L.C. COTET^{1,2*}, C. SALAGEAN^{2,3}, A. MIHIS², I. SZÉKELY^{3,4}, ZS. TOTH⁴, L. BAIA^{2,3,4}, M. BAIA^{2,3}, G. OLTEANU⁵, I. OLTEANU⁵, V. DANCIU¹

ABSTRACT. Three-components suspension, based on a mixture of titania (TiO₂)silica (SiO₂)-functionalized graphene oxide (GO) is prepared and used for surface consolidation of historical andesite stone and mortar. For comparison, monoand bi-component suspensions are also involved in this study. In order to increase the attachment capacity of GO to substrate with silicon, GO functionalized with (3-aminopropyl) triethoxysilane (GO-APTES) was involved. Unmodified and modified by painting with prepared suspensions andesite and mortar samples were investigated by microscopy (Optic and SEM-EDX), XRD, FT-IR and Raman spectra before and after 6 months of exposure to ambient conditions. After investigation, even the amount of used consolidant suspension was low, the stability of the modified samples was found that remains constant and in a long time it is possibly to reach even a higher stability level. This approach provides the idea that the prepared suspension could be an interesting option to be involved in stone and mortar consolidation-restoration field.

Keywords: titanium oxide, cultural heritage, functionalized graphene oxide, surface consolidation, historical stones, historical mortars.

©2022 STUDIA UBB PHYSICA. Published by Babeş-Bolyai University.



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.

¹ Department of Chemical Engineering, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Arany Janos 11, RO-400028, Cluj-Napoca, Romania

² Institute of Research-Development-Innovation in Applied Natural Sciences, Babes-Bolyai University, Fantanele 30, RO-400294, Cluj-Napoca, Romania

³ Faculty of Physics, Babes-Bolyai University, M. Kogalniceanu 1, RO-400084, Cluj-Napoca, Romania

⁴ Nanostructured Materials and Bio-Nano-Interfaces Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babeş-Bolyai University, Treboniu Laurian 42, RO-400271 Cluj-Napoca, Romania

⁵ S.C. Duct S.R.L., Feroviarilor 55, Sector 1, RO- 012206, Bucuresti, Romania

^{*} Corresponding author: cosmin.cotet@ubbcluj.ro

1. INTRODUCTION

Nowadays, there is a growing concern about the degradation of cultural heritage, which is an incalculable legacy for our future. In order to preserve the stone heritage, the intrinsic properties of the stone, the state of conservation, the degradation mechanisms and the environmental factors as well as the appropriate selection of materials and their application procedures must be taken into account. The compatibility, depth of penetration and durability of the selected materials, as well as their effect on water and vapor permeability, and their resistance to biological factors should also be taken into consideration. Until recently, the preservation of cultural heritage was mainly based on traditional conservation and restoration treatments such as the use of synthetic polymers, which often lack vital compatibility with substrate and durability. The development of materials science led to the discovery of nanomaterials with applicability in construction that allowed the improvement of the consolidation and protection of damaged building materials and the maintenance of the architectural heritage [1–3]. Consolidation treatment is an important conservation process that allows to improve the deep cohesion of the damaged stone heritage. However, the irreversibility of the consolidation process and its likelihood of causing unwanted effects makes this treatment one of the riskiest preservation processes. This risk explains the growing development and application of nanotechnology to the preservation of cultural heritage. Nanotechnology allows the design and development of reinforcing nanomaterials compatible with the original stone substrate, with 1-100nm in size and large surfaces, which leads to increased chemical reactivity and easier penetration into the depth of damaged stone monuments [4]. The dramatic increase in the external degradation of historical monuments due to air pollution, respectively the deposition of organic compounds and other pollutants on stone substrates has led to the development of nanomaterials with self-cleaning, antimicrobial and air depollution properties. Over the last 20 years, due to its outstanding ability to decompose pollutants by photocatalytic oxidation and its photoinduced superhydrophilicity [5], titanium dioxide is one of the best-known additives used in building materials, such as cement paste and mortar [6-8]. In addition, it should be noted that titanium dioxide is a cheap, non-toxic, chemically stable photocatalyst [9] and compatible with commonly used building materials [7]. The photocatalytic function of TiO_2 depends on its semiconductor and optical properties. Due to the oxygen vacancies present in its network, TiO_2 is an n-type semiconductor. The photocatalytic action of TiO_2 lies in the ability to simultaneously adsorb two reactants, which are reduced and oxidized

by photonic activation initiated by photon absorption ($hv \ge Eg$). The photoinduced electron transfer to an adsorbed molecule is determined by the position of the valence band and respectively the conduction band of the TiO₂ in relation to the redox potentials of the adsorbed molecules [10]. The energy value of the gap band of TiO₂-anatase is 3.2 eV, which means that it can only absorb UV light ($\lambda \le 387$ nm). Given the fact that the solar spectrum consists of 3-4% ultraviolets, there was the problem of changing the electronic structure of TiO₂ so that it absorbs light from the visible region, and thus working efficiently under natural sunlight. This can be done either by TiO₂-doping with metals and non-metals, TiO₂ coupling with other semiconductors, or by creating network defects [8, 11, 12].

The great discrepancy between the recombination time of the photogenerated electron– hole pairs (10^{-9} s), and the time scale for the chemical interactions of TiO₂ with the adsorbed dirt (10^{-8} to 10^{-3} s) does that the unintended recombination of electron–hole pairs to be much more favourable than for the TiO₂–dirt adsorption which leads to a decrease in the efficiency of the photocatalytic activity of TiO₂ [13].

Due to its special features (specific surface area of $2600 \text{ m}^2 \text{ g}^{-1}$, thermal/chemical stability and mobility of the charge carriers of $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) the graphene increases the adsorption capacity of TiO₂ based photocatalysts acting at the same time as an acceptor of the photo generated electrons from TiO₂, suppressing the recombination between photo-excited electrons and holes. Also, graphene act as a sensitizer extending light absorption range. The localized electrons in the sp² states of the graphene, excited by sunlight, are injected into the conduction band of TiO₂, where they are trapped by the O₂ molecules producing superoxides radicals which oxidize organic compounds [14,15]. The results of the researchers showed that the addition of graphene oxide improves the antibacterial and self-cleaning of the titanium dioxide films in order to use it in practical applications [14, 16, 17].

Another role of TiO_2 -based nanoparticles is to improve mechanical properties (compressive strength, toughness, etc.), and to reduce the shrinkage and permeability of building materials - characteristics that prolong the life of the building material [18]. The positive influence on the impermeability of construction materials (mortar, concrete, etc.) can be explained either by the function of nanoparticles as fillers thus creating less permeable structures, or by their function as "nucleus" that induce the formation and growth of hydration of the cement or which promotes the formation of high-density C-S-H structures [19].

For the TiO_2 photocatalyst application in conservation and restauration of the cultural heritage, the issue was to ensure the durability and adhesion of TiO_2 on the stone or mortar substrates. In recent years, numerous studies have demonstrated the ability of silica-based materials to create durable and well-adherent TiO_2 coatings [20–23].

The TiO₂-SiO₂ coatings proved also high photocatalytic activity, the efficiency increasing as TiO₂ concentration was increased. The positive effects of SiO₂ are due to the increased surface area for adsorption and photodegradation of organic pollutants, to the charge imbalance which determines the creation of Lewis acidic sites, which promotes the adsorption of higher amount of hydroxide respectively a higher photocatalytic efficiency. Furthermore, TiO₂/SiO₂ composite having lower isoelectric point determines the increasing of the concentration of hydroxyl ions which are absorbed on the surface of photocatalysts and reduce the electron/hole recombination rate by blocking the generated holes [24–26].

In our previous study, interesting properties related to the increase of mechanical properties of mortar treated with consolidant based on graphene oxide (i.e. GO, oxidated form of graphene) was obtained [27]. More exactly, an increased value for the compressive strength of about twice time compared to the untreated blank samples and a decrease of the value for the capillary absorption water coefficient with about one order of magnitude in comparison with the untreated blank samples were obtained for mortar samples treated with GO consolidation suspension.

2. EXPERIMENTAL

2.1. Preparation of andesite and mortar as parallelepiped samples

In the case of andesite, a block of andesite was brought from the Pietroasa Bejan quarry and cut at a workshop in Bucharest into 1 cm thick slices, from which 2 cm wide strips were later extracted. The 2x1 cm² strips, obtained at coarse cutting, were cut into 2x2x1 cm³ samples (Figure 1a). The samples thus obtained were sorted by removing the parts with errors, washed in distilled water and stored under normal conditions of temperature and humidity; 20-25 °C and 55-60% relative humidity. Thus, 100 parallelepipedal specimens of 2x2x1 cm³ of andesite were obtained.

The lime mortar is prepared by recipe: one part slaked lime (paste), three parts washed and dried river sand sieved less than 2 mm.

For paste preparation, to 100 g of Ca(OH)₂ 100 ml of water was added to obtain a more fluid mixture that is proper to prepare a mortar with increased porosity. The obtained homogeneous mixture was introduced into the casting patterns by manual pressing. After drying and drawing out from the pattern, 100 samples of lime mortar measuring 2x2x1 cm³ were obtained (Figure 1b). Alteration of the exposure surfaces was performed by treatment with acetic acid solution (6%) in all mortar samples (100 pcs.), by total immersion in the acid solution, exposure for 3 minutes, followed by stopping the reaction by immersing the sample in water.

The not modified faces of mortar samples were reinforced by using an acrylic paint in order to make the samples more enforced during manipulation. The binder has a holocrystalline structure being composed of micron calcite crystals, resulted from the carbonation of calcium hydroxide.

2.2. Preparation of graphene oxide components (i.e. GO and GO-APTES)

2.2.1. Preparation of GO

Graphene oxide (GO) was synthetized using an efficient sono-chemical exfoliation of graphite [28]. In the obtaining pathway besides graphite (7.5g, 99%, powder >0.1mm, Fluka), H_2SO_4 (742mL, 95–97%, SC Nordic Invest SRL, Cluj-Napoca), H_3PO_4 (83mL, 85%, SC Nordic Invest SRL, Cluj-Napoca) and KMnO4 (33g, 995, Sigma Aldrich) that are the main precursors of Marcano-Tour's improved exfoliation method [29], H_2O_2 (550mL, 3%, SC "Hipocrate 2000" SRL, Bucharest), H_2O (550mL, bidistilled homemade), HCI (275mL, 37%, SC Nordic Invest SRL, Cluj-Napoca) and ethanol (275mL, absolute, SC Nordic Invest SRL Cluj-Napoca) were involved into a washing-sonication-centrifugation-decantation process. After 7days of drying, about 14,3g GO was obtained.

2.2.2. Synthesis of GO functionalized with (3-aminopropyl) triethoxysilane (APTES)

Ethanolic suspension of GO (17,5 mL, C=40 mg / ml GO), was placed in a 3necked flask having a capacity of 750 ml. Then, 360 ml (3-aminopropyl) triethoxysilane (APTES) and 360 mg N, N'-dicyclohexylcarbodiimide (DCC) were added under magnetic stirring at 700 rpm. An ascending water-cooled refrigerant was attached to the flask, and the installation was placed in an oil bath heated at 70°C for 24 hours. After the reaction time elapsed, the precipitate of GO functionalized with APTES was allowed to settle, the top layer (colourless) was decanted and the suspension (bottom layer) was centrifuged at 6000 rpm for 15 minutes. The resulted precipitate has been washed three times with 300 ml absolute ethanol. After the last washing and separation by centrifugation, the precipitate of GO functionalized with APTES was dried in an oven at 60°C for 12 hours, yielding 1.0 g of GO functionalized with APTES (GO-APTES).

2.3. Preparation of colloidal solution used in consolidation process

2.3.1. Synthesis of TiO₂ colloidal solution (S1)

To an Erlenmeyer flask (V=50 ml) containing 5 ml of isopropyl alcohol, 30 ml of titanium tetraisopropoxide (98%, MERCK, GE)-TIP were added, in drops and continuous stirring, The obtained solution was added, in drops and continuous stirring, to 175 ml of bidistilled water in a three-necked glass flask (V = 1000 ml).

After 2.5 ml of 65% HNO₃ ml (CHEMPUR, RO) have been added, the flask provided with an ascending refrigerant connected to a water source was immersed in an oil bath at 80°C for 6h continuously magnetic stirring.

2.3.2. Synthesis of TiO_2 colloidal solution with 0.026% GO functionalized with APTES (GO-APTES), (S2)

After 15 minutes of magnetic stirring of the obtained TiO_2 colloidal solution (see 2.3.1), the suspension of GO-APTES (0.053g of GO functionalized with APTES in 5 ml of absolute ethylic alcohol, stirred with ultrasound for 30 min) was added and then the mixture was stirred continuously and kept at 80°C for 8 hours.

2.3.3. Synthesis of TiO₂-SiO₂ (67:33%) colloidal solution (S3)

A mixture of 11.2 ml of tetraethyl orthosilicate (98%, MERCK, DE), 0.05 ml of 65% HNO₃ (CHEMPUR, PL), 1.8 ml of double-distilled water and 26 ml of absolute ethyl alcohol (CHIMREACTIV SRL, RO) was prepared and added, under continuous stirring, to the obtained colloidal solution of TiO_2 (see 2.3.1) that was previously cooled to room temperature. Stirring was continued for 6 hours.

2.3.4. Synthesis of TiO_2 -SiO₂ (67:33%) colloidal solution with 0.023% GO functionalized with APTES (GO-APTES), (S4)

To prepare TiO_2 -SiO₂ (67:33%) colloidal solution with 0.023% GO-APTES, 0.054 g of GO-APTES were weighed and added to 5 ml of absolute ethyl alcohol. After 20 min of ultrasonic stirring, the obtained GO-APTES suspension was added to the colloidal solution of TiO_2 -SiO₂ (see 2.3.3). Ultrasonic stirring was continued for one hour.

2.4. Devices and techniques involved in morpho-structural characterization

2.4.1. Optical microscopy

The optical microscopy analysis was performed with "Motic BA310Pol" device. After a surface cleaning by air blowing, the surface samples were analyzed in adequate lateral illumination.

2.4.2. Scanning electron microscopy (SEM)

The SEM and EDX (electron diffraction X-ray) analysis were performed with a SEM - HITACHI TM4000plus combined with an EDX OXFORD INSTRUMENTS hardware and AZtecOne software.

2.4.3. X-ray diffraction (XRD)

Structural properties of the samples were carried out by using Rigaku MiniFlex II diffractometer with X-ray (Cu-K α ; $\lambda = 0,15406$ nm) radiation equipped with a graphite monochromator. Scan speed was: $1^{\circ} \cdot \min^{-1} (2\theta^{\circ})$ and the diffractograms were taken between 3° -80° ($2\theta^{\circ}$). Samples were scraped with a spatula and transferred into an XRD support.

2.4.4. Fourier Transform Infrared (FT-IR)

Absorption spectra of the investigated samples were recorded at room temperature by employing a Jasco 6000 (Jasco, Tokyo, Japan) spectrometer (in reflection configuration) in the 400–4000 cm⁻¹ range, with a spectral resolution of 4 cm⁻¹. All samples were prepared previously in the form of KBr pellets.

2.4.5. Raman spectroscopy

Raman spectra measurements were recorded with the help of a multilaser confocal Renishaw inVia Reflex Raman spectrometer equipped with a RenCam CCD detector. The 785 nm (NIR) laser line was applied as an excitation source on the samples' surface. The Raman spectra were collected employing a 0.9NA objective of 100 × magnification. The following parameters were used for all spectra: integration time was 20 s, 1200 lines/mm grating, and 50% of the maximum laser intensity - laser power of 150 mW.

3. RESULTS AND DISCUSSION

The study is performed on andesite and lime mortar. The andesite corresponds to the cultural objective Sarmizegetusa Regia, the source of the andesite being the magmatic body from Pietroasa, Bejani Hill, the south-eastern extremity of Deva municipality of Romania. The mortar was prepared in using a mixture of sand, Ca(OH)₂ and H₂O. Parallelepipedal samples of 2x2x1 cm³ were prepared by stone cutting for andesite (Figure 1a) and casting in proper patterns for mortars (Figure 1b). The both sample types were modified by painting with four suspensions (Figure 1c): TiO₂ colloidal solution (S1), TiO₂ colloidal solution with GO-APTES (S2), TiO₂-SiO₂ (67:33%) colloidal solution with GO-APTES (S4).

L.C. COTET, C. SALAGEAN, A. MIHIS, I. SZÉKELY, ZS. TOTH, L. BAIA, M. BAIA, G. OLTEANU, I. OLTEANU, V. DANCIU



Fig. 1. Real images with andesite (a) and mortar (b) samples, and suspensions used in surface modification of the samples (c), (see Chapter 2.3).

In the present study, unmodified samples were also investigated as blanks (S0). Moreover, suspensions with GO (i.e. GO unfunctionalized with APTES) were not mentioned in this study because without GO's functionalization with silicious group a poor fixation of this nanosheet material on samples surface could be achieved. To increase of GO-APTES fixation, SiO_2 component could play a favorable behavior. In order to study the in time structural change, the investigation was performed on unexposed and 6 months ambient atmosphere exposed samples. The suspensions were applied only on a face of the parallelepipedal andesite and mortar samples that consist of $2x2 \text{ cm}^2$. After preparation and analysis, samples were placed in ambient atmosphere for 6 months (from May to October at the climate of Bucharest, Romania). Then, the samples were analyzed again.

3.1. Optical microscopy (OM) analysis of andesite and mortar surfaces

Investigation of andesite and mortar surfaces was performed with the optical microscope using reflected light illumination mode. In Figure 2 a compact structure with zones with different colours (e.g. light-grey, dark-grey) was evidenced for andesite samples. Instead of this, in Figure 3 a more granular structure (i.e. sand particles) linked with the binder component (i.e. calcium carbonate) was shown for mortar samples.



Fig. 2. Optical microscopy images with surfaces of andesite samples unmodified (a) and modified with S1 (b), S2 (c), S3 (d) and S4 (e) before of 6 months for external exposure.



Fig. 3. Optical microscopy images with surface of mortar samples unmodified (a) and modified with S1 (b), S2 (c), S3 (d) and S4 (e) before of 6 months for external exposure.

For both sample types after surface modification with prepared suspensions (see Chapter 2.3), no visual change was evidenced. This could due to the low thickness and the transparent feature of applied layers. The same behavior was evidenced after 6 months of ambient environment exposure (i.e. for simplicity, these images are not presented).

In the case of mortar, microscopic observations show that the mass of the binder is relatively compact and has good adhesion to the aggregate clasps. It is also found that there are several shrinkage cracks in the binder mass, which are poorly connected, with local extension. A slight difference lies in the characteristics of the pore system. The pores have irregular shapes and variable sizes. The microscopically expressed porosity is about 10–15%.

Andesite rock porosity by microscopic examination shows that there are no over capillary pores in its structure. The rock is practically compact, with zero effective porosity and therefore waterproof.

3.2. SEM-EDX analysis of andesite and mortar surfaces

By SEM investigation surfaces with no regular features with zones with cracks were evidenced both for andesite (Figure 4) and mortar (Figure 5) samples and both before and after modification with prepared suspensions (see Chapter 2.3). The same behaviour was shown also after 6 months of ambient exposure (i.e. for simplicity, these images are not presented).



Fig. 4. SEM images with surfaces of andesite samples unmodified (a) and modified with S1 (b), S2 (c), S3 (d) and S4 (e) before of 6 months for external exposure.



Fig. 5. SEM images with surface of mortar samples unmodified (a) and modified with S1 (b), S2 (c), S3 (d) and S4 (e) before of 6 months for external exposure.

The atomic ratios between the percent of Ti and Si (i.e. Ti/Si) were determined by EDX for S2 and S4 consolidant solutions dried on a common support (i.e. not applied on mortar or andesite samples) obtaining hundred micro meters of thickness (i.e. the analysis dose not touch the support). The values were 1.375 for S2 and 1.222 for S4, respectively. This means more Si in S4 in comparisons to S2 (i.e. because of Si from APTES). Moreover, the atomic percent for C (i.e. having GO-APTES as source) for S2 and S4 was not noticed by EDX. This could be because GO-APTES is in a very low concentration that means a low amount of C that is below the detection limit. The atomic percent ratio between Si of S3 and S4 which is 0.888, confirms again the presence of a higher amount of Si for solution prepared with GO-APTES (i.e. because of Si of SiO₂ component in addition to APTES).

3.3. X-ray diffraction (XRD) measurements on andesite and mortar surface

Commercial andesite consists mostly of SiO_2 and various types of Feldspar. In the andesite-unmodified and unexposed sample, we found amorphous SiO_2 and mineral Plagioclase with the following reflections: 21.7°, 23.4°, 24.3°, 27.4°, 30,2°, 35,3°, and 44,3° [30]. A new reflection is also visible in the andesite-unmodified and

L.C. COTET, C. SALAGEAN, A. MIHIS, I. SZÉKELY, ZS. TOTH, L. BAIA, M. BAIA, G. OLTEANU, I. OLTEANU, V. DANCIU

exposed sample: 51.2° [30], which is a reflection of Plagioclase or Pyroxenes. Not all reflections of plagioclase could be observed in the XRD patterns of the unmodified samples because the sample is heterogeneous. The presence of TiO₂, SiO₂ and GO-APTES was not visible in the XRD patterns of the samples. The reason that the mentioned modification could not be seen in XRD patterns, could be that the amount of the TiO₂, SiO₂, and GO-APTES is lower than the detection limit of the XRD. The samples which have been exposed for 6 months are identical to the samples which were not exposed.



Fig. 6. XRD patterns of the unexposed and exposed (6 months) andesite samples.

3.4. Fourier Transform Infrared (FT-IR) measurements on andesite and mortar surface

Andesite is a volcanic rock with a mixed composition, meaning it is the intermediate rock between basalt and rhyolite. It predominantly comprises sodium-rich silicates such as plagioclase, pyroxene, and hornblende. In the FT-IR spectra of all unexposed and exposed andesite samples, the following bands were observed:

O-H stretching vibrations at 3439 cm⁻¹; H-O-H bending at 1636 cm⁻¹ [31]; Si-O asymmetric and symmetric stretching vibrations at 1100, 1026, and 795 cm⁻¹ [32, 33]; Si-O-Si bending a 619 cm⁻¹, respectively Si-O-Al bending at 538 and 483 cm⁻¹ [34]. At first glance, the presence of TiO₂, SiO₂, and GO-APTES cannot be observed from the FT-IR spectra, but it was observed that the ratio of the I_{1026}/I_{1100} bands does change for both types of samples: unexposed and exposed (Table 1), which could hint at structural modifications of the samples. Moreover, from Table 1 it can be observed that the samples' I_{1026}/I_{1100} ratio changes in each sample when comparing it to the blank samples. In the case of the unexposed samples the ratio was below 1, but in the case of the exposed samples it was above 1, indicating that the samples' 6-month exposure did affect their structure.



Fig. 7. FT-IR spectra of the unexposed and exposed (6 months) andesite samples.

Table 1. Ratio changes of the Si-O bands at 1026 and 1100 cm ⁻¹
in the unexposed and exposed samples

Sample	Unexposed	Exposed
	₁₀₂₆ / ₁₁₀₀	₁₀₂₆ / ₁₁₀₀
Andesite Blank	0.910	1.027
Andesite TiO ₂	0.928	1.058
Andesite TiO ₂ + GO-APTES	0.938	1.062
Andesite TiO ₂ + SiO ₂	0.920	1.042
Andesite TiO ₂ + SiO ₂ + GO-APTES	0.924	1.044

L.C. COTET, C. SALAGEAN, A. MIHIS, I. SZÉKELY, ZS. TOTH, L. BAIA, M. BAIA, G. OLTEANU, I. OLTEANU, V. DANCIU



Fig. 8. FT-IR spectra of the unexposed and exposed (6 months) mortar samples.

The building blocks of mortar are lime and an aggregate of sand mixed with water. The mortar samples consist of lime, calcite, and quartz. Concerning the FT-IR spectra of the unexposed and exposed mortar samples, for each sample, the following absorption bands were identified: O-H stretching vibrations at 3643 and 3446 cm⁻¹, which were attributed to the Ca(OH)₂ from mortar [35]; CO₃²⁻ and CO₃ stretching at 1795, 1456, 874 and 712 cm⁻¹, which are related to the calcite and carbonate in the sample [36–38]; Si-O-Si asymmetric, Si-O symmetric stretching, and O-Si-O rocking vibrations at 1081, 777, 721 cm⁻¹, respectively in the 500 - 400 cm⁻¹ region [39, 40].

Regarding the unexposed mortar samples, for all treated samples, a sharp band appeared at 1384 cm⁻¹, in the proximity of the CO₃ band; this can be linked to the presence of impurities on the sample's surface in the form of other ions, species, or even water. Most probably the band at 1384 cm⁻¹ is related to the carbonation of the samples, since it disappears from each sample after 6-months of exposure. Although the presence of other components like metal oxides or graphene oxide from the FT-IR spectra cannot be proven with certainty, it is visible that the intensity of the Si-O-Si bands at 1081 and 777 cm⁻¹ changes in the case of the treated samples—the Si-O-Si bands' intensity changes in both types of samples: unexposed and exposed, and is presented in Table 2. These changes could be caused by the presence of metal oxides or other components like graphene oxide on the samples' surface.

Sample	Unexposed	Exposed
	I ₇₇₇ / I ₁₀₈₁	₇₇₇ / ₁₀₈₁
Mortar Blank	0.449	0.309
Mortar TiO ₂	0.463	0.391
Mortar TiO ₂ + GO-APTES	0.450	0.394
Mortar TiO ₂ + SiO ₂	0.467	0.545
Mortar TiO ₂ + SiO ₂ + GO-APTES	0.457	0.516

 Table 2. Ratio changes of the Si-O-Si bands at 777 and 1081 cm⁻¹

 in the unexposed and exposed samples.

3.5. Raman spectroscopy measurements on andesite and mortar surface

As already mentioned, andesite is a volcanic rock with a mixed composition consisting in sodium-rich silicates such as plagioclase, pyroxene, and hornblende. The Raman spectra recorded from different zones of the andesite samples (lightgrey and dark-grey) are illustrated in Figures 9 and 10. As one can see the spectra are looking different and can be correlated to the specific structural features of the samples. Thus, in the Raman spectra recorded on light-grey zones the most intense bands are located in the 1000-1800 cm⁻¹ spectral region, where appear mainly the stretching vibrations in which Si and O atoms are involved, in structural units such as Q_1-Q_4 [41]. In the low wavenumber region of the spectra, between 110 and 700 cm⁻¹, there are a few low intense bands mainly attributed to bending vibrations of bonds in which Si, O and/Al atoms are involved. On the other hand, in the Raman spectra recorded on dark-grey zones the most intense bands are observed in the low wavenumber region. Moreover, as a consequence of the presence of more disordered structure, the elastically scattered light increased the background of the Raman spectra recorded from these zones. This assumption is confirmed by the attenuated intensity of the bands from the high wavenumber region ($<1500 \text{ cm}^{-1}$), where the stretching vibrations of more connected Si structural units appear. Besides the bands due to the bending vibrations of Si, O and/or Al containing bonds some bands due to hornblende vibrations [42], can be also noticed (around 670 cm⁻¹).

By comparing the spectra of the unexposed samples treated with different solutions a few differences can be observed. Thus, one can notice the presence of the band around 150 cm⁻¹ due to the TiO₆ vibration [43], mostly intense in the spectra of Andesite-S1 and Andesite-S3 samples. Moreover, one can also remark that in all spectra of the Andesite-S1 sample, recorded from light-grey and dark-grey

zones, the bands from the high wavenumber region are less intense as compared to the ones from the 120-700 cm⁻¹ spectral range. This behavior could be due to a reduced number of connected SiO₄ structural units as a consequence of the TiO₂ presence. No clear evidence of the bands given by the GO vibrations can be noticed in the spectra of Andesite-S2 and Andesite-S4 spectra.



Fig. 9. Raman spectra of the unexposed andesite samples.



Fig. 10. Raman spectra of the exposed (6 months) andesite samples.

When analyzing the spectra recorded from light-grey zones of exposed samples in comparison to the ones recorded from the unexposed samples one can see that the band around 150 cm⁻¹ due to the TiO_6 vibrations is more evident in all spectra of exposed samples and the intensity of the bands from the high wavenumber region slightly decreased. This behavior could indicate that the Ti containing structure

is more stable over the exposure period as compared to the Si containing structure. No important differences can be observed between the spectra recorded from dark-grey zones of the exposed and unexposed samples.



Fig. 11. Raman spectra of the unexposed and exposed (6 months) mortar samples.

As mentioned earlier mortar is a mix of sand, water, and a binding agent like cement, lime or plaster. The Raman spectra of the unexposed blank mortar sample present Raman bands at 160, 281, 410, 480, 507, 571, 712 and 1085 cm⁻¹. The sharp band at 1085 cm⁻¹ was attributed to the symmetric stretching mode of carbonate ions, the band at 712 cm⁻¹ corresponds to the in-plane bending vibrations of carbonate, respectively the bands at 281 and 160 cm⁻¹ were attributed to the rotational and translational lattice modes, which are specific for calcite and vaterite [44].

The presence of gypsum in the sample was confirmed by the bands at 410 cm⁻¹. The doublet at 480 and 507 cm⁻¹ was associated with the presence of plagioclase, these bands correspond to the stretching vibrations of the SiO₄ or AlO₄ tetrahedra, whereas the broad band at 571 cm⁻¹ was assigned to the Si-O stretching vibrations [45].

Comparing the unexposed blank mortar sample with the exposed one interesting change can be observed between the two samples' spectra. The intensity of the 1085 cm⁻¹ band decreased and the bands at 712, 507 and 480 cm⁻¹ disappeared, which can be explained by the fact that the sample's surface was covered with pollution. The bands below 300 cm⁻¹ also have disappeared, or shifted to lower wavenumbers, hinting that by exposing the mortar samples to the weather conditions structural changes will occur on the mortar surface. The exposed sample presented new bands at 143, 669, 926 and 953 cm⁻¹. The band at 143 cm⁻¹ was attributed to

the lattice vibrations of Ca-O polyhedra, at 669 cm⁻¹ to the Si-O-Si symmetric bending, respectively the bands at 926 and 953 cm⁻¹ were attributed to the asymmetric stretching of the SiO₄ tetrahedra [46].

The Raman spectra of the Mortar TiO_2 unexposed sample at first glance is similar with the Mortar Blank sample, but it is obvious that the bands at 1085 and 712 cm⁻¹ disappeared, and this was caused probably by the presence of TiO_2 on the samples' surface. The bands at 208, 410, and 638 cm⁻¹ correspond to the TiO_2 anatase phase [47, 48]. After exposing the sample for six months the corresponding TiO_2 anatase phase Raman bands were identified in the spectra at 152, 208, 515 and 638 cm⁻¹. Two other bands were also observed in the exposed sample's spectra at 464 and 1050 cm⁻¹, which were attributed to the silicate and calcite components from mortar.

Two intense Raman bands were observed in the unexposed Mortar $TiO_2+GO-APTES$ sample: at 208 and 464 cm⁻¹, from which the first is linked to the presence of TiO_2 , respectively the second to the presence of an increased number of O-Si-O bonds on the surface. The presence of TiO_2 was also proved by the less intense band at 396 cm⁻¹. After exposing the sample for six months almost identical Raman spectra was obtained for the sample, the most notable difference was that the intensity of the band at 464 cm⁻¹ has increased, respectively it became narrower. Although the corresponding D and G bands for graphene oxide were not observed in the Raman spectra, the very intense band at 464 cm⁻¹ could be caused by the presence of APTES on the sample's surface, since this compound is rich in Si-O-C₂H₅ bonds.

Regarding the Mortar TiO₂+SiO₂ sample, Raman bands corresponding to the TiO₂ anatase phase were observed at 154, 514 and 636 cm⁻¹. Two other bands with relatively small intensity were identified at 1050 and 1085 cm⁻¹, these bands correspond to the silicate and calcite components of mortar. Another band at 1339 cm⁻¹ and a shoulder at 1477 cm⁻¹ were observed in the Raman spectra, which are most probably linked to the presence of calcium hydroxide phosphate and calcium oxalate dihydrate. After the samples were exposed for 6 months the band at [49] 1339 cm⁻¹ and the shoulder at 1477 cm⁻¹ disappeared from the spectra, whereas the bands at 1050 and 1085 cm⁻¹, became more intense and narrower. Corresponding band to anatase TiO₂ were observed at 638, 517 and 154 cm⁻¹. SiO₂ presence on the sample surface was not evident from the Raman spectra.

Concerning the Mortar $TiO_2+SiO_2+GO-APTES$ sample Raman bands were identified at 130, 206, 262 and 464 cm⁻¹. The presence of TiO_2 was evidenced only by the band at 130 cm⁻¹, the band at 514 is masked by the intense band at 464 cm⁻¹, respectively the band at 636 cm⁻¹ was a very broad and low intensity shoulder. The bands at 206 and 262 were cm⁻¹ attributed to the presence of SiO₂ [50].

Although the sharp and intense band at 464 cm⁻¹ is generally attributed to SiO₂, in this context it is worth mentioning, that this band corresponds to the Si-O-Si/O-Si-O bridging vibrations [51], which could prove the presence of APTES. After exposing the sample for six months to the weather conditions, the same bands were observed as before (130, 206, 262 and 464 cm⁻¹), but in this case also the bands had higher intensity and were narrower. Another band specific for SiO₂ was observed at 355 cm⁻¹. After the exposure two modifications were observed in the Raman spectra: a doublet at 1309 and 1320 cm⁻¹, respectively a shoulder at 1591 cm⁻¹. The bands at 1309 and 1591 cm⁻¹ can be attributed to the D and G bands of the functionalized graphene oxide (GO-APTES) [52].

According to the Raman spectra of the unexposed and exposed samples we can draw the conclusion that blank mortar stability decreases after being exposed to the weather conditions for six months. However, by adding only three layers of TiO_2 , $TiO_2+GO-APTES$, TiO_2+SiO_2 or $TiO_2+SiO_2+GO-APTES$ colloidal solution, the stability of the mortar samples remains constant, or possibly it reaches even higher stability, leading to the conclusion that this method of applying colloidal solution on the samples' surface is a viable option.

CONCLUSIONS

A mixture of three components (TiO2, SiO2 and GO-APTES) was tested for consolidation of the surface of two sample types (i.e. andesite and mortar). Also, suspensions that contains TiO₂, TiO₂+GO-APTES, TiO₂+SiO₂ were investigated as blanks for three-components suspension. The unmodified and modified with different suspensions samples were investigated with microscopic techniques (optic and SEM), X-ray diffraction (XRD and EDX), FT-IR and Raman techniques before and after 6 months of ambient exposure.

After investigation was found that the stability of the three-components treated samples remains constant, or possibly it reaches in time even higher stability. This leading to the conclusion that the obtained suspension is a viable option in stone and mortar consolidation-restoration field.

ACKNOWLEDGMENTS

The authors acknowledge UBBTeMATIC-Art P_40_374 project for the financial support. L. B. would like to acknowledge the financial support provided by STAR-UBB Advanced Fellowship.

REFERENCES

- L. Dei and B. Salvadori, "Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay," *J. Cult. Herit.*, vol. 7, no. 2, pp. 110–115, 2006, doi: 10.1016/j.culher.2006.02.001.
- [2] A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results," *Chem. Rev.*, vol. 95, no. 3, pp. 735–758, 1995, doi: 10.1021/cr00035a013.
- [3] P. Munafò, G. B. Goffredo, and E. Quagliarini, "TiO2-based nanocoatings for preserving architectural stone surfaces: An overview," *Constr. Build. Mater.*, vol. 84, pp. 201–218, 2015, doi: 10.1016/j.conbuildmat.2015.02.083.
- [4] A. Sierra-Fernandez, L. S. Gomez-Villalba, M. E. Rabanal, and R. Fort, "New nanomaterials for applications in conservation and restoration of stony materials: A review," *Mater. Constr.*, vol. 67, no. 325, 2017, doi: 10.3989/mc.2017.07616.
- [5] R. Wang *et al.*, "Light-induced amphiphilic surfaces [4]," *Nature*, vol. 388, no. 6641, pp. 431–432, 1997, doi: 10.1038/41233.
- [6] A. Maury and N. de Belie, "State of the art of TiO2 containing cementitious materials: Self-cleaning properties," *Mater. Constr.*, vol. 60, no. 298, pp. 33–50, 2010, doi: 10.3989/mc.2010.48408.
- [7] J. Chen and C. sun Poon, "Photocatalytic construction and building materials: From fundamentals to applications," *Build. Environ.*, vol. 44, no. 9, pp. 1899–1906, 2009, doi: 10.1016/j.buildenv.2009.01.002.
- [8] M. Pelaez *et al.*, "A review on the visible light active titanium dioxide photocatalysts for environmental applications," *Appl. Catal. B Environ.*, vol. 125, pp. 331–349, 2012, doi: 10.1016/j.apcatb.2012.05.036.
- [9] O. Carp, C. L. Huisman, and A. Reller, "Photoinduced reactivity of titanium dioxide," *Prog. Solid State Chem.*, vol. 32, no. 1–2, pp. 33–177, 2004, doi: 10.1016/j.progsolidstchem.2004.08.001.
- [10] M. Batzill, "Fundamental aspects of surface engineering of transition metal oxide photocatalysts," *Energy Environ. Sci.*, vol. 4, no. 9, pp. 3275–3286, 2011, doi: 10.1039/c1ee01577j.
- [11] J. Schneider *et al.*, "Schneider et al. 2014 Understanding TiO 2 Photocatalysis Mechanisms and Materials(2).pdf," *Chem. Rev.*, vol. 114, no. 9, p. 9919–9986, 2014.
- [12] J. Chen, F. Qiu, W. Xu, S. Cao, and H. Zhu, "Recent progress in enhancing photocatalytic efficiency of TiO2-based materials," *Appl. Catal. A Gen.*, vol. 495, pp. 131–140, 2015, doi: 10.1016/j.apcata.2015.02.013.
- [13] X. Kang, S. Liu, Z. Dai, Y. He, X. Song, and Z. Tan, *Titanium dioxide: From engineering to applications*, vol. 9, no. 2. 2019.
- [14] N. Zhang, Y. Zhang, and Y. J. Xu, "Recent progress on graphene-based photocatalysts: Current status and future perspectives," *Nanoscale*, vol. 4, no. 19, pp. 5792–5813, 2012, doi: 10.1039/c2nr31480k.

- [15] S. Linley, Y. Liu, C. J. Ptacek, D. W. Blowes, and F. X. Gu, "Recyclable graphene oxidesupported titanium dioxide photocatalysts with tunable properties," ACS Appl. Mater. Interfaces, vol. 6, no. 7, pp. 4658–4668, 2014, doi: 10.1021/am4039272.
- [16] E. SOLANO BERRAL, "Sobre un caso de cervicitis gonocócia y gestación.," Medicamenta (Madr)., vol. 10, no. 215, p. 224, 1952.
- [17] J. Shen, B. Yan, M. Shi, H. Ma, N. Li, and M. Ye, "One step hydrothermal synthesis of TiO2-reduced graphene oxide sheets," J. Mater. Chem., vol. 21, no. 10, pp. 3415–3421, 2011, doi: 10.1039/c0jm03542d.
- [18] D. Feng *et al.*, "Portland cement paste modified by TiO2 nanoparticles: A microstructure perspective," *Ind. Eng. Chem. Res.*, vol. 52, no. 33, pp. 11575–11582, 2013, doi: 10.1021/ie4011595.
- [19] Z. Li, S. Ding, X. Yu, B. Han, and J. Ou, "Multifunctional cementitious composites modified with nano titanium dioxide: A review," *Compos. Part A Appl. Sci. Manuf.*, vol. 111, pp. 115–137, 2018, doi: 10.1016/j.compositesa.2018.05.019.
- [20] C. Mendoza, A. Valle, M. Castellote, A. Bahamonde, and M. Faraldos, "TiO2 and TiO2-SiO2 coated cement: Comparison of mechanic and photocatalytic properties," *Appl. Catal. B Environ.*, vol. 178, pp. 155–164, 2015, doi: 10.1016/j.apcatb.2014.09.079.
- [21] A. Naumann, I. Stephan, and M. Noll, "Material resistance of weathered wood-plastic composites against fungal decay," *Int. Biodeterior. Biodegrad.*, vol. 75, pp. 28–35, 2012, doi: 10.1016/j.ibiod.2012.08.004.
- [22] C. Kapridaki, L. Pinho, M. J. Mosquera, and P. Maravelaki-Kalaitzaki, "Producing photoactive, transparent and hydrophobic SiO2-crystalline TiO2 nanocomposites at ambient conditions with application as self-cleaning coatings," *Appl. Catal. B Environ.*, vol. 156–157, pp. 416–427, 2014, doi: 10.1016/j.apcatb.2014.03.042.
- [23] S. Khannyra, M. Luna, M. L. A. Gil, M. Addou, and M. J. Mosquera, "Self-cleaning durability assessment of TiO2/SiO2 photocatalysts coated concrete: Effect of indoor and outdoor conditions on the photocatalytic activity," *Build. Environ.*, vol. 211, p. 108743, 2022, doi: 10.1016/j.buildenv.2021.108743.
- [24] M. Zhang, L. Shi, S. Yuan, Y. Zhao, and J. Fang, "Synthesis and photocatalytic properties of highly stable and neutral TiO2/SiO2 hydrosol," J. Colloid Interface Sci., vol. 330, no. 1, pp. 113–118, 2009, doi: 10.1016/j.jcis.2008.10.038.
- [25] X. Li and J. He, "Synthesis of Raspberry-Like SiO 2 TiO 2 Nanoparticles toward Antire fl ective and Self-Cleaning Coatings," 2013.
- [26] R. Fateh, R. Dillert, and D. Bahnemann, "Preparation and characterization of transparent hydrophilic photocatalytic TiO2/SiO2 thin films on polycarbonate," *Langmuir*, vol. 29, no. 11, pp. 3730–3739, 2013, doi: 10.1021/la400191x.
- [27] M. C. Dudescu, I. Olteanu, L. C. Cotet, and V. Danciu, "APTES Functionalized Graphene Oxide for Silane-Based Mortar Performances," vol. 20, no. xx, pp. 1–9, 2020, doi: 10.1166/jnn.2020.18958.

L.C. COTET, C. SALAGEAN, A. MIHIS, I. SZÉKELY, ZS. TOTH, L. BAIA, M. BAIA, G. OLTEANU, I. OLTEANU, V. DANCIU

- [28] L. C. Cotet, K. Magyari, M. Todea, M. C. Dudescu, V. Danciu, and L. Baia, "Versatile selfassembled graphene oxide membranes obtained under ambient conditions by using a water-ethanol suspension," J. Mater. Chem. A, vol. 5, no. 5, pp. 2132–2142, 2017, doi: 10.1039/C6TA08898H.
- [29] D. C. Marcano *et al.*, "Improved synthesis of graphene oxide," ACS Nano, vol. 4, no. 8, pp. 4806–4814, 2010, doi: 10.1021/nn1006368.
- [30] M. Pavlovic, M. Dojcinovic, R. Prokic-Cvetkovic, L. Andric, Z. Ceganjac, and L. Trumbulovic, "Cavitation wear of basalt-based glass ceramic," *Materials (Basel).*, vol. 12, no. 9, 2019, doi: 10.3390/ma12091552.
- [31] A. T. Djowe, S. Laminsi, D. Njopwouo, E. Acayanka, and E. M. Gaigneaux, "Surface modification of smectite clay induced by non-thermal gliding arc plasma at atmospheric pressure," *Plasma Chem. Plasma Process.*, vol. 33, no. 4, pp. 707–723, 2013, doi: 10.1007/s11090-013-9454-8.
- [32] Y. Liu, F. Zeng, B. Sun, P. Jia, and I. T. Graham, "Structural characterizations of aluminosilicates in two types of fly ash samples from Shanxi Province, North China," *Minerals*, vol. 9, no. 6, pp. 1–16, 2019, doi: 10.3390/min9060358.
- [33] L. Y. Yu, Z. X. Huang, and M. X. Shi, "Synthesis and characterization of silica by sol-gel method," Adv. Mater. Res., vol. 1030–1032, pp. 189–192, 2014, doi: 10.4028/www.scientific.net/AMR.1030-1032.189.
- [34] J. T. Kloprogge, *Infrared and Raman Spectroscopies of Pillared Clays*, 1st ed., vol. 8. Elsevier Ltd., 2017.
- [35] A. Eisazadeh, K. A. Kassim, and H. Nur, "Solid-state NMR and FTIR studies of lime stabilized montmorillonitic and lateritic clays," *Appl. Clay Sci.*, vol. 67–68, pp. 5–10, 2012, doi: 10.1016/j.clay.2012.05.006.
- [36] R. Babilas, A. Bajorek, A. Radoń, and R. Nowosielski, "Corrosion study of resorbable Ca60Mg15Zn25 bulk metallic glasses in physiological fluids," *Prog. Nat. Sci. Mater. Int.*, vol. 27, no. 5, pp. 627–634, 2017, doi: 10.1016/j.pnsc.2017.08.011.
- [37] M. A. Legodi, D. De Waal, J. H. Potgieter, and S. S. Potgieter, "Technical note rapid determination of CaCo3 in mixtures utilising FT-IR spectroscopy," *Miner. Eng.*, vol. 14, no. 9, pp. 1107–1111, 2001, doi: 10.1016/S0892-6875(01)00116-9.
- [38] F. B. Reig, J. V. G. Adelantado, and M. C. M. Moya Moreno, "FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method. Application to geological samples," *Talanta*, vol. 58, no. 4, pp. 811–821, 2002, doi: 10.1016/S0039-9140(02)00372-7.
- [39] A. V. Oancea *et al.,* "Multi-analytical characterization of Cucuteni pottery," *J. Eur. Ceram. Soc.*, vol. 37, no. 15, pp. 5079–5098, 2017, doi: 10.1016/j.jeurceramsoc.2017.07.018.
- [40] B. J. Saikia, "Spectroscopic Estimation of Geometrical Structure Elucidation in Natural SiO₂ Crystal," J. Mater. Phys. Chem., vol. 2, no. 2, pp. 28–33, 2014, doi: 10.12691/jmpc-2-2-3.
- [41] J. J. Freeman, A. Wang, K. E. Kuebler, B. L. Jolliff, and L. A. Haskin, "Characterization of natural feldspars by raman spectroscopy for future planetary exploration," *Can. Mineral.*, vol. 46, no. 6, pp. 1477–1500, 2008, doi: 10.3749/canmin.46.6.1477.

- [42] A. I. Apopei, V. Diaconu, C. Muzeal, J. Neamţ, and A. Buzatu, "The composition and source of the raw material of two stone axes of Late Bronze Age from Neamţ County (Romania)-A Raman study," no. March, 2018, [Online]. Available: http://geology.uaic.ro/auig/.
- [43] Y. Zhang, C. K. Chan, J. F. Porter, and W. Guo, "Powders Prepared By Vapor Hydrolysis," vol. 13, no. 9, 1998.
- [44] F. C. Donnelly, F. Purcell-Milton, V. Framont, O. Cleary, P. W. Dunne, and Y. K. Gun'ko, "Synthesis of CaCO3 nano- and micro-particles by dry ice carbonation," *Chem. Commun.*, vol. 53, no. 49, pp. 6657–6660, 2017, doi: 10.1039/c7cc01420a.
- [45] J. R. Johnson, S. J. Jaret, T. D. Glotch, and M. Sims, "Raman and Infrared Microspectroscopy of Experimentally Shocked Basalts," J. Geophys. Res. Planets, vol. 125, no. 2, pp. 0–3, 2020, doi: 10.1029/2019JE006240.
- [46] S. Ortaboy *et al.*, "Effects of CO2 and temperature on the structure and chemistry of C-(A-)S-H investigated by Raman spectroscopy," *RSC Adv.*, vol. 7, no. 77, pp. 48925– 48933, 2017, doi: 10.1039/c7ra07266j.
- [47] R. Taziwa, E. Meyer, and N. Takata, "Structural and Raman Spectroscopic Characterization of C-TiO 2 Nanotubes Synthesized by a Template-Assisted Sol-Gel Technique," J. Nanosci. Nanotechnol. Res., vol. 1, no. 1, pp. 1–11, 2017, doi: 10.4229/EUPVSEC20172017-3DV.2.103.
- [48] R. Kaveh, M. Mokhtarifar, M. Bagherzadeh, A. Lucotti, M. V. Diamanti, and M. P. Pedeferri, "Magnetically recoverable TiO2/SiO2/γ-Fe2O3/rGO composite with significantly enhanced UV-visible light photocatalytic activity," *Molecules*, vol. 25, no. 13, 2020, doi: 10.3390/molecules25132996.
- [49] G. Marucci, A. Beeby, A. W. Parker, and C. E. Nicholson, "Raman spectroscopic library of medieval pigments collected with five different wavelengths for investigation of illuminated manuscripts," *Anal. Methods*, vol. 10, no. 10, pp. 1219–1236, 2018, doi: 10.1039/c8ay00016f.
- [50] O. F. S. Polymorphs, "DEPENDENCE SPECTRA a resolution," pp. 347–359, 1987.
- [51] P. Schmidt, L. Bellot-Gurlet, A. Slodczyk, and F. Fröhlich, "A hitherto unrecognised band in the Raman spectra of silica rocks: Influence of hydroxylated Si-O bonds (silanole) on the Raman moganite band in chalcedony and flint (SiO 2)," *Phys. Chem. Miner.*, vol. 39, no. 6, pp. 455–464, 2012, doi: 10.1007/s00269-012-0499-7.
- [52] M. Musielak, A. Gagor, B. Zawisza, E. Talik, and R. Sitko, "Graphene Oxide/Carbon Nanotube Membranes for Highly Efficient Removal of Metal Ions from Water," ACS Appl. Mater. Interfaces, vol. 11, no. 31, pp. 28582–28590, 2019, doi: 10.1021/acsami.9b11214.