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Present Status and Perspectives of Graphene and Graphene-related Materials in Cultural Heritage

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Cultural heritage faces recurring degradation processes and natural aging phenomena, demanding the envisioning of innovative preservation solutions inspired by cutting-edge scientific research. Over extended time frames, current preservation strategies often prove inadequate in preserving the different constituent materials of cultural assets, which are thus threatened by their inherent fragility and by the complex interactions with the surrounding environment. The distinctive properties of graphene and graphene-related materials (GRMs) now offer unexplored opportunities in the field of cultural heritage, addressing various forms of deterioration phenomena. This work critically analyzes early-stage literature on the use of graphene and GRMs. Strengths, weaknesses, and limitations in anti-corrosion, anti-fading, and consolidation properties of graphene and GRMs are thoroughly investigated, along with their possible applications in smart sensors to monitor the state of health of endangered artifacts. The aim is to elucidate how specific characteristics of graphene and GRMs can be applied to the conservation, diagnostics, and monitoring of artistic and archaeological assets. Future perspectives in the design of stable, long-lasting, and compatible graphene-based solutions for cultural heritage protection are highlighted, providing a detailed discussion on potentials and pitfalls.

1. Introduction

Since its discovery in 2004, graphene has been attracting the attention of the scientific community[1–8] due to its outstanding combination of physico-chemical properties. Graphene is a one-atom-thick material[9] that is exceptionally strong,[10] flexible,[11,12] thermally conductive,[13] impermeable to all gases,[14] and with a remarkable charge carrier mobility,[15] while absorbing only 2.3% of visible light.[16,17] These properties offer significant prospects for meeting various requirements in the preservation, conservation, and diagnostics of cultural heritage artifacts, which are inherently susceptible to damage, deterioration, or even failure when interacting with the surrounding environment for extended periods.

Artifacts, composed of stone, glass, metals, paper, inks, and dyes, constitute intricate systems characterized by significant chemical and structural heterogeneity. The long-term impact of factors like light,

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temperature, humidity, pollution, and biological microorganisms on these diverse materials asks for tailored solutions, which might be effectively provided by innovative materials. In the last decades, there has been growing interest in the potential of carbon-based nanomaterials as encouraging candidates to usher into the next generation of protective and consolidating materials for cultural heritage.[18–23] Within this realm, graphene and graphene-related materials (GRMs) have shown promise in addressing a range of issues (**Figure 1A**), including corrosion, UV-aging, and reversibility.[24–31] These issues are sometimes not fully addressed by current strategies,[32–35] or by conventional treatments.[36–41]

Over the last 19 years, extensive research on graphene and GRMs[42–48] has paved the way for their application in a wide range of fields, such as (opto)electronics, sensing, biomedicine, and energy storage.[49–57] This progress has catalyzed substantial growth in the industrial market for graphene, which has demonstrated capabilities for cost-effective mass production[58,59] Worldwide production of graphene and GRMs has surged from just a few tons/year in 2009 to several thousand tons/year in present times.[60,61] The commercial availability[60,62] at a relatively low cost of these materials opens up exciting possibilities in various fields with lower investments, such as cultural heritage.

In this review, we explore the opportunities and challenges associated with using graphene, graphene oxide (GO), reduced graphene oxide (rGO), and other GRMs in the preservation of historical, archaeological, and artistic objects. As numerous seminal works are indeed laying the foundation for innovative strategies with significant potential in the field of conservation and monitoring technologies, we critically assess the current state-of-the-art in this field, providing guidance for research design and optimization. We also address the challenges and prospects of such use, emphasizing the importance of a multi-disciplinary approach.

1.1. Current Approaches in the Conservation Field

The protection of cultural heritage assets from deterioration demands cutting-edge solutions from the fields of chemistry, material science, and engineering, as the technologies currently in use present limitations and drawbacks. Traditional restoration practices and methodologies encounter significant challenges, such as the need for frequent re-applications coupled with time-consuming procedures, and the use of harmful compounds or materials lacking physicochemical compatibility with the original artifacts.

Current conservation strategies rely on the use of several natural and synthetic materials such as polymers, waxes, and varnishes, scientifically developed in the 20th century for restoration applications. Natural and synthetic waxes are commonly employed for providing protection against external harmful agents, representing an important tool for restorers, particularly in view of their ease of application.[63,64] However, their effectiveness against corrosion is significantly limited, particularly in the case of metal artifacts in outdoor environments. Microcrystalline waxes represent another viable option, under both outdoor and indoor exposure conditions, but their long-term durability raises major concerns.[63] The addition of anti-corrosion compounds is,

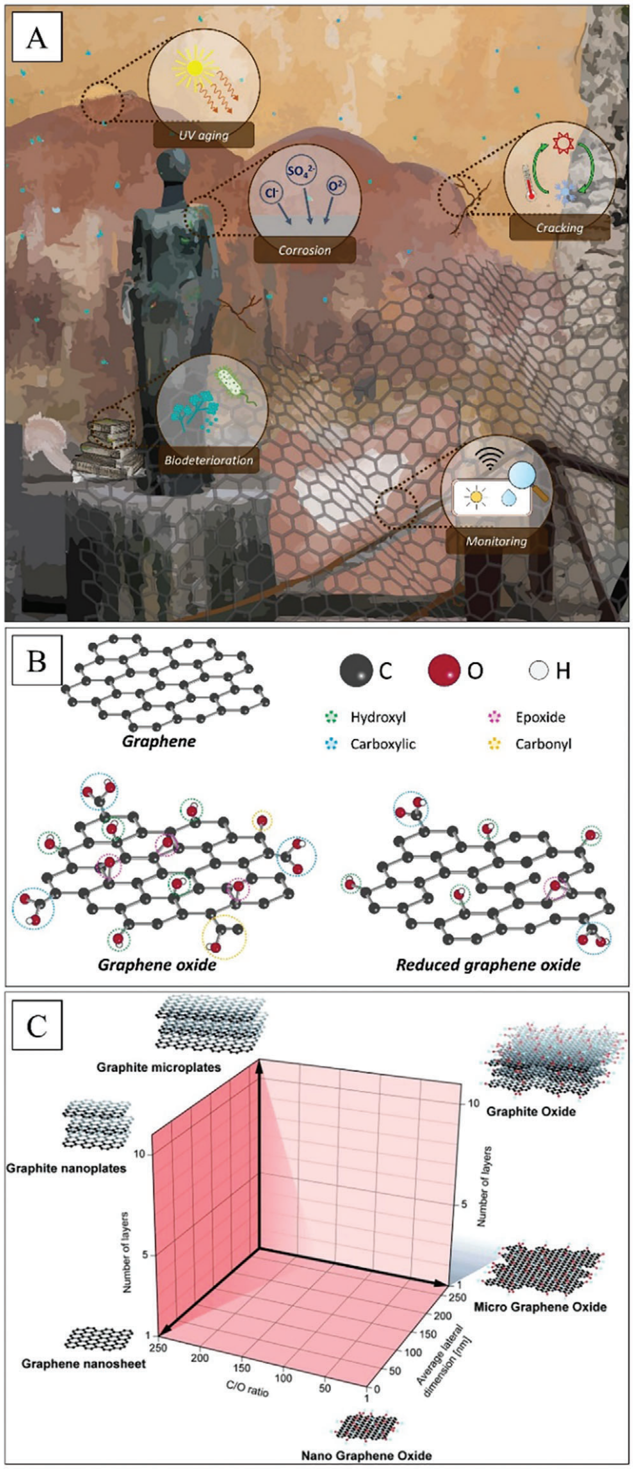

Figure 1. A) Illustration of the potential applications of graphene and graphene-related materials in cultural heritage; B) Chemical structure of graphene, graphene oxide, and reduced graphene oxide, with a focus on the different functional groups; C) Classification of the different graphene types according to the number of layers, the average lateral dimension, and the atomic carbon/oxygen ratio. Reproduced with permission.[42] Copyright 2014, Angewandte Chemie.

thus, often necessary to enhance their corrosion resistance.[65] The integration of benzotriazole, for example, is effective in hampering the corrosion of bronze artifacts by promoting the formation of a protective layer.[66] However, its proven toxicity[67] necessitates the development of alternative non-hazardous inhibitors.

Polymer-based varnishes and resins represent one of the most common approaches for surface protection and structural consolidation as they do not compromise the aesthetic and optical quality of artworks, exploiting properties like transparency, strong adhesion, and enhanced mechanical and chemical response.[41] However, they suffer from thermal degradation, photo-oxidation, and stress-induced cracking, which may compromise their appearance and physico-chemical properties.[68] Acrylic and vinylic polymers and co-polymers, in particular, are commonly used as coatings, consolidants, and adhesives.[63,69] Yet, they also present issues related to long-term stability and aging.[70] Epoxy resins are being widely employed to form homogeneous thin films over the surface of the objects to enhance their hydrophobicity.[71] However, their ability to form a strong hydrophobic barrier can impede natural water vapor permeability through porous structures.[72,73] The general susceptibility of polymeric materials to degradation and aging significantly impacts their use in the field since it leads to subsequent changes in the physicochemical properties of the artwork itself.[74] Furthermore, their removal requires restoration interventions that pose challenges to conservators, as they need to be performed in a controlled, gradual, and selective manner without affecting the original components. These difficulties have prompted the development of advanced formulations like gel-based matrices, containing active components. Polymer-based gel systems are designed to confine the cleaning fluids at the gel–artifact interface, where the fluids can safely swell or detach undesired layers. Therefore, thanks to this ability to deliver, in a highly controlled way, cleaning fluids, they allow safe cleaning interventions without the need for lengthy steps, thus making the operations time-effective and safer.[21,75]

Nanotechnology has emerged as a forefront player in developing innovative solutions for the restoration and conservation of cultural heritage over the past two decades. Considering that degradation processes initiate at the nano- and meso- scale of the surface and interfaces of artifacts, the use of materials such as nanoparticles, composite nanomaterials, and highly engineered nanosystems is ideal for addressing the deterioration mechanisms at their onset. Moreover, the use of nanoparticles and the control of their self-assembly offers great advantages and possibilities in the design of materials that closely match key features of the treated substrate such as porosity, achieving controlled penetration through the structure.[76] This strategy has demonstrated its effectiveness in the consolidation, cleaning, and protection of various artworks with diverse artistic and historical origins.[77]

An example of the successful application of nanomaterials in conservation is the use of calcium hydroxide nanoparticles, commonly known as nanolime. The use of these nanoparticles represents an alternative to conventional consolidation materials employed in the restoration of carbonate-based materials, overcoming the compatibility issue of synthetic polymers. Another fundamental class of nanomaterials largely adopted in stone consolidation is that of SiO_2 nanoparticles (also used in combination with $Ca(OH)_2$), which are employed to strengthen stone-based substrates or buildings that have been degraded by erosion and weathering.[78] Additionally, biodeterioration phenomena are successfully tackled with nanoparticles, such as ZnO and MgO, which have a proved inhibitory activity against the growth of specific fungal species by limiting their colonization activity.[79]

The characteristics of cultural heritage substrates could hinder the efficacy of treatments based on nanoparticles. This issue has been raised for the self-cleaning and anti-biofouling properties of TiO_2 nanoparticles on stone materials:[36] on highly porous and rough surfaces, a high amount of nanoparticles is necessary to achieve an elevated concentration of nanoparticles at the surface, but this potentially alters the aesthetic appearance of the artworks. 2D materials could represent a valid support material to trap the nanoparticles at the outer surface, limiting penetration within the bulk of the structure. Therefore, innovative solutions based on the synergy between nanoparticles and graphene, GRMs, and other 2D materials could represent a valid approach to overcome current limitations. The recent scientific developments could unlock a wide range of opportunities for developing innovative materials. As the scientific community delves into tailoring the properties of these emerging materials, the outlook for unprecedented applications in the realm of cultural heritage becomes increasingly promising.

1.2. Graphene and Graphene-Related Materials

Graphene is the first strictly 2D material to be isolated and experimentally studied. It is a single atomically thin layer of graphite, with carbon atoms arranged in a honeycomb lattice. Graphene was originally isolated via mechanical exfoliation of graphite,[8] a technique yielding flakes with sizes limited to tens of micrometers. Due to its unique band structure, single-layer graphene (SLG) offers a 97.78% light transmission in the visible region of the light spectrum, independently from the wavelength of the incident photon, and ≈30% in the UV region, effectively being transparent to the naked eye. Moreover, graphene was demonstrated to be impermeable even to really small molecules thanks to a combined effect of the closed-spaced carbon atoms and high electron-density.[80] Nowadays, the concept of graphene is also extended up to a few layers (< 10) of vertically stacked single layers.[2] GRMs, such as graphene quantum dots (GQDs),[81,82] GO[83,84] or rGO,[85] have been synthesized as well (Figure 1B,C).[86] These materials possess different properties, depending on the crystallinity, the variation in size and geometry, and the density and type of defects, which are in turn linked to the production method.

The main techniques for the production and processing of graphene and GRMs can be divided into bottom-up approaches, where the fabrication stems from individual components, and top-down approaches, where single carbon layers are obtained from the bulk material.[86] An example of a top-down approach is liquid phase-exfoliation (LPE),[87] which produces graphene flakes dispersed in solution (**Figure 2A**). Instead, bottom-up techniques, such as chemical vapor deposition (CVD) (Figure 2B), provide high-quality large-area samples with good thickness control and typically high crystallinity, whose lateral size can extend up to several tens of square meters.[88,89] These two approaches will be discussed in the next section.

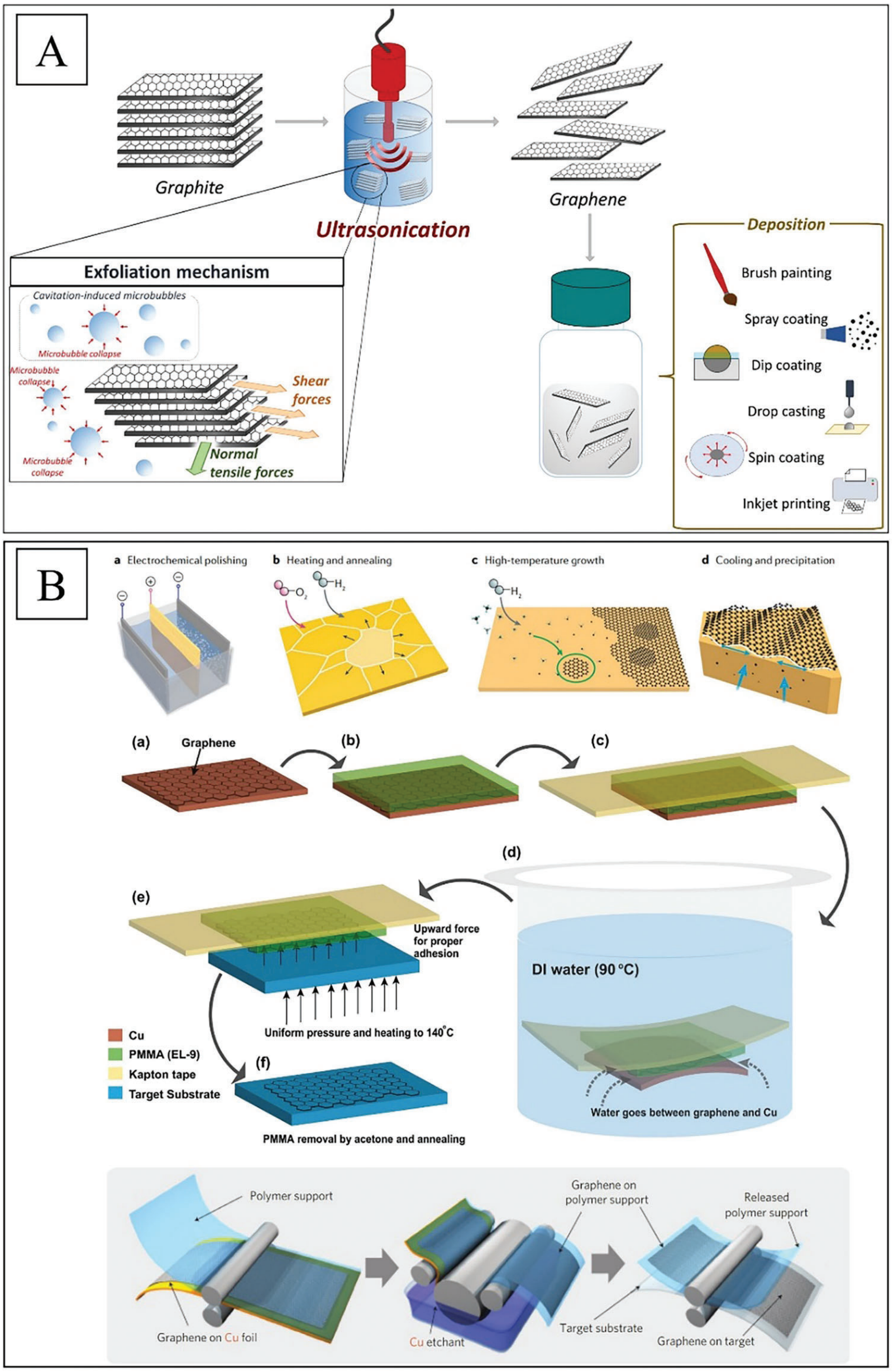

Figure 2. A) Liquid phase exfoliation of graphene-related materials and related deposition methods. In the inset: schematic representation of the exfoliation mechanism used for the top-down production protocols; B) Principle of chemical vapor deposition growth of graphene on Cu and examples of transfer mechanisms: wet transfer by delamination, and semi-dry roll-to-roll transfer. Reproduced and adapted with permission.[90] Copyright 2021, Nat Rev Methods Primers. Reproduced with permission.[91] Copyright 2014, Sci Rep. Reproduced and adapted with permission.[88] Copyright 2010, Nature Nanotech.

1.2.1. Graphene Production Methods

Liquid-phase exfoliation of graphite is the simplest among the top-down approaches and typically involves three steps: 1) the dispersion of graphite powder in an adequate solvent, 2) its exfoliation (usually involving ultrasonication), and 3) the purification.[92,93] Advantages of LPE are versatility, ease of scalability (depending on the exfoliation method), and cost-effectiveness.[94] Conversely, it is challenging to obtain precise control over size and thickness during the exfoliation.[95,96] The liquid dispersion of graphene layers represents an ideal platform for producing films or coatings on rigid and flexible substrates. Methods such as inkjet printing,[57] drop casting[97] and dip casting,[98] spin coating,[99] and spray coating[100] can be employed depending on the needs of the substrate and the final purpose of the formulation.

On the other hand, in a CVD process graphene synthesis takes place starting from gaseous precursors, thanks to the interaction with a suitable substrate where the chemical reaction occurs, leading to graphene formation.[101–104] An important aspect regarding CVD graphene is its adherence to the underlying substrates: this takes place thanks to the nature of van der Waals bonds, which are weak enough to allow easy mechanical removal from the growth substrate and yet strong enough to allow adhesion to the target.[105] This characteristic is exploited to transfer CVD-grown graphene films onto the materials of interest since the high temperatures required in CVD typically do not allow direct production of graphene on the chosen object. Transfer methods can be summarized in terms of wet, semi-dry, and dry transfer techniques (Figure 2B), depending on the amount and type of chemicals, as well as the physico-chemical processes, used to implement the transfer.[106,107]

In cultural heritage, commercial graphene and GRMs dispersions produced by LPE protocols are typically preferred due to their versatility and ease of application on diverse substrates. CVD graphene is however ideal for coating flat objects and can cover large areas while guaranteeing high transparency. Nevertheless, the presence of grain boundaries and inherent difficulties with graphene transfer may pose issues, as will be discussed later.

1.2.2. Graphene Oxide and Reduced Graphene Oxide Production Methods

GO consists of graphene-like sheets that contain oxidized groups that impart hydrophilicity, such as hydroxyls, epoxides, and carboxylic groups.[108] The synthesis of GO is achieved by the oxidation of graphite and the subsequent exfoliation into GO flakes, usually through the LPE method. The most common method for graphite oxidation[96] is the Hummers' method,[109] which consists of refluxing graphite in the presence of a strong oxidizer in acidic solvents. One of the main advantages of GO is its ease of functionalization, which can take place directly during the first stage of the process, or after the synthesis is complete.[110]

Parallelly, rGO is the reduced form of GO, in which oxygen functional groups are removed via chemical, thermal, or electrochemical reduction.[96] Besides these processes, rGO can also be exfoliated by means of LPE, starting from pristine graphite oxide as a precursor with the subsequent addition of different oxidation and reduction agents.[111]

Electronic and optical properties are dependent on the presence of defects, which are produced during the oxidation and reduction processes.[112,113] Compared to graphene, electron mobility, electrical conductivity, and thermal conductivity decrease in GO, but can be increased in rGO.[112,114] GO and rGO can attain almost full transparency as a single layer, but they can reach almost full absorption in the visible spectrum if the optimal conditions are not met.[115]

In the domain of cultural heritage, GO and rGO have been mostly used for applications on stone-based substrates, as protective coatings and reinforcing additives. Their hydrophilicity facilitates the dispersion in the water-based and alcohol-based solvents generally employed for cultural heritage coatings and favors the interaction with the treated materials. Attention has also been dedicated to the use of these GRMs against biodeterioration phenomena in stone-based artifacts and wood.

2. Applications in Cultural Heritage

2.1. Painted Artworks

2.1.1. Graphene Protection Against Color Fading

Kotsidi et al. leveraged the possibility of obtaining large and high-quality graphene sheets (30 inches graphene)[88] via CVD on flexible substrates and exploiting them as a protective coating for artworks.[25,26] The authors reported that CVD graphene films of sizes up to 30 × 30 cm^2 can be transferred with a tailored roll-to-roll approach on paper, cardboard, and canvas in order to block UV light, oxygen, moisture, and corrosive agents. The ability to act as a superior barrier against external agents was tested by observing the color fading. Indeed, single-, bi-, and tri- layers of pure graphene veils proved to be highly efficient, with a protection factor of >70% in the case of tri-layers (**Figure 3A**). The higher protection in the tri-layer case was associated with a gradual darkening of the covered surfaces (as each graphene layer absorbs 2.3% of visible light), but in all cases, graphene performed better than commercially available products for the prevention of color fading.[25] The strategy adopted for the transfer process played a key role: the use of pressure-sensitive adhesive film enabled graphene wetting on the final substrate and maximized the contact area and the van der Waals interactions. Moreover, the low adhesion between the polymer and graphene, compared with the better adhesion between graphene and the destination surface, facilitated the transfer, which could be carried out at mild pressure and temperature conditions, without the use of surface modifiers and adhesives. This experiment highlights the need for a full understanding of the physico-chemical properties of the surface of the artwork in order to tailor the graphene transfer process. The Raman-active defect-sensitive graphene D peak was used as a measure of the transfer-induced damage, proving that the transfer was optimal on glossy paper and cardboard. On canvas, the process led to higher defect density due to the roughness of the substrate, posing the question of the applicability of this approach on artworks with highly inhomogeneous surfaces.

Regarding the protection mechanisms of graphene, it is necessary to separately evaluate the aging process of the single

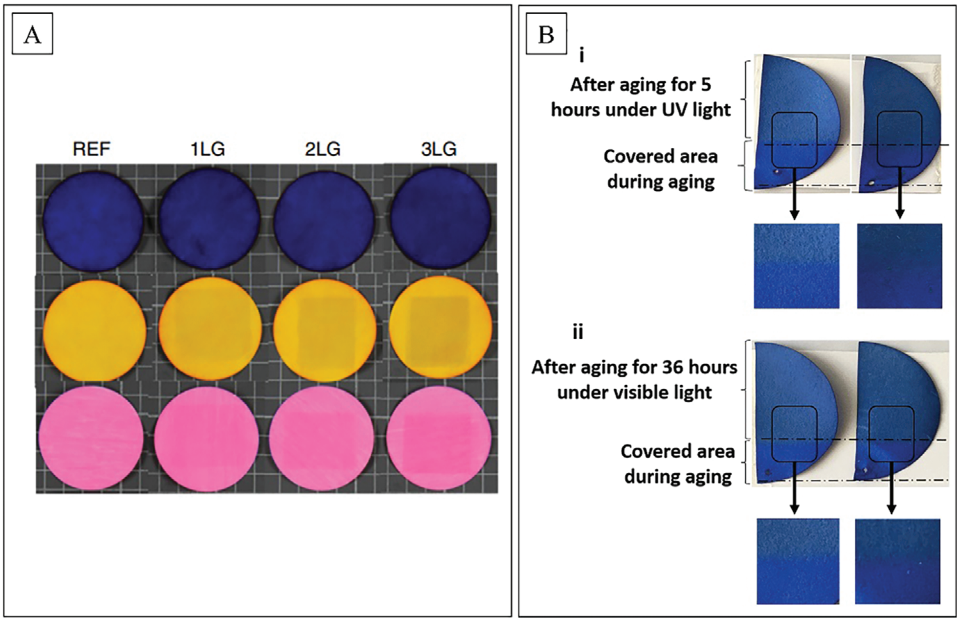

Figure 3. A) Images of painted mock-ups coated with graphene veils (mono-, bi-, or tri- layer). Reproduced with permission.[25] Copyright 2021, Nat. Nanotechnol. B) Images of painted mock-ups coated with graphene nanoplatelets after accelerated aging under UV radiation and under visible light. Reproduced and adapted with permission.[116] Copyright 2023, Nanoscale.

components. Commonly, paints are composed of a coloring agent, a binder (e.g., vegetable oil), and a solvent, and the three components are subjected to different kinds of degradation. Oils typically degrade due to photooxidation and photolysis of their polyunsaturated fatty acid carbon chains,[117] which cause yellowing of the color and chalking/embrittlement of the texture; instead, pigments and dyes are subjected to the action of free radicals formed due to both oxygen exposure and UV light, which fade the pigment color and bring further damage to the surrounding materials.[118] After proving the feasibility of the transfer and the quality achieved, Kotsidi et al. demonstrated the underlying mechanism of protection.[25] A dye containing an azo group, subjected to photolytic degradation (involving oxygen or singlet oxygen species generated by UV light) was used for this purpose. Indeed, the ability of graphene to absorb UV light and its impermeability to oxygen, volatile organic compounds, and water molecules are the key properties that impart superior protective abilities to graphene coatings.[25,26] However, these properties are strongly hampered by the presence of defects (i.e., wrinkles, gaps, and tears) that break the barrier and open a wound in the protective film. To overcome this issue, the stacking of additional layers strengthens the barrier effect, as subsequent layers cover any discontinuity present on the underlying graphene layer. This has strong consequences on the color difference index (ΔE), as the application of an increasing number of graphene layers leads to a substantial increase in the absorbance in the visible range. The value of 2.3% absorption of incident visible light from a single graphene layer significantly increases due to the random stacking of the hexagonal lattices of the upper and lower layers. This issue requires major consideration, together with the design of experiments, in which the role of defects is addressed in detail. However, it is important to highlight that the ΔE values for graphene are substantially lower than those measured on the same set of samples covered with commercial products based on the acrylic polymers commonly employed for the prevention of color fading. Furthermore, these polymeric materials pose several issues in the subsequent steps as they often need to be removed from the artwork surface.

In parallel, innovative solutions achieved by leveraging synergistic materials and approaches shall be developed. Kotsidi et al. also proved that graphene further imparts hydrophobicity to the substrate, an important property for the protection of artworks, and prevents the penetration of oils on porous substrates.[25] These properties could play a key role in conservation but require extensive research and studies on the long-term performance.

Another important property of the newly developed class of coatings that was also tested is reversibility. Since the interaction between graphene and the surface consists of weak van der Waals bonds, the authors report that it is possible to remove the film simply by employing a soft rubber eraser, through which a mechanical action is applied on the treated surface. However, the removal was performed immediately after the application, and further studies are needed to evaluate the effects of coating aging on reversibility.

Additionally, Kotsidi et al. demonstrated that the use of graphene and GRMs as additives in inks and paints hinders fading effects with a protection factor reaching ≈40% (Figure 3B).[116] The authors identified different mechanisms of action for the different types of graphene adopted. Graphene nanoplatelets act thanks to the synergy between two main actions: preventing oxidation due to the absorption of the radiation in the UV range and scavenging free radicals, such as $OH^{\bullet}$. On the other hand, the activity of GO is limited to its capability of absorbing UV light, whilst providing a physical barrier to further penetration and diffusion of oxidants within the matrix. Indeed, GO does not show high activity as a hydrogen donor.

However, the authors discovered that GO can be reduced in water by UV light, and this in situ chemical modification leads to an increase of graphene-like structures and, hence, antioxidant capabilities, leading to higher protection for a longer exposure time. Interestingly, GRMs were also proven to add important features to the paints, such as elasticity (thanks to the addition of graphene nanoplatelets) and electrical conductivity (due to the presence of functional groups on GO) at concentrations as low as 0.1%. This important work proves that careful choice of graphene types is necessary to achieve specific features, and that multifunctionalities can be obtained by taking advantage of graphene-related properties.

2.1.2. Composite and Hybrid Materials for Surface Protection and Consolidation

As previously discussed for canvas, wall paintings are also threatened by UV damage and oxidation, major factors affecting several critical components such as pigments and binders. GRMs and their composites can counteract these deterioration phenomena thanks to the absorption of dangerous radiation, whilst consolidating the fragile substrates beneath the pigments, subject to flaking, hollowing, and cracks.[119–123] The combination of GRMs and materials already in use for consolidation purposes in the cultural heritage field could overcome the limitations of current approaches, leveraging on the synergy between the different properties of the components.[124–126] Given the opportunities offered by this synergistic strategy, Zhu et al. proposed a nanohybrid material based on $Ca(OH)_2$ and GQDs, synthesized by following a facile aqueous method that produces uniform, small, and less aggregated materials.[124] The thickness of the GQDs was in the order of 1–2 nm, which corresponds to a few layers of graphene. Upon interaction with $Ca(OH)_2$, the quantum dots formed clusters on the surface of the nanoparticles (**Figure 4A**).

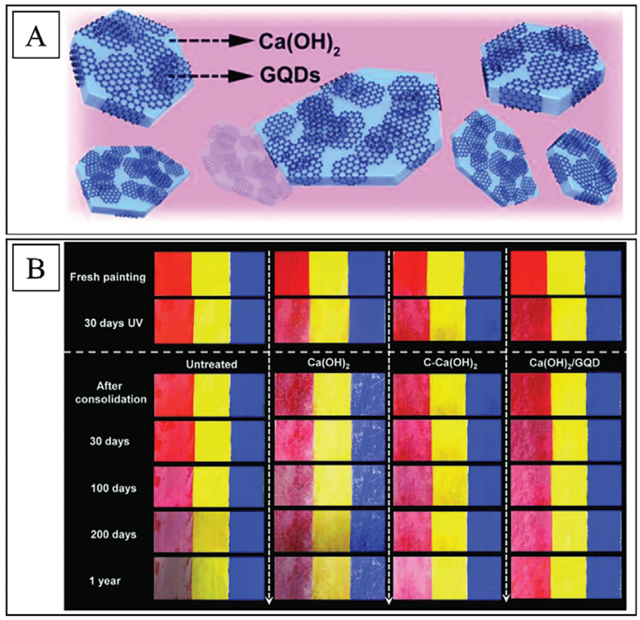

Figure 4. A) Schematic illustration of the arrangement of graphene quantum dots on the surface of $Ca(OH)_2$ nanoparticles. Reproduced with permission.[124] Copyright 2018, Adv. Funct. Mater. B) Color change (compared to untreated samples) of the pigments on surfaces consolidated with as-prepared, commercial, and graphene quantum dots-stabilized $Ca(OH)_2$ nanoparticles; images acquired at different drying times (top) and at different aging times (bottom).[124] Copyright 2018, Adv. Funct. Mater.

Their size varied strongly compared to the pristine samples, presumably due to the presence of the GQDs which may play the role of surfactants, preventing the growth of the $Ca(OH)_2$ crystals. Application of the nanohybrid formulation onto simulated wall paintings was obtained by brushing until the painting surface could not be any further infiltrated, followed by a carbonation step at controlled relative humidity and temperature. The flexural strength was reported to be significantly increased after applying the nanohybrid materials, as well as the bonding strength, which was evaluated by measuring the sample weight loss. The improved performance in terms of flexural and bonding strength was attributed to the high degree of carbonation process, transforming completely $Ca(OH)_2$ to $CaCO_3$ in the stable calcite phase. The authors further reported an anti-UV absorption ability, as well as an enhancement in penetration depth, attributed to the smaller particle size and higher stability of the nanohybrids. Lastly, the surface color change was evaluated upon the application of the nanohybrids onto the surfaces of wall paintings and reported to be low at different aging times. In particular, the gradual fading of the red, blue, and yellow pigments after short-term aging (several days) and relatively long-term (up to 1 year) was lower for the nanohybrids, when compared with the effect of the other formulations (Figure 4B). This work proves how GQDs have multiple roles: on the one hand, they absorb damaging radiation whilst, on the other hand, they provide stability to the $Ca(OH)_2$ nanoparticles, limiting their growth and, thus, favoring the carbonation process. Furthermore, the authors proved that the nanohybrids show superior efficiency compared to commercial $Ca(OH)_2$ materials: those based on $Ca(OH)_2$ and GQDs can penetrate deeper into the substrates, providing better consolidation.

Similarly, in another report, a nanocomposite material based on polyacrylic acid-functionalized graphene integrated with nano-$Ca(OH)_2$ was proposed for the reinforcement of murals.[125] Simulated wall painting samples were painted with cinnabar, ultramarine, yellow ochre, and malachite pigments after carbonation was reached in ambient room conditions. The nanocomposite formulation, dissolved in ethanol, was brushed on the surface of the mural specimens, which were subsequently placed into a humidity chamber to allow carbonation. The authors report the absence of any significant color changes upon the application of the coating as well as an improvement in bonding strength. The improvement in the consolidation performance was also partially attributed to the ability of graphene to capture and store carbon dioxide and to the high specific surface of the nanocomposites, as reported elsewhere.[124]

Another approach to the protection and consolidation of ancient wall paintings relates to the formulation of a composite coating based on the combination of GO and a widely used fluoropolymer resin. Commercial GO was modified to form aqueous solutions at different concentrations.[127] The formulations were applied onto rectangular boards which consisted of wood as support material, and pigmented mortar to simulate the second and third layers of the ancient paintings. The authors investigated the color change of the samples in response to the application of GO. For the formulations that contained only low concentrations, the aesthetic alterations of the surfaces were reported to be minimal. On the contrary, for relatively high concentrations, the colors became darker. It needs to be pointed out, though, that the colors tested in this work were vermilion, ultramarine, and emerald-green (i.e., darker colors than the ones in the majority of reports, for which, presumably, color alterations are more difficult to be discerned in comparison to brighter/lighter colors). The mechanical response of the coated samples was also evaluated by measuring the hardness and shear strength, but these properties were found to only be marginally enhanced, while the presence of the resin rendered the formulation unremovable from the substrate. Finally, the authors compared the film containing GO with two commercial products, FEVE and Paraloid B72. The samples treated with the formulation containing GO showed higher resistance to salts and better UV light shielding performance, leading to improved resistance to aging.

2.2. Natural and Artificial Stone-Based Materials

2.2.1. Environmental Climatic Damage

Cultural heritage features a wide variety of stone-based materials, both natural and man-made, which may suffer from deterioration due to physical and chemical weathering, biodeterioration, and anthropic deterioration (e.g., pollution, vandalism, climate change).[128–130]

The prolonged exposure of monuments made of sedimentary stones (e.g., limestone and dolomite) to weathering and harsh environmental conditions, like intense rainfall and extreme temperature changes, brings about tremendous consequences. To tackle this problem, a controlled application of aqueous GO coatings has been proposed to shield these vulnerable surfaces. In the report authored by Gonzàlez-Campelo et al.,[131] LPE-produced GO was obtained in the form of an additive-free aqueous colloidal suspension, which was easily and efficiently applied by airbrushing on dolomitic stone specimens of varying sizes, high coherence, and low porosity. The samples were subjected to artificial thermal changes and rainfall, to simulate 20 years of weathering. Protection of the dolomite stone against rain-induced wear was achieved after applying the suspension four times over the surfaces; the effectiveness of the formulation points to a strong binding at the interface of the two distinct materials. Additionally, an improvement of the mechanical properties, specifically of the compression stress was observed, while also highlighting the absence of any alteration of the aesthetics of the original surface since only a minimal chromatic variation could be detected by the naked eye. Lastly, the main challenge was related to the slight darkening of the GO coating after aging, attributed presumably to a spontaneous GO reduction upon prolonged exposure to visible light. The authors further expanded their work toward the evaluation of the performance of GO as a protective coating for dolostone surfaces against more harsh environmental conditions and prolonged timescales. Indeed, GO demonstrated a protective response against surface erosion attributed to acid rain and extreme thermal changes, yet the high heterogeneity of the material itself must account for the variation in responses.[132,133] On the other hand, issues about durability on more extended timescales require further investigation. It should be stressed that sedimentary stones belong to a family of materials that vary strongly in porosity, chemical composition, grain structure, and therefore mechanical and structural integrity and durability. The subsequent decay of such materials is, thus, dependent on multi-scale parameters that need to be thoroughly investigated.

Other types of climatic damage are the recrystallization of compounds in the pores and the dissolution of the compounds constituting the substrate itself, which are typically induced by variations in humidity and temperature (freeze-thaw cycles). These dissolution-recrystallization phenomena can cause mechanical stress in the stone, leading to cracking and even detachment. Furthermore, chemical weathering erodes the stone since acidic pollutants, dissolved in rain, react with the stone constituents, and form soluble compounds. Along with oxidation and hydration, these mechanisms affect the structural integrity of the substrate.[128] These deterioration phenomena might possibly be limited by the application of graphene or GO, thanks to their gas impermeability, which facilitates the streaming away of rainwater down the stone surface.

The efficacy of GO in terms of concrete surface protection has also been evaluated by varying the GO content at different stages of hardening and aging.[134] Encouraging results were obtained after submersion and brushing on freshly prepared concrete (one day of hardening), and a linear relationship between the content of GO and the consequent protection was established. It was also reported that the use of GO for the surface treatment of concrete limits water penetration and capillary water adsorption while improving the resistance of the treated concrete to freeze and thaw cycles.[135]

2.2.2. Biodeterioration

Besides being susceptible to climatic weathering, such as high humidity and heavy rain, historical buildings made of stone-based materials further suffer from biodeterioration and subsequent aesthetical damage.

GRMs represent interesting candidates as antimicrobial agents since their antimicrobial activity has been associated with their ability to provoke damage to bacteria via the combination of physical and chemical interactions.[136] This unique mechanism of action could overcome or delay the ability of microbial cells to develop resistance, a major issue in the effort to produce antimicrobial materials and substances. Several reports suggest that only certain types of GRMs have antimicrobial ability. Indeed, the majority of studies report that GO is the most effective thanks to the ability to damage the microbial cells with mechanical interaction of sharp edges as well as to generate reactive oxygen species.[137]

Others found that rGO in the form of nanowalls was the most effective due to the higher hydrophobicity, sharp edges, charge transfer, and its interaction with a hydrophobic layer of lipid in the microbial cell surface. Since the physico-chemical interaction of GRMs with microbial cells is key to exhibiting antimicrobial activity, GRMs in solution apparently have a higher ability to interact with free-floating microbial cells, thus leading to strong antimicrobial behavior.[138] In the case of coatings and antimicrobial surfaces, GRMs exposed on the surfaces should either prevent bacterial attachment, inhibit microbial growth or damage the microbial cells. Therefore, it is key to engineer the surfaces to present exposed GRMs with adequate roughness, density, and distribution, so as to maintain the antimicrobial behavior observed in solutions.[136]

Considering the ability of GRMs to fight microbial growth, several studies have focused their attention on applying these features to prevent biodeterioration in cultural heritage. However, the field is still in its infancy, and there are contradictory results. A report has focused on the properties of GO in combination with other nanomaterials to block biodeterioration in mortars. Indeed, the synergistic effect of GO and Ag nanoparticles or ZnO nanoparticles and their antibacterial properties have been investigated. Prodan et al. report that GO itself presents antibacterial properties since it can generate reactive oxygen species and physically penetrate membranes with its sharp edges.[139] However, in a later report, the test of GO against three bacterial strains showed no bacterial inhibition.[140] Despite these contradictory results, the synergy with nanoparticles characterized by antibacterial properties has been proven to enhance and strengthen its action, and a satisfactory antibacterial effect was described for GO mixed with Ag and ZnO, while also combined with fly ash and TiO_2, respectively. Satisfying results were also reported for nano-additives obtained by combining graphene, cadmium sulfide, and diatomaceous earth. The self-cleaning action of these additives in mortar samples was evaluated through the monitoring of microalgae biofilm degradation and growth inhibition. The authors report that the presence of graphene provides the formulation with biocide properties both in the presence and absence of ultraviolet radiation and suggest that this could be due to the onset of oxidative stress in microalgae.[141]

To address the alteration of stone surfaces upon biodeterioration effects, the literature also reports the combined use of graphene with metal and metal oxide nanoparticles, to formulate nanostructures with antimicrobial properties.[141] Aqueous colloidal suspensions based on ZnO nanorods with controlled shape and density, decorated onto multilayer graphene nanoplatelets, have been tested to overcome the limitations of single-component formulations.[142] The effect of these hybrid nanostructures against strains of Gram-positive *Staphylococcus aureus* and Gram-negative *Pseudomonas aeruginosa*, two deteriorative bacteria commonly found in wall paintings, was evaluated in terms of viability in both suspensions and solid substrates. In the case of solid surfaces, antimicrobial tests were performed on plywood samples. The suspension was drop-cast onto the surfaces and let air-dry. Then, after UV-sterilization, the bacteria suspensions were spotted on the surfaces. As reported, bacterial survival was significantly inhibited, due to a severe mechanical interaction with the nanorods, which caused the perforation of the cell wall of the organism (**Figure 5**A).

The role of the graphene nanoplatelets is to promote the growth of the rods in a specific orientation (vertical with respect to the substrate), achieving a needle-like configuration. Therefore, their penetration through the cell membrane is favored, leading to higher efficacy in terms of bacterial surface damage. Further, in view of the importance of maintaining the aesthetics of the original surfaces, it is highlighted that the grey coloration of graphene is mitigated by the whitening effect of ZnO. The aqueous suspensions were also airbrushed onto Noto stone, Carrara marble, and yellow brick specimens until full coverage was ensured, to evaluate the effect of porosity and pore size.[144] The uneven distribution of the nanoparticle formulation on the surface of stone samples with high porosity and diverse pore size resulted in a slight reduction of the antibiofilm effect, while for samples of lower porosity, the distribution was more uniform. The role of graphene within this formulation is not primary in terms of antibacterial properties, yet its presence promotes a favorable configuration for the structure to exert the necessary forces for cell wall damage to be achieved. Disruption of the cell membrane for model bacteria like *E. coli*, upon direct contact with graphene nanosheets is well established in the literature,[143] while the antimicrobial properties of the different types of graphene have attracted immense attention.[145–150] The antimicrobial mechanism of the different GRMs is achieved via a three-step process: 1) cell deposition on the graphene-based hybrids, 2) exertion of stress on the membrane due to direct contact with the sharp nanosheets, and 3) oxidative stress. Evidently, GRMs with tailored and optimized physicochemical properties (e.g., size, solubility, and conductivity) and a particular density of functional groups may well mediate such membrane and oxidative stress for bacterial cytotoxicity. This, of course, requires direct contact between the cells and the nanosheets, as well as an optimal dispersion state with individual nanosheets of small size (Figure 5B).

Stone-based materials may also be compromised in terms of mechanical strength and durability due to the presence and growth of plant species such as moss that contribute to pitting and erosion phenomena. To control moss colonization on weathered sandstone, the use of GRMs within a complex matrix has been proposed and evaluated. A formulation composed of CuO nanoparticles anchored on GO sheets was mixed with an inorganic magnesium-based consolidant and was applied by brushing on actual moss-covered samples collected from a cultural heritage site.[151] The capability of the consolidant to inactivate moss spores was evaluated by monitoring their survival ratio. Consolidation of the substrate before and after moss contamination was investigated, to estimate the ability to inactivate existing moss, as well as to prevent new colonization. The survival ratio of the moss spores was sharply reduced, as the consolidant effectively inactivated moss spores and already-grown moss (**Figure 6**).

However, this formulation raises issues about the mechanical response of the substrate in terms of compressive strength and surface hardness, which are compromised in comparison with samples treated only with consolidant. The pristine consolidant significantly improves both properties, while the composite consolidant exhibits a reduced, but still measurable enhancement. Further, discoloration of the surface of the specimens has been reported upon the application of the formulations. It is evident that the consolidation effect is attributed to the presence of the inorganic phase in this formulation, while the role of GO is limited to the improvement of the binding force between the CuO nanoparticles and the stone matrix material. Considering this preliminary report, it emerges that GO constitutes a good candidate as a filler to serve different purposes in multi-component formulations in view of its available functional groups.

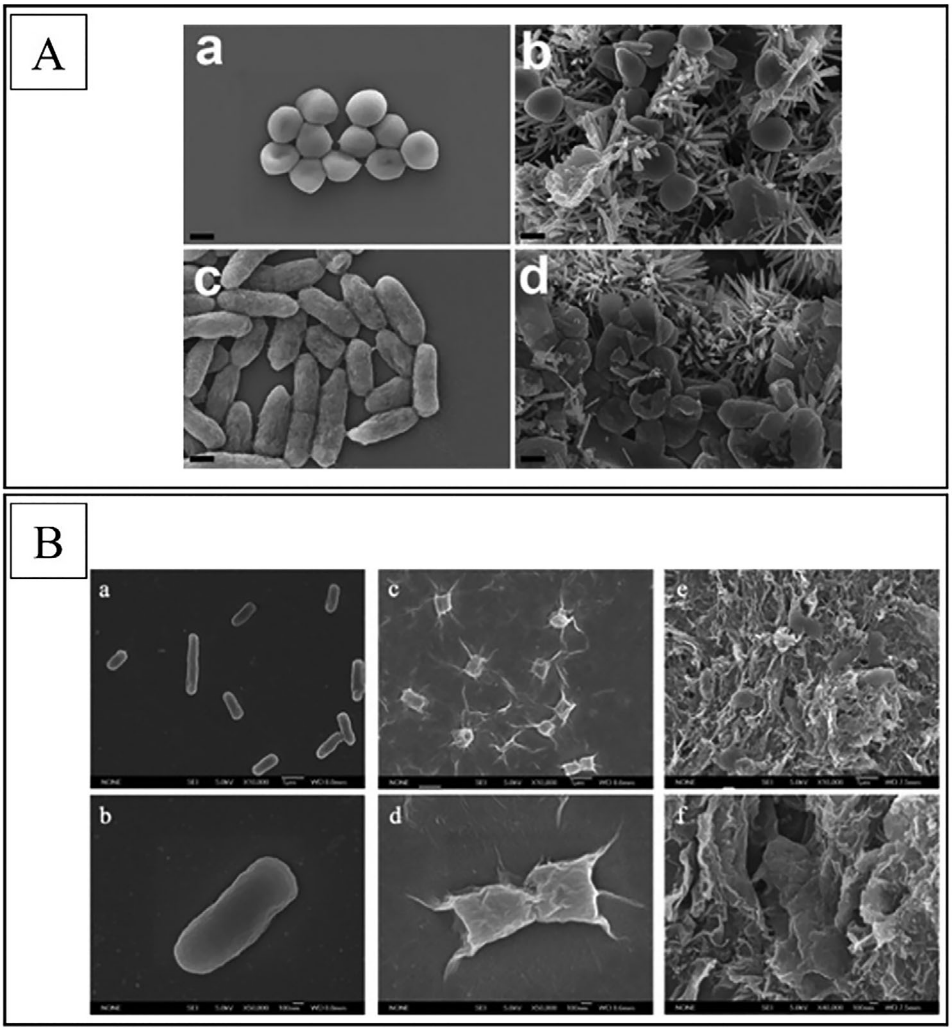

Figure 5. A) FE-SEM images of a,c) pristine *S. aureus* and *P. aeruginosa* bacterial cells and b,d) after being exposed to the hybrid nanomaterial of graphene nanoplatelets decorated with ZnO nanorods solution exhibiting mechanical injuries and perforation of the cell wall (scale bar 400 nm). Reproduced with permission.[142] Copyright 2017, Nanobiotechnol. B) SEM images showing *E. coli* bacteria cells a,b) and their interactions with the graphene-related materials as these lose their integrity after incubation and upon exposure to graphene oxide c,d) or reduced graphene oxide e,f) dispersions. Reproduced with permission.[143] Copyright 2011, ACS Nano.

2.2.3. Loss of Structural Integrity

GRMs are not only limited to being employed as coatings, but they can also be used as consolidants within materials developed for repair, remedial measures, and rehabilitation of historical buildings. Indeed, restoration materials are necessary to tackle the degradation of a variety of building materials ranging from archaeological and medieval mortars to Portland cement from the XIX century. In built heritage sites, GO shows potential for a wide range of applications, spanning from an additive in cement, necessary for the repair of built heritage constructions from the industrial revolution, to mortars, prepared following historical recipes.[152] It is particularly important to overcome major issues affecting the performance of the products currently in use, and drastically improve their toughness and tensile strength and their long-term resistance to cracking.

GO shows promise for the development of building materials, although the structure-function relationship within the cement and/or mortar matrix still needs to be investigated. Until now, three main hypotheses have been evaluated. First, GO might act as a nano-reinforcer in the matrix, helping to slow down the cracking phenomena observed after exposure to environmental factors. Secondly, more than one research group has theorized that this bidimensional material might act as a nucleation site for hydration products, favoring their formation and leading to denser structures.[153–155] Lastly, the oxygen-containing functional groups, characteristic of GO, might be responsible for the stronger interaction with the calcium silicate hydrate gel, stabilizing the modified-matrix. Overall, all these mechanisms might work in synergy and result in a material with an optimized performance. It is, thus, difficult to differentiate among the individual contributions: the key point is the dispersion state of GO. Poorly dispersed GO in the matrix compromises its strengthening

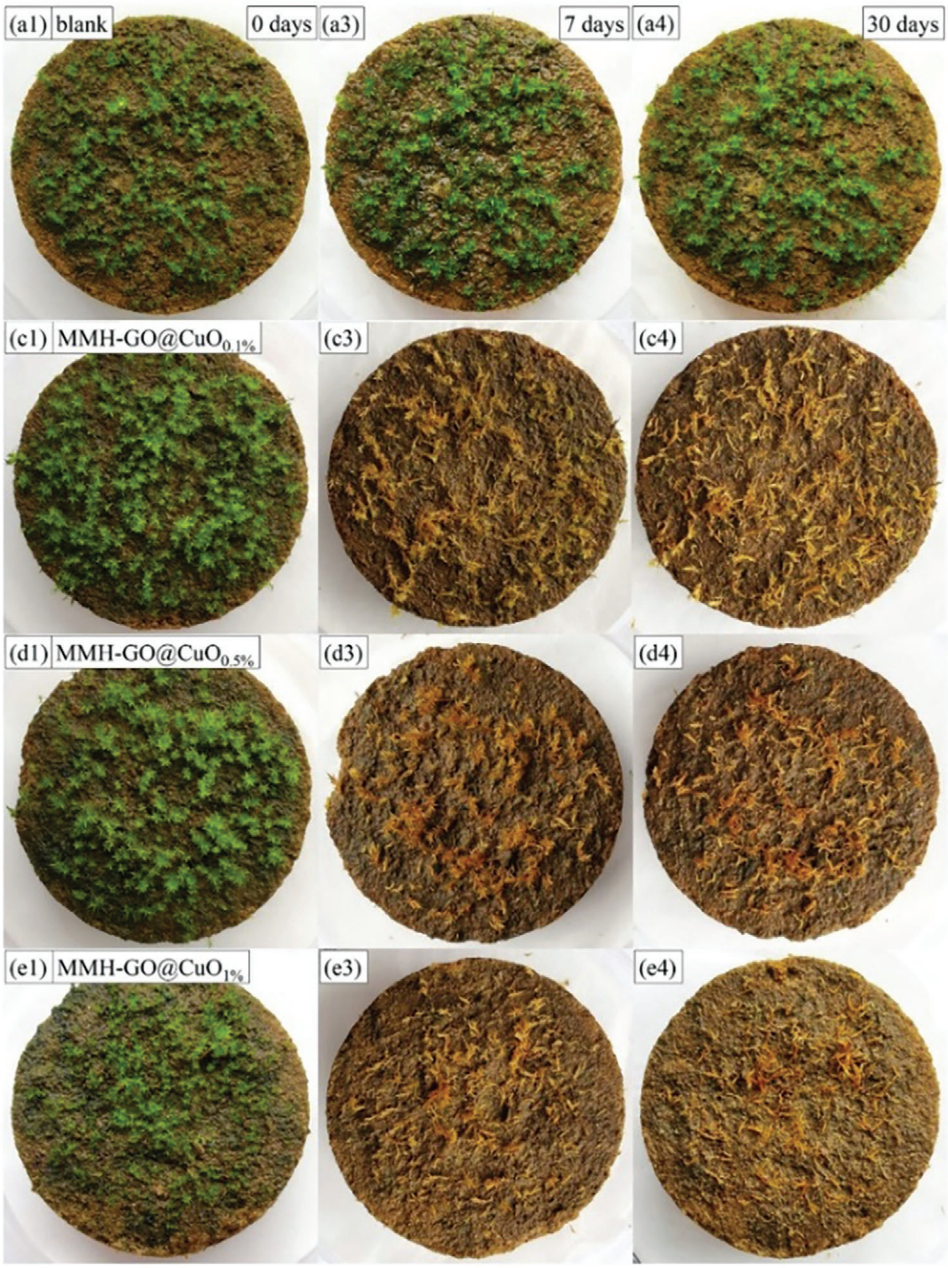

Figure 6. Images of moss colonization on weathered sandstone surfaces a) before and c–e) after application of the consolidants at different concentrations, after 7 and 30 days of consolidation treatment. Reproduced and adapted with permission.[151] Copyright 2023, J. Cult. Herit.

effect on cement substrates. The aggregation of GO into the matrix lowers the number of nucleation sites available, together with their specific surface area, reducing the positive effect of GO. At the same time, the presence of high amounts of K^+, Na^+ and Ca^{2+} can diminish the electrostatic repulsion between the GO sheets, leading to aggregation phenomena that negatively affect the interaction with the cement components. To overcome this issue, chemical modification of GO could represent a valid approach, but it is time-consuming, expensive, and, most of all, a potential source of impurities in the matrix. On the other hand, the addition of a second material or compound compatible with both GO and the cement components is an interesting strategy. Polycarboxylate superplasticizer, one of the most important superplasticizers for concrete due to its superior performance, is receiving great attention as it allows to obtain good dispersion of GO while maintaining adequate compatibility with the cement, thanks to its capability to be adsorbed on the surface of GO. However, within the complex matrix, polycarboxylate superplasticizer might interact preferentially with the cement matrix rather than with GO and this could lead to a reduction in its ability to disperse GO.[153,155] There are also other strategies to improve the dispersion of GO (such as the addition of mineral dopants), but more

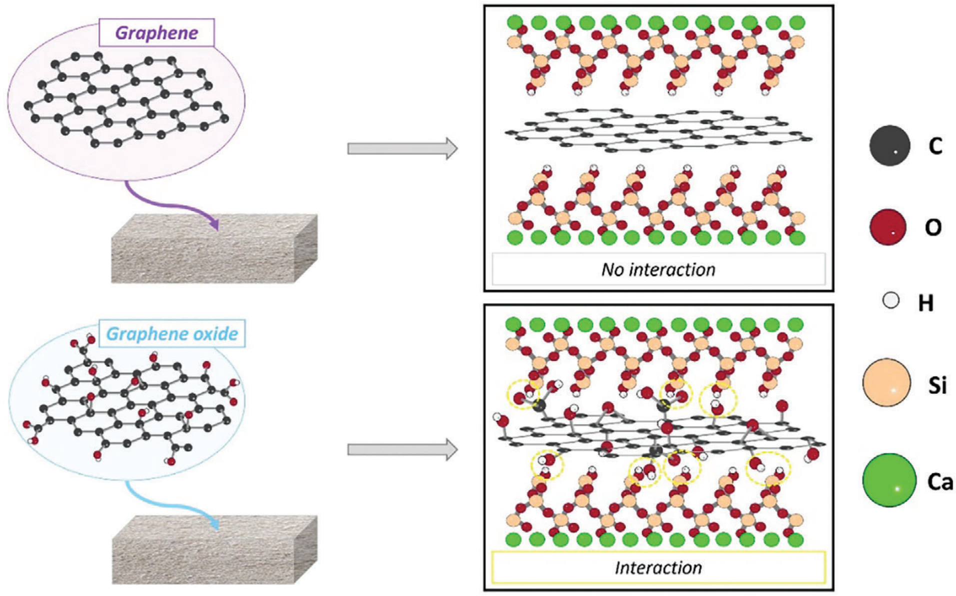

Figure 7. Schematic comparison of the interaction of graphene and graphene oxide with a typical cementitious matrix, mostly comprising a hydrated calcium silicates gel network.

advanced studies are needed to assess their potential. Further research needs to be devoted to establishing structure-function relationships that could drive and optimize the design of improved and long-lasting construction materials powered by GO.

The research on mortars with the addition of GO aimed at cultural heritage applications is at its beginning, as the few reports presented in the literature are generally not aimed at restoration. The data demonstrate that GO can improve to a certain extent the mechanical properties of hydraulic lime mortars,[153,154] due to the action of this material in the pore structure of the matrix. Indeed, besides the increase in the hydration process rates, GO can fill the pores leading to the formation of a denser and more durable structure. However, whilst improving the above-mentioned properties, GO can reduce the workability. This is probably due to the encapsulation of water within the agglomerated structures formed by GO, which leads to a problematic reduction in the available water/cement ratio.[153,155]

Further work from Dimou et al. showed no significant changes in the flexural strength due to the addition of GO, but an improvement in the compressive strength, which was reported to increase by 20–30% compared with the reference mortar.[156–158] Besides investigating these properties, Dorin et al. proved that GO addition only slightly improves the adhesion of the modified mortar. In these studies on the influence of GO on the performance of natural hydraulic mortars, different concentrations of GO in different physical forms (aqueous dispersions or powder) have been tested.[159,160] However, the results are preliminary, and it is difficult to draw a conclusive remark. In lime-pozzolan-cement pastes, Alexopoulos et al. proved that the incorporation of GO, rGO, and carboxilated graphene improved the compressive strength with a 33% increase achieved due to the addition of rGO. Additionally, the flexural strength of the pastes increased with the addition of GO and rGO, respectively 14% and 7%.[161] Further work needs to focus on the design of new approaches that take into consideration the complexity of the building materials, GRMs, and their intricated interactions.

Considering the application of graphene and rGO in building materials, the main issue is represented by the hydrophobicity of graphene, an obstacle in the aqueous environment of cement and hydraulic mortars (**Figure 7**). Strategies to overcome this obstacle rely on the addition of surfactants together with mechanical stirring and ultrasonication.

Once dispersed within the cement matrix, graphene nanoplatelets[162] as nano-additives have demonstrated a remarkable improvement in the mechanical properties[163] of cement. Moreover, graphene nanoplates are also able to affect the durability of concrete thanks to the barrier effect (particularly against chloride-mediated degradation mechanisms), whilst remarkably improving the electric and thermal conduction even at low concentrations. Noteworthy, the inclusion of GRMs in cement-based materials allows the production of smart concrete with sensing properties.[164–166] This provides the ability to continuously monitor the degradation state of the restoration materials, performed by the material itself without the frequent need for specialized personnel. Finally, graphene nanoplates have shown great potential as anti-biofouling agents within cementitious mortars, opening the way to extensive research on this application.

2.3. Glass, Cellulose-Based Materials, and other Substrates

Further categories of cultural heritage materials that require a conservation effort are glass, wood, and paper, among others. Veltri et al. evaluated the response of thin and optically transparent nanocomposite films, exhibiting antibacterial properties against *E. coli*, over a range of materials of both industrial and architectural interest including glass, granite, bronze, marble, and

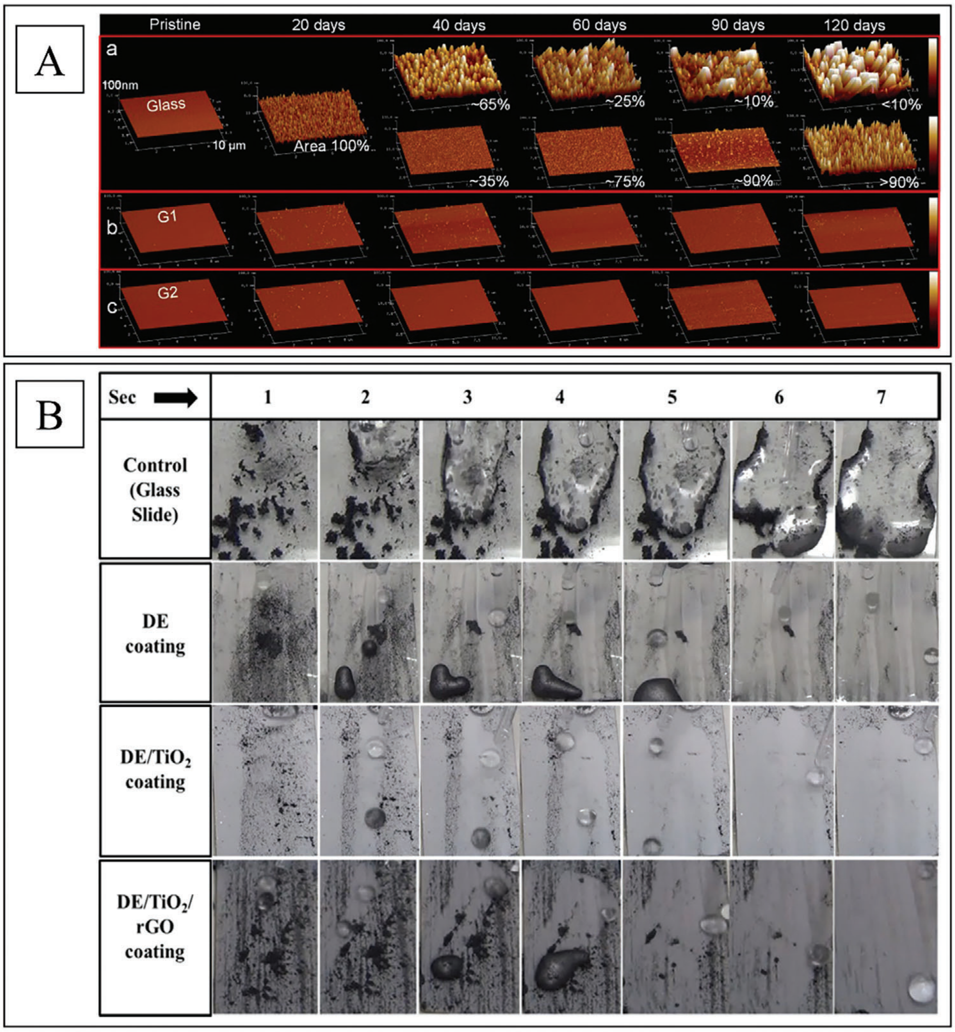

Figure 8. A) AFM analysis showing the topography and the surface structural changes of bare and graphene-coated glass immersed in water at different times. Reproduced with permission.[168] Copyright 2016, ACS Nano. B) Images of glass slide surfaces showing the uncoated control samples and the self-cleaning action for the coated samples upon artificial contamination with graphite microparticles for the different formulations. Reproduced with permission.[169] Copyright 2015, ACS Appl. Mater. Interfaces.

ceramic substrates.[167] Nanocomposite materials in the form of nanofilms, containing graphene flakes, were proposed for the treatment of large-scale objects exposed to challenging environmental conditions. Their application was achieved by using an airbrush or paintbrush for large-scale specimens, or by following a drop cast method for small-scale applications. Graphene flakes were chosen in the study by hypothesizing an interaction mechanism between them and the external cell membrane of the bacteria (i.e., the graphene flakes would exert stress onto the cells following their deposition or adherence to the substrate). For granite and bronze, the authors report a strong bactericidal response, while for glass, marble, and ceramic substrates, the findings suggest that the bacteria were able to proliferate. However, given that the nanocomposite films were formulated by using a polymeric matrix, which required either elevated temperatures or long waiting times for polymerization to occur, concerns are raised regarding their potential use and application within the cultural heritage field.

Besides the threat imposed by bacterial growth, glass substrates further suffer from corrosion phenomena. To particularly address water-induced corrosion issues, CVD graphene, grown on Cu and subsequently transferred onto a silicate glass plate, was used and its response was evaluated.[168] The underlying mechanism is based on the inhibition of the diffusion of sodium from the glass surface to water and the generation of hydroxide species upon the presence of the graphene coating over the glass substrate. The pristine and graphene-coated glass samples were immersed in unbuffered deionized water, to perform corrosion experiments over a period of 20 up to 120 days (**Figure** 8A). The authors report that the pristine glass samples exhibited an increase in surface roughness after immersion, which, along with the presence of defects, resulted in a pronounced reduction of the fracture strength, while graphene-coated glass samples exhibited only limited surface morphological changes with a slight roughness increase.

Given that glass substrates are prone to degradation consequent to exposure to environmental contamination, researchers have also evaluated the effect of a multifunctional composite coating based on a mixture of materials (i.e., polydimethylsiloxane, rGO sheets, SiO_2 nanoparticles, and TiO_2 nanoparticles) as a self-cleaning and corrosion-protective layer.[169] The formulation was applied on glass substrates by following the methods of spraying, brushing, and dipping. To assess the self-cleaning action of the prepared coatings, bare and dip-coated glass slide substrates, artificially contaminated with graphite microparticles, were subjected to continuous water dropping to monitor the action of the water carrying away the graphite powder. As anticipated, the coated surfaces exhibited a sharp self-cleaning action as they allowed the removal of the black graphite microparticles by the water droplets, while untreated glass slides showed an accumulation of powder without any appreciable removal. However, the results suggest that the presence of rGO had no appreciable effect on the self-cleaning response of the formulation, but rather its integration upon small additions yielded an improvement in mechanical stability and corrosion resistance (Figure 8B). Yet, despite the preliminary results, color alterations and compromised transparency are still major issues for glass-based materials.

Wooden and bamboo artifacts constitute other types of materials, which require protection since their surface is susceptible to UV radiation damage and fungal biodeterioration. Relevant works have utilized graphene for the fabrication of coatings by exploiting layer-by-layer self-assembly action.[170,171] Indeed, minor improvements have been reported upon the deposition of the coatings over the respective surfaces, but as the studies are preliminary, further work is required in this direction. Other applications of GRMs leverage key features such as conductivity response, light absorption, and fluorescence. However, few reports discuss these opportunities, leaving unanswered questions. It is worth mentioning that a composite hydrogel based on acrylamide, montmorillonite, and GO was proposed for the electrochemical cleaning of stained paper-based artworks.[172] Moreover, GRMs can find applications as UV absorber materials in cellulose-based substrates,[173] or as tracer materials for the detection of repaired areas in artworks and artifacts.[174]

2.4. Corrosion Protection of Metals

Corrosion is a common and natural, yet majorly deteriorative, process in metallic artifacts.[175] The properties of GRMs could be useful to address this phenomenon whilst preserving the aesthetic, mechanical, and conductive qualities of the treated metals.[176] However, the protection of cultural heritage metal artifacts by applying coatings based on graphene and GRMs is a research field still in the early stages. Up to now, only a few experimental works on the use of rGO on historically relevant metal substrates have been reported, paving the way for extensive research and advanced studies.[177] Mokhtarifar et al. proved that rGO nanosheets together with the γ-Fe_2O_3 nanoparticles enhance the self-cleaning properties of composite TiO_2 films deposited on metallic Ti specimens and, hence, reduce metal alterations due to contact with acid rain and pollutants. The role of rGO is mainly linked to the improvement in charge separation efficiency necessary for the photocatalytic process since the rGO layer acts as an electron acceptor, finally improving light harvesting and consequent light-induced wettability conversion.

Considering the limited experimental reports on metal artifacts, we expand on the topic of anti-corrosion properties of graphene coatings investigated in the industrial context. These works represent a solid starting point for the development of graphene-based protective coatings aimed at conserving cultural heritage metallic artworks (**Figure 9A–C**) and allow a critical and evidence-based analysis of the potential of graphene and GRMs.

To date, several studies have been conducted employing CVD graphene as a protective coating for metals.[24,178–180] Indeed, as already introduced in this review, high-quality (i.e., highly crystalline) graphene is known to be impermeable to various gases and thus is an ideal barrier. The ability of graphene to provide oxidation resistance to the surface of Cu and Cu/Ni alloy has been investigated,[178] finding that homogeneous and well-deposited layers of CVD graphene can limit or completely inhibit the formation of oxidized species on metals that were exposed to high temperatures (200 °C) or immersed in H_2O_2 solution for 2 min (Figure 9A). Yet, this remarkable protective action requires high-quality graphene, as micro-corrosion phenomena can be detected where defects are present and near the grain boundaries. Exposed graphene edges (in a non-continuous film) act as centers for Fe oxidation and propagation, while detached graphene can trap highly reactive species, such as Cl atoms, thus worsening the degradation of metal substrates due to corrosion.[181] When defects, grain boundaries, incomplete coverage, and detached areas are present, CVD-grown graphene is effective at limiting Cu oxidation and corrosion only over short timescales, due to the barrier effect against gases and moisture. Over long timescales, small molecules, such as O_2, may infiltrate through defects and cause the oxidation and corrosion of the underlying substrate. The high electrical conductivity of graphene coatings facilitates the occurrence of a galvanic reaction at exposed grain edges and boundary defects, both across the surface and through the bulk of the metallic substrate (Figure 9B). Pinholes, cracks, or scratches on the graphene coatings could in fact lead to accelerated local corrosion as graphene acts as a cathode and most metals act as anodes like in a galvanic cell and, even with very low mass loss, such local corrosion can strongly weaken the material.[182] These results highlight once again the importance of obtaining a homogeneous layer of graphene well attached to the surface and free of defects for long-lasting protection. It has been shown that the use of a continuous CVD tri-layer graphene provides a good barrier preventing oxidation of the native Cu substrate even at temperatures higher than 40 °C and in highly humid environments.[183] In environmental conditions, the protection of Cu from oxidation with CVD graphene has been verified for up to 3 years.[183] However, one should note that the performance of graphene coatings depends strongly on the type, structure, and oxidation state of the underlying metal surface. This aspect was investigated in detail by Dong et al.[180] They found that the deposited graphene film improved Cu corrosion properties for a short period of time. Indeed, after prolonged immersion in a NaCl solution, the graphene film detached from the Cu substrate and no longer provided barrier protection, leading to more severe corrosion in this sample than in the uncoated non-annealed one. The influence of the annealing process should be considered since it leads to higher corrosion rates, independently of graphene. The

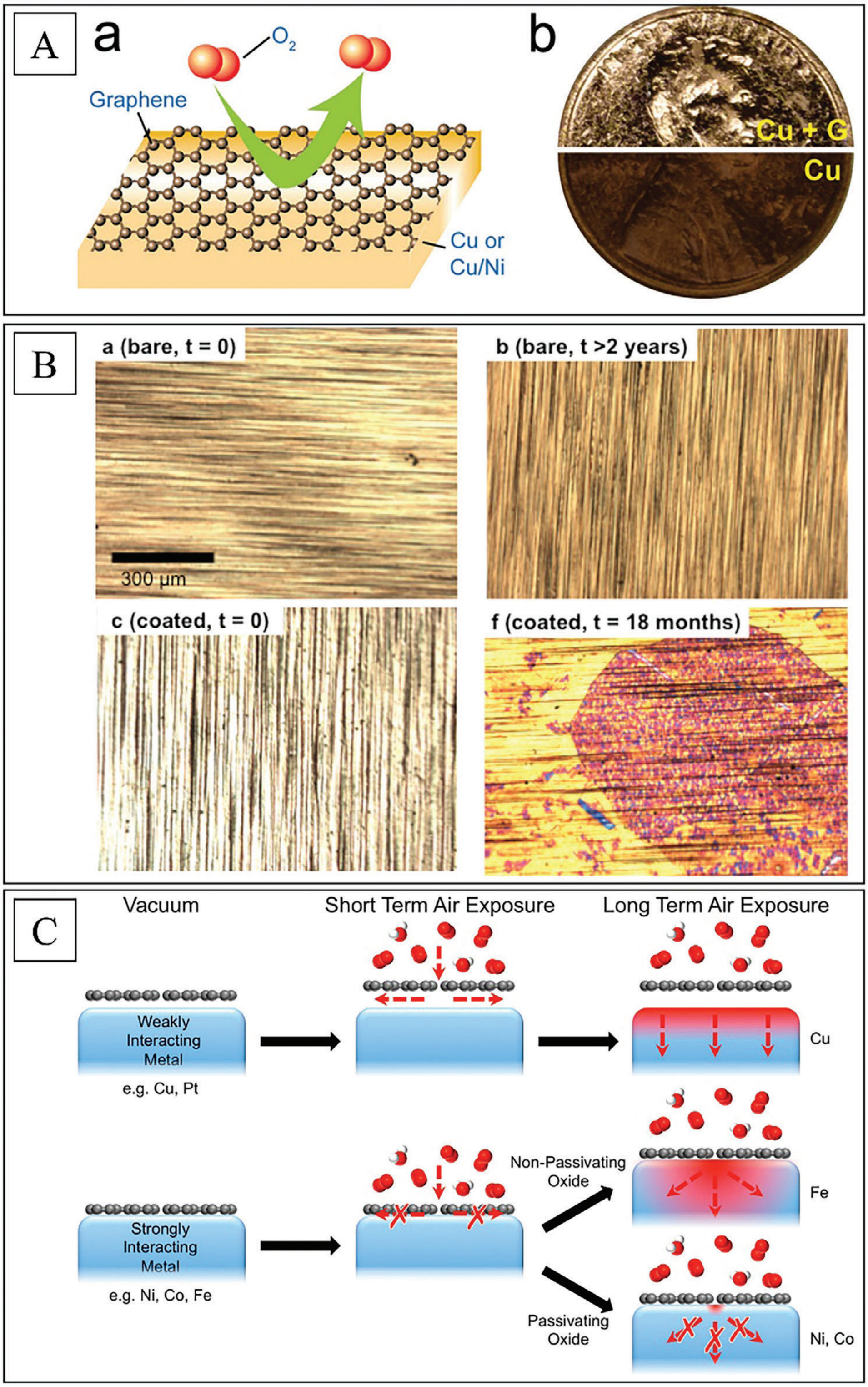

Figure 9. A) Schematic illustration showing a graphene film as a molecular diffusion barrier protecting the metal beneath from reactive agents (left) and photograph of a graphene-coated (top) and uncoated (bottom) coin after exposure (right). Reproduced with permission.[178] Copyright 2011, ACS Nano. B) Optical micrographs of bare and CVD graphene-coated Cu substrate stored under ambient conditions, showing (top) bare Cu at time 0 and after two years, and (bottom) room-temperature oxidation of Cu at time 0 and after 18 months. Reproduced and adapted with permission.[24] Copyright 2013, ACS Nano. C) Schematic drawing illustrating the graphene passivation behavior on different metal substrates during atmospheric air exposure for weakly and strongly interacting metals. Reproduced with permission.[179] Copyright 2015, J. Am. Chem. Soc.

high temperatures required by the process (940 °C)[180] provoke in fact the recrystallization of Cu substrate into different grain crystallographic orientations, resulting in the establishment of new preferential nucleation centers located near the modified grains, where corrosion phenomena preferentially develop.

Additionally, graphene on different metals or alloys yields diverse anti-corrosion protection: Weatherup et al. demonstrated that SLG coatings perform differently on various polycrystalline transition metals (i.e., Ni, Co, Fe, and Pt).[179] Following the exposure of the coated materials to atmospheric conditions, they reported that Ni substrates remained mostly unoxidized on the surface (if not for the formation of some small oxide species), while Cu surfaces did not show similar long-term passivation behavior when protected with SLG (Figure 9C). The significant difference between these two systems lies in the strength of the metal-graphene interaction: in weakly interacting metals (e.g., Cu), graphene gets decoupled from the substrate by the intercalation of oxidizing agents, which as a result can access the bare metal and give rise to rapid oxidation processes. Contrarily, in strongly interacting metals (e.g., Ni), graphene remains coupled to the surface and the oxidant species are only able to react on the portions closer to graphene defects. In addition, in metals that form a passivating oxide, the regions near defects can be plugged by the oxide formation, which could represent protection from corrosion.

Besides CVD graphene, different forms of top-down-produced graphene have been tested as anti-corrosion coatings.[31,184,185] Indeed, the application of multilayer graphitic films has been found to result in flexible barrier films that are highly impermeable to gases, liquids, and aggressive chemicals.[176] Multilayer graphene exhibits an improved response against oxidation over SLG on coated Cu substrates, attributed to the fact that the oxidation process proceeds slowly within the multilayers.[186] Moreover, graphene can be incorporated in organic polymeric coatings, where the barrier effect can be improved due to the increased tortuosity of diffusion pathways, although the complexity of the system could currently be seen as a drawback.[31] Another promising approach is the use of composite coatings where graphene is combined with microcapsules or nanocontainers characterized by self-healing and corrosion inhibition properties. Finally, GO and rGO have been embedded within coating matrices such as polymers and oil, and studied as anti-corrosion barriers.[31,187] In these specific cases, GRMs were added with the aim of improving the coating efficiency. For this task a good dispersion of the sheets as well as their relative orientation within the matrix are decisive, the latter being still at this time of research a difficult factor to control. In all the solutions presented above and involving thicker graphene layers, it remains to be investigated whether such approaches would be suitable for cultural heritage metallic substrates, as multiple graphene layers may diminish the optical properties of the coated surface.

2.5. Preventive Conservation

2.5.1. Indoor Environmental Control

Preventive conservation represents the first line of action in the management of cultural heritage.[188] This entails controlling the conditions of storage, exhibition, usage, handling, and transportation.[189] Within dedicated areas, such as museums, artifacts are exposed to different agents that can potentially be harmful (i.e., light, temperature, relative humidity, and indoor air pollution).[190,191] This underlines the need for strict control over indoor conditions, defining tailored solutions for different classes of materials.[192] Storage boxes and glazing frames should be designed to address specific needs and to meet multiple protection requirements (e.g., multi-pollutants atmosphere, humidity, and light).

Considering this challenging task, the use of alternative materials is required, and graphene and GRMs could play an important role in developing effective strategies. Preliminary work has demonstrated that the barrier effect of graphene can be exploited for the protection of artworks from oxygen, moisture, and volatile organic compounds (VOCs).[25,176] Following these encouraging results, boxes modified with GRMs have been proposed as smart solutions not only for transportation but also for storage purposes. The internal walls of conventional archive boxes can be coated with GRMs or, alternatively, a coated carrier (e.g., cardboard panels) can be interposed between the stored object and the internal walls. Thanks to the barrier effect of GRMs, these boxes can mitigate humidity changes and block the interaction with VOCs. Indeed, the multilayered structure of graphene nanoplatelets represents a barrier to small molecules (i.e., O_2) that are trapped in the tortuous porous structure.[193,194] Besides the structural characteristics of GRMs, their barrier properties are also attributed to the density of aromatic rings on the plane, which hinders the penetration of gases and establishes a high energy barrier. At the same time, GRMs can provide optimal shielding from UV radiation due to their photostability and strong absorption in the UV region.[195,196] To exploit the potential of this property, GO has been applied to glazing materials (i.e., glass and acrylics) as a UV-shielding species.[197] This approach provides UV protection and an improvement in hardness and abrasion resistance.

To further benefit from the barrier effect of GRMs, GO has been combined with polyvinyl alcohol to create stand-alone films or coated corrugated boards, which can then be inserted in the storage boxes. To determine their ability as VOCs adsorbers, three polar compounds have been selected: formic acid, formaldehyde, acetic acid, and acetaldehyde. GO can interact and, consequently trap these molecules thanks to its oxygen-containing functional groups, which make it affine to polar species.[30] Parallelly, protection from nonpolar VOCs might also be achieved by leveraging the hydrophobicity of graphene.[198,199] In the action of the polyvinyl alcohol/GO film, the interaction mechanism appears to mainly involve surface complexation, π–π stacking, and electrostatic interactions.[30] Most importantly, the authors report that the adsorption mechanism is reversible, possibly allowing to reuse of the PLA/GO film after it has reached its maximum capacity. The performance of this nanocomposite has been reported to be comparable or superior to the one based on rGO combined with ionic liquids[200] or hexagonal boron nitride[201] in terms of VOCs adsorption. The improvement is probably associated both with the different polarity of GO compared to rGO and with the different structure of film and aerogel. Indeed, rGO presents a differently functionalized surface, which might disfavor the interaction with polar VOCs. However, the interaction is still based on the high specific area of rGO and on its π structure. On the other hand, the use of aerogels instead of films plays an important role as it increases the percentage of available surface area. Indeed, aerogels are nanomaterials in which their porosity can be fine-tuned depending on the size and shape of the nanoparticles used as precursors, with the possibility of achieving a particularly high surface area.[202] These aerogels are impressively light, 3D structures characterized by high mechanical strength. Moreover, their adsorption capacity is associated with high electrical conductivity and thermal resistance, which opens the way to multi-functional applications.[202]

In a recent report, the potential of rGO-based aerogels containing an ionic liquid has been studied as a preventive conservation strategy against VOCs and fungi (i.e., *Aspergillus niger*) colonization.[200] Both the adsorption and the desorption of VOCs have been investigated, proving a more stable aerogel-aldehydes interaction and a quicker desorption for the organic acids. This suggests that both chemisorption and physisorption occur simultaneously. The study concludes that the interaction between VOCs and the adsorber is improved due to the simultaneous presence of the ionic liquid with rGO, which leads to the formation of stronger hydrogen bonds. This hybrid material also presents antifungal properties as it achieves growth inhibition against specific microorganisms. This preliminary result has also been confirmed by Sawangphurk et al., who tested rGO nanosheets against *Aspergillus niger*, *Aspergillus oryzae*, and *Fusarium oxysporum*.[203] They found that the inhibitory concentrations of rGO are 2-fold lower than those of conventional formulations containing essential oils and ZnO nanoparticles.

Other synergies have also been explored within this context. The addition of hexagonal boron nitride platelets to rGO improves its adsorption capability since the adsorption of VOCs and water vapor is enhanced in the presence of the hexagonal boron nitride.[201] The system has been tested against formaldehyde, hydrochloric acid, and acetic acid. The hybrid material outperforms rGO only in the adsorption of formaldehyde, while rGO by itself appears to result in better results for the adsorption of hydrochloric and acetic acids. The authors hypothesize that formaldehyde can strongly interact with the hexagonal boron nitride thanks to its high specific surface area and to the presence of hydroxyl and amino groups on the surface, which can form hydrogen bonds with formaldehyde itself. This chemisorption could be possibly followed by a disproportionation mechanism through which this molecule reacts to form formic acid and methanol, underlining that these hybrid materials could be especially useful for the conversion of dangerous VOCs into less toxic species. The potential double function of these aerogels for both the adsorption of pollutants and their catalytic decomposition is of great interest, opening the way for even more complex applications involving the abatement of harmful species.[204,205] Androulidakis et al. reported an improved water vapor adsorption for the hybrid material, compared to rGO by itself.[201] This observation is correlated to the increase in the hydrophilicity of the hybrid material due to the addition of hexagonal boron nitride. Remarkably, the hybrid material has also been tested in terms of electrical and thermal conductivity, expanding its multi-functionality to the real-time monitoring of environmental conditions. Besides the potential of this hybrid material, graphene and GRMs have also been considered valuable components in sensors of VOCs and of other physico-chemical key parameters. High charge-carrier mobility, a reduced power requirement, and compatibility with currently-in-use electronic devices have already opened the way to the use of graphene and GRMs in advanced monitoring and sensing devices.[206,207]

2.5.2. Monitoring Technologies and Sensors

The current practice in museology entails preservation and conservation actions based on extensive diagnostic analyses, such as continuous monitoring through sensors and specific assessments of the alteration in progress.[208] Considering these strict requirements, easy-to-use, portable, and fast diagnostic tools consisting of sensitive, accurate, and multi-parameter sensors are fundamental for conservators to check the correct preservation of paper, pigments, paints, and metals.[209] In both diagnostic and monitoring applications, the key properties of GRMs can dramatically enhance the current technology and deliver the next generation of continuous monitoring devices and point-of-use diagnostics characterized by high sensitivity and selectivity, coupled with the potential to be used directly on the object.

GO properties have already been tested for the development of screen-printed electrodes to discriminate metals (e.g., Fe) and metalloid compounds (e.g., As): this voltammetric approach was used to identify the redox state of Fe and As.[210] The determination of the redox status of these two elements within the pigments,[211] together with their speciation, is important for understanding the physico-chemical properties of artworks even when present in trace amounts.[212] This determination can be carried out by removing a tiny amount of sample from the artwork,[213] or by direct contact of the sensor with the pigment; in this case, the electrolytic contact is obtained with hydrogels, paving the way for the implementation of screen-printed electrodes modified with GO in already existing restoration and conservation methodologies.[214]

Graphene can also have an impact on the realization of highly performing electrochemical immunosensors, which constitute innovative diagnostic tools for providing selective analyses of several organic components on a defined spot of the artwork.[215] Indeed, GRMs can stably immobilize a high number of antibodies suitable for the specific interaction with the target analyte on the artifact, an approach already successfully tested in cultural heritage for the determination of keratin in ancient wools.[216] A wider detection range and a much lower detection limit of keratin compared to traditional indirect enzyme-linked immunosorbent assay (ELISA) was achieved, paving the way for a new strategy to investigate the origin and diffusion of ancient textiles. Considering the versatility of antibodies and the great richness of options offered by the chemical versatility of GRMs, ultrasensitive electrochemical immunosensors can identify residual traces of the original binders or coatings that are hardly detectable with traditional spectroscopy techniques (e.g., FTIR, Raman). Potentially, cheap, and on-site miniaturized biosensors based on graphene materials could be used directly on the surface of artworks, which constitutes a new approach to continuous monitoring.

Further work proved that a hybrid montmorillonite (MMT)/rGO film applied on pristine and consolidated tuff stone can be used as a sensor for the monitoring of water adsorption and desorption.[217] The advantage of this approach is the possibility to directly apply it to the item, to achieve an in situ continuous monitoring of the humidity levels. The high sensitivity of the sensor response for small variations of water content is ascribed to the carboxylic group of rGO. Therefore, MMT/rGO sensors can be used to evaluate water adsorption–desorption of tuff in real-time: the in situ monitoring allows us to predict degradation phenomena associated with the effect of water and to plan restoration interventions accordingly.

GRMs also have the potential to impact one of the most used diagnostics in conservation science, namely Raman spectroscopy, which enables rapid, non-destructive, precise, and in situ molecular identification. The weakness of the Raman signal is a major limitation of this technique, which can be overcome by surface-enhanced Raman spectroscopy (SERS) thanks to an enhancement substrate (generally plasmonic materials like Au and Ag nanoparticles). The application of SERS to cultural heritage has been extensively explored on cross sections of important paintings and different artistic objects stored in museums and conservation departments.[218–220] Recently, graphene has attracted significant attention as a SERS enhancement substrate with or without plasmonic nanoparticles,[221] introducing the graphene-enhanced Raman spectroscopy (GERS).[221] In cultural heritage, GERS applications are not yet reported but they could represent a fast and in situ improvement of SERS technology. Indeed, the presence of the fluorescence background is a notorious obstacle to Raman spectroscopy for organic materials. This can be overcome thanks to the effective quench of the photoluminescence of fluorescent dyes,[222,223] which can be achieved with the use of graphene, without the need of bleaching the sample.[224]

Beyond these applications as external sensors, GRMs could also be used as a sensing system within complex matrices such as cementitious materials.[225] A seminal work from Dimou et al.[156] proposed a binary paste matrix (natural hydraulic lime and metakaolin) modified with rGO as reinforcement for the development of cultural heritage restoration mortars. The addition of rGO provokes a decrease in electrical resistance that indicates a good distribution of the electrically conductive nanomaterials within the binder, forming an efficient electrical network. Parallelly, in lime-pozzolan-cement paste, the addition of GO, rGO, and carboxylated graphene provides excellent piezoresistive properties.[161] Noteworthy, in the sample with carboxylated graphene, a 70% fractional change in electrical resistance was recorded upon cyclic loading and unloading at a level of 50% of the compressive strength. These results pave the way for the potential use of the nano-composite binder for the structural health monitoring of cultural heritage architectural monuments.

In addition, the previously mentioned graphene aerogels can play an important role in sensing, since they combine large surface area, due to porosity, with conductive properties, making them a promising electrochemical sensor for the detection of gases, oils, and organic compounds.[202]

Finally, the next generation of sensors for the continuous monitoring of artifact conservation are Tattoo sensors, whose use has already been proposed in cultural heritage and which are designed to not alter the color, whilst providing high conductivity and contact over large areas. The use of GRMs in these devices can impart high sensitivity, whilst not affecting the optical properties of the artifact, and offers the option of loading the tattoo sensors (**Figure 10**A,B) with reserve chemical reagents, allowing the device to become a smart actuator, capable of releasing inhibitors, chelating, and consolidation agents from nanometer-sized containers.[226]

3. Challenges and Opportunities

Without a doubt, a decade of rigorous research on graphene and GRMs[228] has unequivocally showcased their potential to emerge as a groundbreaking innovation capable of slowing down, if not halting, the degradation of artworks (**Table 1**). Nevertheless, it is still necessary to engage in further critical discussions, opening a comprehensive dialogue about both the opportunities and challenges in their application that should involve material scientists, chemists, physicists, engineers, and cultural heritage experts in a multidisciplinary approach.[22,23] In the following paragraphs, we will endeavor to outline what we have identified as challenges that must be considered and accounted for in the development of graphene-based products for cultural heritage, as well as the additional benefits they can offer and that can be leveraged.

3.1. Targeting Production and Deposition of Solution-Based Graphene and GRMS for Cultural Heritage Applications

A great advantage of graphene and GRMs in liquid dispersions is the chance of tuning their properties depending on the application needs, by controlling the synthetic process. Indeed, chemical functionalization of these materials can be flexibly performed during their production, affecting properties such as their affinity to water or electrical conductivity, with small modifications of the standard synthetic route. The flexible and cost-effective production of graphene-based liquid dispersions is however counterbalanced by a not always easy control of their quality due to possible variations in the thickness and size of the 2D dispersed flakes. To date, this has sometimes led to mistrust toward their adoption.[229] In the coming years, the diffusion of globally shared quality-check protocols with commonly available spectroscopic and microscopic techniques would be beneficial to avoid conflicting results due to the quality of the 2D material rather than to its effectiveness in a certain application. Reliable controls of the physico-chemical properties of graphene and GRMs are extremely important when considering applications in cultural heritage, where researchers often rely on commercial materials and focus their attention on the applications rather than on the material itself. This issue clearly emerges from a critical literature review: graphene and GRMs quality and resulting properties strongly affect the outcomes of all studies, especially when dealing with complex substrates and heterogeneous artifacts. Therefore, reproducibility and rigorous quality standards throughout the entire production stage are decisive for future applications in cultural heritage.

Considering deposition methods, most conservation strategies are based on graphene and GRMs in liquid dispersions, which can be applied through submersion, spraying, or paint-brushing.

Table 1. Summary of graphene (Gr) and graphene-related materials (GRMs) applications on various substrates and materials. Relevance to the cultural heritage (CH) field is denoted with a checkmark (✓). Production and deposition methods are noted. Results and remarks are briefly mentioned for each study.

Substate	Gr or GRMs	Production method	CH	Type and deposition method	Results and Remarks	Refs.
Painted artworks						
Inks, paints, and dyes	GO, rGO	HM (GO), thermal treatment (rGO)		A	Highly effective hydroxyl radicals scavengers for the protection of a variety of molecular targets from oxidation	[29]
	Gr NPs	CP	✓	A	Protective barrier against fading (due to UV and visible light) with an improvement of up to 40%	[116]
	Gr	CVD	✓	C (RtR)	Removable single-layer or multilayer to prevent color fading with a protection factor of up to 70%	[25]
Wall paintings	GQDs + $Ca(OH)_2$	Chemical method in water	✓	C, CO (BR)	Conservation efficiency and promising potential for consolidation, increase in flexural and bonding strength, anti-UV absorption ability, minor color changes	[124]
	Gr + $Ca(OH)_2$	HM	✓	C, CO (BR)	Reinforcement and consolidation of murals, improvement in bonding strength with no significant color changes	[125]
	GO + resin	CP	✓	C	Minor improvement of mechanical properties, minimum aesthetic alterations for low concentrations but more pronounced with color darkening for higher concentrations	[127]
Natural and artificial stone-based materials						
Dolomitic stone	GO	LPE, MHM	✓	C (SC)	Prevention of rain-induced wear and climatic erosion, improvement of compression stress, minimal chromatic alteration but more pronounced with darkening of the coating after aging	[131]
	GO	LPE, MHM	✓	C (SC)	Protection against surface erosion due to acid rain and extreme thermal changes, durability on extended timescales remains to be studied	[133]
	GO				Protection against acid rain	[134]
Concrete	GO	HM		C (BR)	Improvement of concrete durability	[135]
Sandstone	CuO NPs on GO sheets	CP	✓	CO (infiltration method)	Prevention of moss growth and inactivation of moss spores, mechanical properties, and discoloration issues require further investigation	[151]
Noto stone, Carrara marble, yellow brick	Gr NPs + ZnO	LPE, CP	✓	C (SC)	Antibacterial and antibiofilm activity; time- and dose-dependent bactericidal effect, mitigation of color alteration thanks to the whitening effect of ZnO	[144]
Hydraulic lime mortars	GO + Ag NPs + Fly ash, $ZnO+TiO_2$	HM	✓	A	Improvement of the physical properties and bacterial inhibition	[140]
	GO + Ag NPs,Fly ash, ZnO,TiO_2		✓	A	Improvement of the mechanical properties and resistance to chemical attack	[160]
	rGO + hydraulic limes; Metakaolin	GO Reduction	✓	A	Mechanical reinforcement of the mortars	[158]
	GO	MHM		A	Improvement of the mechanical and physical properties	[159]

(*Continued*)

Table 1. (Continued).

Substate	Gr or GRMs	Production method	CH	Type and deposition method	Results and Remarks	Refs.
Glass, cellulose-based materials, and other substrates						
Glass, granite, bronze, marble, ceramics	Gr flakes	CP	✓	C (DRC, BR)	Thin, transparent films based on polymeric matrix for protection against bacteria proliferation and penetration (substrate-dependent response)	[167]
Glass	rGO sheets + particles	MHM + reduction		C (DC, SC, BR)	Self-cleaning action of coated surfaces; the presence of rGO in the formulation has no appreciable impact on it	[169]
Silicate glass	Gr	CVD		C (TR)	Water-induced corrosion of silicate glass is inhibited with minor surface alterations and a slight roughness increase	[168]
Wood	Gr nanosheets	Oxidation + Thermal exfoliation		C (LbL)	Multilayer membrane with thermal stability and effective protection against UV damage	[170]
Bamboo	rGO nanoplates	MHM		C (LbL)	Minor improvement in antifungal activity against specific fungal types only	[171]
Paper	rGO	MHM	✓	Hydrogel	Electrochemical removal of stains on paper-based artworks; graphene promotes the electrical conductivity of the hydrogel	[172]
	GO + CMC, PEI		✓	C	UV-aging protection and general reinforcement	[173]
Metals						
Cu	Gr	CVD		C (CVD)	Protection of the areas uniformly covered by graphene; onset of corrosion on defects and grain boundaries	[24]
Cu, Ni	rGO	HM + reduction		C (RC, SC)	Corrosion protection of multilayer graphitic films from acids at different concentrations	[176]
Ti	rGO + TiO_2, γ-Fe_2O_3	CP	✓	C (DC)	Enhancement of self-cleaning property of TiO_2 by rGO (which also increases surface roughness)	[177]
Cu, Cu-Ni	Gr	CVD		C (CVD)	Inhibition of oxidation for a short period of time	[178]
Cu	Gr	CVD		C (CVD)	Short-term corrosion protection, but strong influence of substrate microstructure on detachments	[180]
Ni, Co, Fe, Cu, Pt	Gr	CVD		C (CVD)	Long-term protection of Ni surfaces against oxidation under atmospheric conditions by coverage with single-layer graphene thanks to strong graphene–metal interaction	[179]
Fe	Gr	CVD		C (DRC, TR)	Non-uniform graphene layer can detach and promote local corrosion on grain boundaries and defects	[181]

(Continued)

Table 1. (Continued).

Substate	Gr or GRMs	Production method	CH	Type and deposition method	Results and Remarks	Refs.
Cu	Gr	CVD		C (CVD)	In vacuum atomic oxygen conditions multilayer graphene has better anti-oxidation ability than monolayer graphene	[186]
Indoor environmental control						
Archive boxes	GO + PVA	MHM	✓	Stand-alone film or coated carrier	Humidity regulation and VOCs adsorption	[30]
Glazing frames	GO	MHM	✓	C (spin coating)	increase in glass glazing hardness and UV-radiation shielding	[197]
Archive boxes	rGO + IL	MHM + chemical reduction	✓	Aerogel	Antifungal aerogels with VOCs adsorbing properties	[200]
Archive boxes and display cases	rGO + hBN platelets	MHM + chemical reduction	✓	Aerogel	Electrically conductive aerogels for the adsorption of VOCs	[201]
Monitoring technologies and sensors						
Glass and ceramic	GQDs			C	Waterborne epoxy-based fluorescent adhesive with GQDs used for the reconstruction or repair of artifacts	[174]
Pigmented leather cover book	GO	Oxidative unzipping	✓	Screen printing machine	Screen-printed electrodes as sensitive and non-invasive approach to monitor oxidation state of pigments	[210]
Ancient wool	GO	CP	✓	A	Electrochemical immunosensors with enhancement of detection limit for keratin trace	[216]
Tuff stone	rGO	CP	✓	A	Sensitive on-site continuous sensor based on hybrid montmorillonite /GO to monitor water adsorption and desorption sensor	[217]
Lime-pozzolan cement	GO/rGO			A	GO imparts piezoresistive properties to the cement potentially useful to monitor the conservation state	[156]
Potentially on paper	GRMs		✓		Tattoo sensors- potentially novel smart sensor and actuator capable of monitoring and releasing restorative agents	[226]

GRMs: nanoparticles/nanoplatelets (NPs); Graphene Quantum Dots (GQDs); Carboxymethyl cellulose (CMC); Polyethyleneimine (PEI); ionic liquid (IL); polyvinyl alcohol (PVA); hexagonal boron nitride (hBN). Production method: Commercial Powder (CP); Liquid Phase Exfoliation (LPE); Hummers Method (HM); Modified Hummers Method (MHM). Type: Additive (A); Coating (C); Consolidant (CO). Deposition method: Chemical Vapor Deposition (CVD); Spray-Coating (SC); Dip-Coating (DC); Brushing (BR); Drop-Casting (DRC); Hydrothermal Treatment (HT); Transfer (TR); Rod-Coating (RC); Roll-to-roll (RtR); Layer-by-layer self-assembly (LbL).

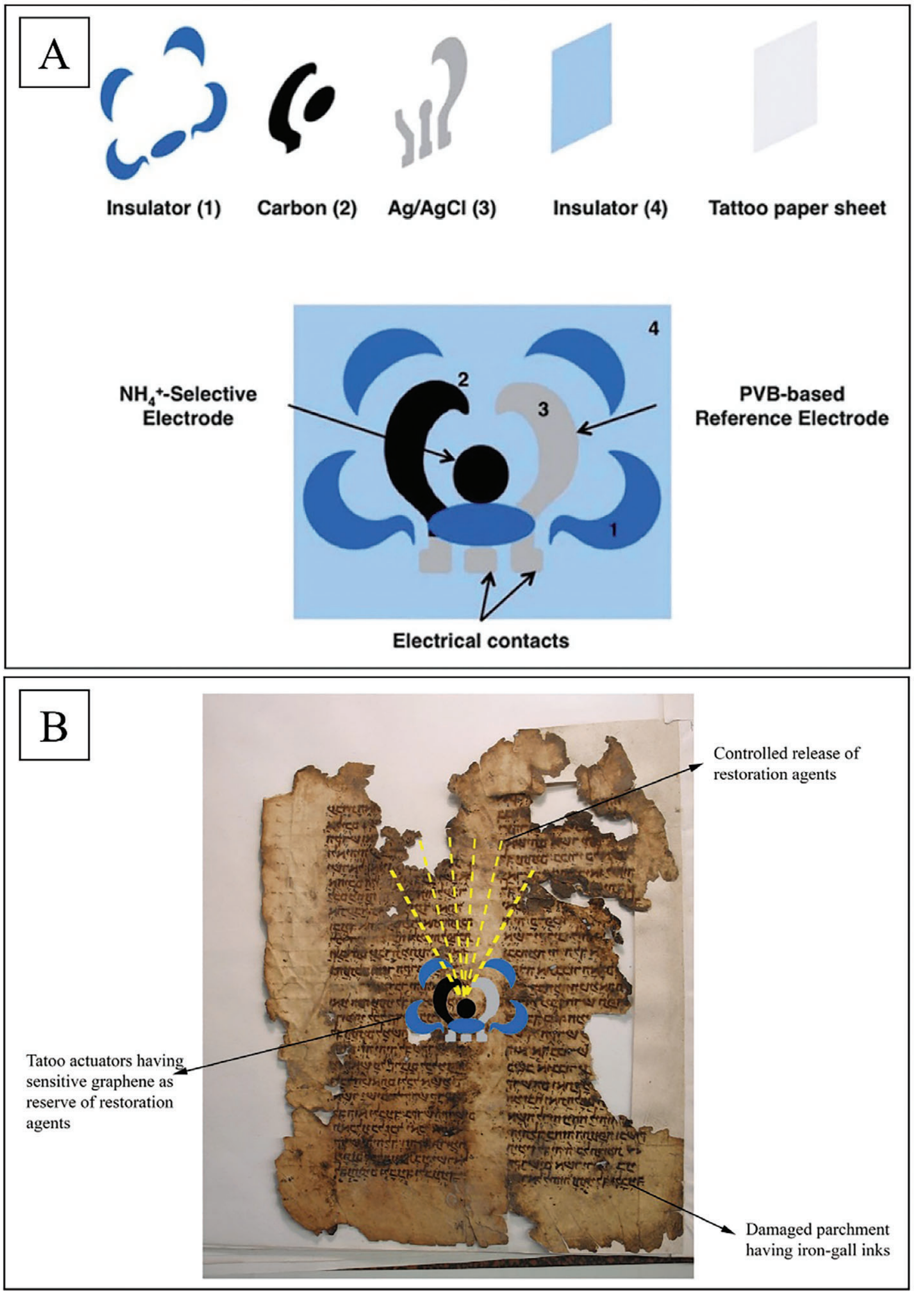

Figure 10. Graphene-based tattoo sensor for in situ detection and real-time monitoring of pollutants and damage on cultural heritage surfaces. A) Layer-by-layer fabrication of the potentiometric tattoo sensor. Reproduced with permission.[227] Copyright 2018, Sensors. B) Application of the tattoo sensor for cleaning, restoration, and consolidation of damaged artwork surfaces. Reproduced with permission.[226] Copyright 2020, Sensors.

Typically, these approaches do not allow for easy control of the number of deposited graphene layers due to a chaotic disposition of the flakes in solution and their non-planar arrangement during the application. Consequently, liquid-dispersion-based coatings can present significantly low transparency, which is a considerable issue in the protection of artifacts.[87,115] This issue is challenging, and a focused research effort should be devoted to the optimization of tailored deposition methods, granting control over the flakes assembly at the surface and, hence, over the final properties of the substrate.

3.2. Tailoring CVD Graphene Synthesis and Transfer for Cultural Heritage Applications

Contrarily to the deposition of liquid dispersions, CVD graphene can be prepared with high crystallinity, large crystal domains, and great thickness control. Substrate selection is key, as its chemistry and crystallinity affect the quality of the produced graphene. Commercially available CVD graphene is typically polycrystalline, hence presenting grain boundaries that negatively affect the material impermeability. Those shall be minimized for the successful adoption of CVD graphene as a transparent protecting coating for artifacts made of canvas, paper, or even metal. Indeed, on metals, not only do grain boundaries limit the protection against corrosion, but they could also favor galvanic mechanisms,[182] worsening the conditions of the treated substrate. The solution for the conservation of metallic artifacts is in fact aiming at obtaining a uniform film on the surface to guarantee perfect coverage, impermeability from ions, and protection against other oxidizing agents. Presently, research laboratories have demonstrated the possibility of achieving high-quality single-crystal CVD graphene on oriented metallic substrates,[230] and an increase in the commercial availability of this material can be expected over the next few years.[231]

Besides this, the transfer processes of CVD graphene should be crafted to avoid damage to the delicate destination artifacts and to mold graphene to irregular and rough surfaces. However, significant work is required as CVD graphene films have- until now- only been applied on smooth surfaces.

Cracks, defects, and folds are caused by non-uniform forces applied between graphene and the destination substrates, as well as by the roughness of the substrate: mechanical parameters and interactions between the materials are therefore the key questions to be addressed. For example, in roll-to-roll the quality of the transferred film depends on roller diameter, speed, and film separation angle, some mechanical factors that are worth investigating.[231]

Ultimately, one could envision that the future protection of selected artifacts (from aging processes such as oxidation and color fading) could be successfully achieved without the need for multiple CVD graphene layers (which negatively affect transparency) but with the deposition of a single-crystal CVD graphene single layer following a substrate-tailored transfer process.

3.3. Interaction with Surfaces and Interfaces

The interaction between artifacts' surfaces and graphene, GRMs and graphene-based composites, and hybrid materials is a key issue. Surface properties will determine different adhesion strengths and different durability of the coatings, strongly influencing the protective strategy. In this direction, specific solutions should be devised through tailored engineering of graphene and GRMs coatings. Early results on protective coatings for metal substrates already show how a strong interaction between the metal surface and graphene is effective in long-term corrosion protection.[232] However, strong interactions are typically obtained through invasive procedures (such as high-temperature CVD growth), which are hardly suitable for cultural heritage. Moreover, further work is needed to evaluate coating-substrate interactions on porous, and inhomogeneous materials, as well as substrates with a mixture of hydrophilic and hydrophobic areas, and composite materials with organic components that can experience natural outgassing, given that continuous-layered graphene is gas-impermeable.

In the case of formulations with nanoparticles, polymers, and other inorganic materials, the complexity of the final composites or hybrid materials complicates the studies aimed at unraveling the mechanisms of interaction between the graphene and GRMs, the other components, and the heterogeneous substrates. Tailored studies should be devised to investigate and decipher the actual role of GRMs in such complex matrices and the change of the original properties of each single component in the mixture. The parameters that need monitoring are numerous as both the synergy between the components themselves and their activity on the substrates should be considered.

From a mechanical point of view, it is evident that the structural integrity of materials within the cultural heritage field is significantly affected or even compromised upon their exposure to concurrent degradation processes. The integration of graphene and GRMs into such fragile and disrupted structures can potentially enhance their mechanical response, provided that specific requirements are met.[233,234] In particular, the interaction of graphene and GRMs with the existing substrate should be designed to achieve synergistic interactions by controlling bonding strength, adhesion, and efficient stress transfer between interfaces.

3.4. Composite, Hybrid, and other 2D Materials

The synergy of graphene and GRMs with nanoparticles and polymers is opening a vast panorama of possibilities for creating materials with tailored functionalities, improved performance, and enhanced sustainability. As researchers continue to explore the advanced properties of composite and hybrid materials, the potential for groundbreaking innovations in cultural heritage becomes increasingly promising.

The diversity of size, shape, structures, and surface properties of nanoparticles offers a wide spectrum of options to overcome inherent limitations, add functionalities, and engineer smart stimuli-responses. The richness and complexity of polymers further provide a platform from which advanced functional materials with tailored properties can be developed. Moreover, the synergistic combination of graphene and GRMs represents an alternative to overcome the inherent limitations of the approaches currently in use. Graphene and GRMs could confer UV protection or impart barrier effects to gas permeation, overcoming major drawbacks of currently used coatings. However, the use of hybrid and composite materials requires a major scientific effort as the role and contribution of each single component and the synergistic mechanism need to be elucidated in depth.

Other bidimensional materials such as hexagonal boron nitride (hBN) also represent an interesting new road. Indeed, it has been demonstrated that hBN and hBN/polymer hybrid coatings protect metals from corrosion[235,236] and oxidation,[237] and that hBN-based composite nanomaterials have antibacterial properties.[238,239] Moreover, these materials share common features with graphene, including high transparency, low reactivity, flexibility, and van der Waals adhesion.[240] However, the low maturity of fabrication techniques for hBN hinders further investigations as it does not offer large-area single-layer films alike graphene.[241]

3.5. Convergence of Protective and Diagnostic Technologies

Graphene and GRMs open the important opportunity to simultaneously protect and monitor artifact conservation, thanks to their properties. Coatings based on these materials can be designed to be transparent, highly conductive, and with extensive contact with the surface underneath. Therefore, on one side, graphene and GRMs can work as protective coatings, providing a shield to the piece of art. On the other side, they can act as high-performance sensing materials thanks to their remarkable electrical conductivity and high surface nominal area, whilst not affecting the appearance of artifacts (in particular, metals, dark-colored stone-based materials, and inks). Therefore, they can be used as invisible tags. This opens unprecedented ways to overcome a dichotomy in conservation science that has seen diagnostics and monitoring technologies separated from protective approaches, posing several issues and challenges. The synergistic combination of protective and sensing capabilities offers a comprehensive approach that addresses both preventative conservation and monitoring needs. Major scientific and technological effort together with synergies between complementary approaches is needed to develop this important breakthrough in cultural heritage conservation.

3.6. Long-Term Stability and Reversibility

Long-term stability of treatments stands as a fundamental aspect to be considered when preserving and restoring cultural heritage objects. The chemical, optical, and mechanical stability during the aging process, need to be evaluated on diverse and complex materials and this critical analysis should encompass both tests on replicas that mimic the morphology and composition of the artifacts, as well as assessments on real case studies.[242] Moreover, in-depth evaluations of the performance of protective coatings and consolidants are key aspects, particularly for artifacts exposed to outdoor environments, which endure challenges like rainfall, drastic temperature fluctuations, and potentially extreme climatic events. Understanding the response of the protective treatments is an important step and should be studied in situ during prolonged exposure times. To expedite this process, simulation models able to mimic standard aging conditions represent a key tool.[243] Once long-term stability has been evaluated, it becomes imperative to investigate the level of reversibility. The chance of removing graphene and GRMs exists theoretically, as these materials mainly interact with the substrate through weak van der Waals forces. However, the removal process should be carefully assessed at different timescales, including a thorough characterization of the artifact, to identify any residual or unstable chemical species. Indeed, the aging process could have a strong impact on this property as the modification and deterioration of the subsurface and the graphene and GRMs could have important consequences on reversibility after extended periods of time.

4. Conclusions

The preservation and conservation of cultural heritage represents a complex and ambitious endeavor, requiring customized protective and preventive solutions for a variety of materials exposed to changing environmental conditions. In this review, we have outlined the most relevant applications of graphene and GRMs on different substrates, ranging from metals to stone-based materials. We have also critically examined their potential as innovative alternatives to traditional formulations and treatments.

The advancements in graphene and GRMs in this realm are promising, but as demonstrated by this collection of works on the subject, which are relatively limited in number, there is still much work to be done. Deeper and more accurate investigations are needed to expand our understanding of the behavior of graphene and GRMs on various cultural heritage materials, as currently, the available results are case-dependent and limited by substrate and material type.

When used as protective coatings for paintings and figurative art, graphene, and GRMs have proven to be effective 2D barriers against not only light but also oxygen, moisture, and other harmful agents. Remarkably, treatment reversibility has also been demonstrated. Against the erosion of stone monuments exposed to harsh weather conditions and environmental factors, graphene, and GRMs provide valuable opportunities for the development of advanced surface protection treatments. When applied to building materials, they could play a significant role in mitigating biodeterioration phenomena. The remarkable bactericidal activity of graphene and GRMs against a wide range of bacteria has been largely reported, but the exact mechanism of action for the different materials remains elusive. The existing literature primarily focuses on the combined use of GRMs with other nanomaterials and future studies should focus on unraveling the bactericidal effect of each constituent. Comprehensive research efforts and the implementation of novel advanced characterization techniques are necessary steps to engineer surface coatings that provide the necessary roughness, density, and distribution needed to enhance their antimicrobial properties. Finally, the potential of graphene and GRMs as protective coatings of metal-based historical artifacts has not yet been explored, but they have demonstrated promise as potential solutions to mitigate corrosion of metallic substrates in industrial contexts. The existing literature already offers a valuable foundation for the design of graphene and GRMs-based coatings capable of achieving effective anti-corrosion performance on cultural heritage samples.

Regarding the consolidation of building materials, graphene, and GRMs represent a significant opportunity for the development of highly effective consolidants, even if currently the mechanism of interaction between GRMs and the complex cement matrix is not clear. A deeper understanding of such interactions is necessary to support the development of an experimental design based on a clear structure-function relationship. Key features such as size, surface properties, and presence of functional groups require major attention, as well as the development of advanced techniques to study the complex structure formed upon the addition of GRMs. A similar scientific advancement is also important for hybrid and composite materials in which the incorporation of graphene and GRMs can impart new properties necessary to enhance surface protection and consolidation. The paucity of reports in the existing literature underscores the need for further extensive scientific endeavors. These pursuits should focus on elucidating the physico-chemical properties of hybrid and composite materials, as well as the synergistic mechanisms emerging from the combination of different components.

Lastly, graphene and GRMs unlock outstanding possibilities in both diagnostic and monitoring applications. Properties of graphene-based composites and hybrid materials, like transparency and high conductivity, have the potential to significantly pave the way for the development of a new monitoring technology. They could usher in the next generation of continuous monitoring devices and point-of-use diagnostics characterized by high sensitivity and selectivity, with the added advantage of being directly applicable to the object itself.

We anticipate that the growing interest in employing graphene and GRMs for the purposes of treating cultural heritage could, in the coming years, result in significant advancements in the areas of protection, consolidation, and monitoring and ultimately expedite the development of advanced smart coatings and composites for the preservation of these assets.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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