detection methods, such as gas chromatography or mass spectrometry, are beyond conservators' purposes, requiring filters or cartridges for sampling and time-consuming laboratory analysis. Moreover, despite offering a complete air composition overview, there is a delay between contamination and detection, which excludes the possibility of a real-time monitoring. Other analyte-specific indicators based on traditional technologies[3] have been used to monitor cultural heritage, but issues of sensitivity, applicability and cost-effectiveness remain major obstacles. The most common qualitative method for air monitoring in museums is the Oddy test.[4] This method involves visual inspection of clean metal coupons to detect potential pollutant hazards but has long evaluation time. Optical devices, instead, offer advantages in terms of speed, sensitivity, and selectivity. In this sense, colorimetric sensor arrays have emerged as low-cost optoelectronic noses for the detection and identification of individual compounds and complex mixtures.[5] Among these, a class of sensors based on noble metal nanoparticles (NPs) has recently gained interest. Gold or silver NPs, functionalized with specific receptors, have found applications in many fields, including monitoring the environment.[6] In particular, capped AgNPs have been used as dosimetric detectors for the ultrasensitive monitoring of airborne pollutants in museums and the detection of volatile compounds emitted from deteriorated artifacts.[7] The mechanism behind these sensors relies on changes in the localized surface plasmon resonance (LSPR) through NPs aggregation occurring upon the presence of the analyte, resulting in a shift of the plasmonic absorption and a corresponding color change. These detection substrates are portable, easy to use and sustainable. However, they provide none or limited structural information about the analytes, because of the detection methods exploited (colorimetry, fluorescence).

One application of NPs, still based on LSPR and well-developed for trace-detection, is Surface Enhanced Raman Scattering (SERS) spectroscopy, consisting of the amplification, by several orders of magnitude, of the Raman signal of analytes in proximity of the metal NP, occurring due to the LSPR near field enhancement. This highly sensitive vibrational spectroscopic technique offers molecule-specific fingerprint signals and has a wide range of applications. The use of NPs arrays as capturing probes (exploiting functionalized NPs) to boost the affinity between small gaseous molecules and the NPs, combined with SERS spectroscopy has shown good possibilities for gas phase detection of pollutants such as NOx and SOx.[8] Further, SERS has proven to be a valuable tool in conservation science[9], widely utilized for the identification of organic colorants due to its ability to enhance Raman signal, while minimizing the fluorescence background. These features mark SERS as a crucial technique for the detection of dyes, usually strongly fluorescent and present in Cultural Heritage matrices at very low concentrations. Several studies prove the efficiency of SERS for the identification of historical natural dyes in lakes and textiles[9], while in the last years the research has even been focused on the SERS detection of synthetic dyes in different typologies of matrices.[10] Notably, Ag-colloids and Ag-colloidal pastes are commonly employed as plasmonic nano-systems for cultural heritage studies. However, both substrates are intrinsically invasive. In fact, in order to promote the close contact between the NPs and the analytes, the sampling from the object of interest and the following extraction of analytes are required, while the direct deposition of AgNPs on the artwork must be avoided because it involves an addition of non-original material and it could cause a chromatic variation of the surface. In recent years, many SERS strategies have been proposed for the study of natural dyes, which could be minimally invasive. Examples include polymer-based gel beads imbibed with water/DMF/EDTA [11], cellulose Ag-films [12] and agar agar hydrogels.[13] However, a common challenge with these matrices is the necessity for water-based solutions to extract analytes, posing difficulties for artworks sensitive to moisture. Attempts have been made for a dry-state extraction of colorants, such as Ag-nanoisland[14] or AgNPs synthesis directly over rigid glass slides.[15] Nevertheless, the inflexibility of these substrates makes them impractical for application on complex and curved surfaces. Other non-invasive SERS probes based on Ag-PDMS composite have been proposed, but limited by complex fabrication procedures.[16] Also, the need for sustainable, cost-effective, uniform and flexible SERS platforms has recently attracted great attention for trace detection of various analytes.[17] Based on these premises, this project is intended to develop a SERS based sensor with the twofold application for the detection of both harmful air pollutants and volatile compounds (generated from the deterioration of plastics and other organic materials in cultural heritage objects) and for the extraction and detection of synthetic organic colorants from contemporary art. In this way, one NPS-based strategy is proposed to solve two different risk factors for the conservation of precious objects: 1) the damage from pollutants noxious for the preservation of Cultural Heritage and 2) the intrinsic risk connected to analytical sampling in artworks.

Objectives

Overall objective: creation of a new ultrasensitive, green and cost-effective integrated platform to provide for a sustainable environmental monitoring and diagnostics of cultural heritage in both indoor and outdoor context.

Specific objective: definition of an experimental approach, based on SERS spectroscopy, through the fabrication and characterization of a suitable substrate capable of the untargeted detection of volatile and non-volatile compounds of interest in the cultural heritage field. The methodology could help overcome the limited applicability of SERS in the gas sensing field and the drawbacks of sampling organic analytes. Hence, NAIADE main focus is the creation of a green sustainable sensor made of properly functionalized silver nanoparticles (AgNPs) fixed on a polymeric substrate, for instance cellulose, to be used both as sampling device and detection system.

Implications and applications

The NAIADE project's implications and applications encompass a wide range of fields, from environmental monitoring and analytical chemistry to cultural heritage preservation and material analysis. It offers an eco-friendly, cost-effective, and non-invasive approach to detect and characterize various analytes, making it a valuable tool in multiple scientific and practical contexts. In particular, the implications and applications of the project could be summarized in the four following points:

- *Flexible substrates for analyte detection*: the integration of AgNPs into a porous polymer network provides a flexible structure that permits the sampling even on most complex surfaces, while ensuring a wide surface area of interaction for gaseous molecules and trace detection of various analytes.[6] Additionally, polymer networks provide for a good stability, sensitivity and simple (one-step) fabrication processes. Their structure offers abundant binding and stabilizing sites for the NPs, ensuring a secure anchoring and a homogeneous deposition of plasmonic layer. Also, in the case of cellulose substrates, the background interference is reduced due to its weak response to SERS.[18] This can have broad applications in environmental monitoring, offering a more sustainable alternative to traditional detection methods that may involve hazardous chemicals or expensive equipment.
- *Plasmonic properties for rapid detection (colorimetry)*: The plasmonic properties of AgNPs can serve as a colorimetric sensor for rapid, ultrasensitive, and quantitative detection of small gaseous molecules. This means that the system can quickly indicate the presence and concentration of specific gases, making it useful for environmental monitoring, safety, and industrial applications.
- *SERS spectroscopy for molecule-specific analysis*: The project also utilizes AgNPs as a SERS substrate for molecule-specific fingerprint analysis. SERS is a powerful analytical technique that provides detailed information about the chemical composition of materials. It has applications in the preservation and restoration of cultural heritage objects, such as artworks and historical artifacts. SERS spectroscopy has been already employed for the identification of dyes[9] and proved to be suitable for VOCs and other environmental pollutants.[19]
- *Dry-extraction for organic material detection*: The project's approach could potentially be exploited for a dry-extraction method that is solvent-free for the detection of organic materials, such as synthetic dyes in inks and textiles. This is a valuable application for conservators and researchers who need to analyze the composition of historical materials without the risk of damage or contamination. Furthermore, the implementation of this system can help mitigate risks associated with direct contact between NPs and the object surface, offering a non-invasive and safer way (both for the environment and the operator) to analyze and monitor artifacts.

Work plan

The research project is divided into several tasks, some of which are composed of sub-tasks. The conclusion of each task will lead to a specific milestone that concours to achieve the final objective of the project. The PhD activity will be composed as follows:

T1. Literature review, technique familiarization and formation: the first period (approximately two months) will be spent conducting a comprehensive literature search on the state of the art on plasmonic applied to environmental monitoring and cultural heritage diagnostics. At the same time this period will include the formation on some experimental techniques (synthesis, instrumentation). Also, seminars, workshops and institutional courses will be followed during the first and second year of PhD program as part of the training period.

T2. Sensor development: the development of the AgNP-based array will take approximately 15 months and the work will be organized in the following subtasks:

T2.1. Synthesis and Assessment of the Nano-System: this subtask involves the synthesis of different Ag nano-systems to identify the most versatile probe for capturing analytes, including small gaseous molecules and non-volatile organic compounds related to cultural heritage. Tests on different systems will be led to enhance their affinity for small gaseous molecules.

T2.2. Characterization of AgNPs: the characterization of AgNPs will be conducted with Scanning Electron Microscopy (SEM) for the morphology and Dynamic Light Scattering (DLS) to provide information on their size. Additionally, Light Transmission Spectroscopy (LTS) will be helpful to determine the actual concentration and size of the colloidal system, offering valuable insights into the AgNP properties.

T2.3. AgNP Synthesis on Cellulose Net: filter paper will be used in this step as a pilot substrate to synthetize the AgNPs directly inside the cellulose net. First attempts will be led by soaking stripes into $AgNO_3$ solution and adding reducing agents. Two different protocols (one adding hydroxylamine hydrochloride[20] and the other one using sodium borohydride[18] as reducing agents) will be compared. Also, the use of a polymer network[21] will be explored to anchor the NPs to the substrate.

M1. Plasmonic substrate for the ultrasensitive detection of volatile and non-volatile molecules

T3. Dosimetric Testing: an extended period (approximately seven months) will be spent in conducting trials with different known gases and their mixtures at different concentrations to verify the dosimetric capabilities of the selected system by monitoring the interaction with volatile molecules.

M2. Creation of a colorimetric and spectroscopic database of the most widespread airborne pollutants in the field of cultural heritage.

T4. Preparation of Textile and Ink Mockups: Inks will be obtained mixing ethylene glycol and some dispersive agents with the most widespread dyes in contemporary art (azo and triarylmethane dyes). Wool and cellulosic threads will be dyed with the same colorants.

T5. Dry-extraction Testing: the paper-based AgNPs array will be tested in this phase as a swab remover for a solvent-free extraction from mockups. The non-invasiveness of the procedure will be assessed using Fiber Optic Reflectance Spectroscopy (FORS) and colorimetry.

M3. Creation of a spectroscopic database of the most widespread synthetic organic colorants in modern and contemporary art.

T6. Case studies: Some artifacts from the Istituto Centrale del Restauro (ICR) of Rome and street art works will be eventually selected as case studies for the extraction and analysis of synthetic dyes. In this final stage the AgNP-based sensor will be tested directly on real case studies both as sampling swabs on works of art and monitoring platforms for volatile organic compounds (VOCs) and pollutants. Also, the methodology will be exploited – during the period abroad – for the monitoring of airborne pollutants in some of the monuments under study at the University of Athens (Greece).

Dissemination plan

Dissemination will be articulated by publishing scientific papers on indexed journals (e.g. Journal of Raman Spectroscopy, Sensors, Colloids and Surfaces) and by presenting the results of the research in several national and international conferences of interest in the field (e.g. SCI ABC Conference, ECIS, Technart). Dissemination will also include the creation of two open-access spectroscopic databases that will be published online and on dedicated journals (e.g. Spectrochimica Acta part. A).

List of activity

During the first two years, several courses within the Earth Science PhD program offer will be attended. Furthermore, soft skills workshops offered by Sapienza University will be followed and summer schools on topics of interest.

International mobility

During the three years of the PhD program, a period of 6 months will be spent at the National Technical University of Athens (NTUA), under the supervision of Dr. Katerina Delegou, whose research group is investigating environmental impact on the conservation of cultural heritage and with whom Sapienza University has already an established collaboration. During this period, the methodology will be exploited for the monitoring of airborne pollutants in some of the monuments under study at NTUA.

Gantt chart

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