



Preventing colour fading in artworks with graphene veils

M. Kotsidi^{1,2}, G. Gorgolis¹, M. G. Pastore Carbone¹, G. Anagnostopoulos¹, G. Paterakis^{1,2},
G. Poggi³, A. Manikas², G. Trakakis¹, P. Baglioni³ and C. Galiotis^{1,2}✉

Modern and contemporary art materials are generally prone to irreversible colour changes upon exposure to light and oxidizing agents. Graphene can be produced in thin large sheets, blocks ultraviolet light, and is impermeable to oxygen, moisture and corrosive agents; therefore, it has the potential to be used as a transparent layer for the protection of art objects in museums, during storage and transportation. Here we show that a single-layer or multilayer graphene veil, produced by chemical vapour deposition, can be deposited over artworks to protect them efficiently against colour fading, with a protection factor of up to 70%. We also show that this process is reversible since the graphene protective layer can be removed using a soft rubber eraser without causing any damage to the artwork. We have also explored a complementary contactless graphene-based route for colour protection that is based on the deposition of graphene on picture framing glass for use when the direct application of graphene is not feasible due to surface roughness or artwork fragility. Overall, the present results are a proof of concept of the potential use of graphene as an effective and removable protective advanced material to prevent colour fading in artworks.

Heritage assets promote economic development through tourism and the art industry, and improve quality of life in the general population, favouring social inclusion and equality¹. Therefore, strong efforts should be made for the preservation of art ensuring its transfer to future generations. New materials and techniques usually display marked sensitivity to environmental conditions, resulting in the short lifetime expectancy typical of modern and contemporary artworks². For example, the exposure of artworks to ultraviolet (UV) and visible light in the presence of oxidizing agents triggers colour changes, yellowing and fading³. The consequence of the above degradation mechanisms is the severe and irreversible alteration of artworks that are inestimable legacies of mankind. A notable example that has recently been reported⁴ is the colour change of Van Gogh's 'Sunflowers', in which crystals of red lead have turned into white plumbonacrite due to the reaction of paint impurities with light and CO₂. It is well known that the selective reflection of visible light by dyes results in their corresponding colours. The absorbed photons, however, especially those of higher energy, can excite molecules from the ground state, triggering a series of chemical reactions resulting in colour changes or fading. Photodegradation processes induce irreversible colour alterations that cannot easily be predicted or prevented. Among all the environmental parameters that can affect art materials, light exposure is evidently the only one that cannot be controlled without any impact on the visual appearance of the artwork.

Recent scientific developments can provide innovative solutions and methodologies capable of preserving our artistic, historical and architectural patrimony. Some researchers have pioneered the use of nanomaterials for the conservation of cultural heritage, which have been successfully tested over the years on several art masterpieces⁵. Herein we examine the applicability of graphene as a protective coating for artworks such as graphic art pieces and drawings. One important characteristic of graphene is that it exhibits high in-plane stiffness and strength^{6,7} but it can easily be flexed due to its

extremely small (atomic) thickness. Furthermore, it is impermeable to harmful compounds, such as oxygen, moisture⁸ and corrosive gases^{9,10} and can adhere quite easily to substrates through the formation of van der Waals bonds^{11,12}. Thanks to these properties, along with hydrophobicity¹³ and light absorbance¹⁴, graphene appears to be an ideal candidate for the protection of artworks belonging to museums, collections and galleries, during storage and transportation. In addition, graphene adheres to any clean surface but, due to its atomic thickness, can easily be removed from it, in contrast to currently available commercial polymeric coatings. Thus, it exhibits a competitive advantage over other protective materials and substances for the protection of artworks from colour fading.

Nowadays, chemical vapour deposition (CVD) graphene films of up to 30 × 30 cm² can be routinely produced, while continuous roll-to-roll processes have been recently developed commercially¹⁵. Transfer of high-quality, large-area CVD graphene on different flexible substrates has been developed^{16–18} and several attempts to deposit graphene on bare paper have been reported^{19,20}. However, the direct deposition of graphene on artworks may not be straightforward since the wet transfer and hot lamination conditions can be detrimental for fragile painted substrates. The strategy we designed to prepare CVD layers of graphene and transfer them on mock-ups and real artworks using a tailor-made roll-to-roll approach²¹ is shown in Fig. 1 and Supplementary Fig. 1. In particular, high-quality CVD monolayer graphene was employed in the process (Supplementary Fig. 2). The use of a pressure-sensitive adhesive film (PSAF) in the transfer process has been demonstrated to enable graphene wetting on the final substrate²², thus maximizing the contact area and van der Waals interactions. Also, the low work of adhesion between the PSAF and graphene, compared with that between the graphene and the destination surface, facilitates the transfer (see theoretical analysis reported in Supplementary Discussion and Tables 1 and 2) that can be carried out at mild pressure and temperature conditions (Methods), without the use of surface modifier or adhesives¹⁹.

¹Institute of Chemical Engineering Sciences, Foundation for Research and Technology – Hellas (FORTH/ICE-HT), Patras, Greece. ²Department of Chemical Engineering, University of Patras, Patras, Greece. ³CSGI & Department of Chemistry, University of Florence, Sesto Fiorentino, Italy. ✉e-mail: c.galiotis@iceht.forth.gr

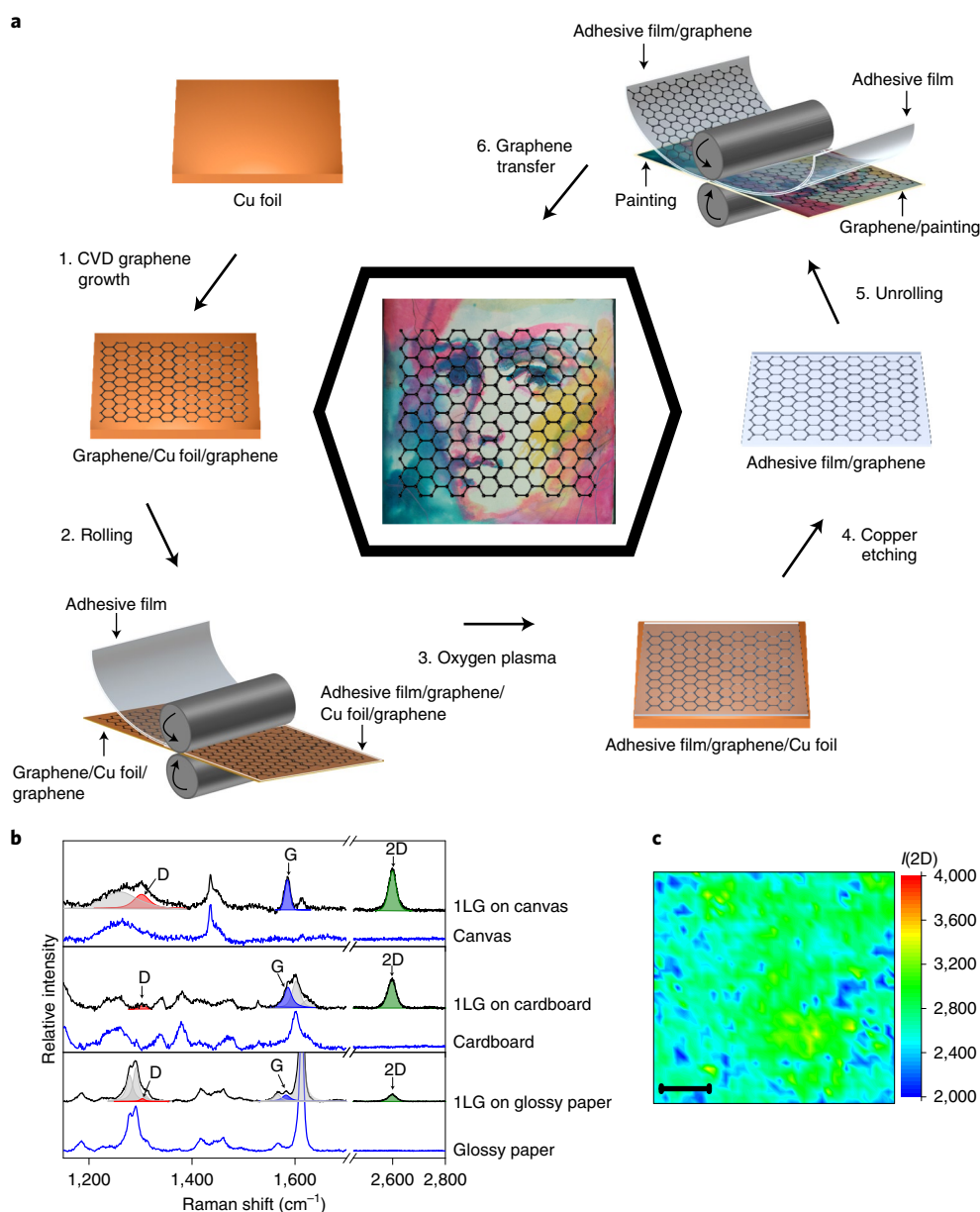


Fig. 1 | Graphene deposition onto artworks. **a**, Schematic illustration of the roll-to-roll process used to transfer graphene onto mock-ups and real artworks⁴⁴. **b**, Representative Raman spectra of bare and coated substrates with a monolayer graphene veil (1LG). Lorentzian function fits (coloured peaks) are superimposed on the experimental data. **c**, Spatial distribution of the intensity of the 2D peak, $I(2D)$, for large-sized CVD graphene sheet on glossy paper. Scale bar, 200 μm .

Furthermore, we demonstrate that the proposed roll-to-roll method does not affect the mechanical integrity of typical paper substrates used in graphic arts (Supplementary Fig. 3).

Using the proposed method, graphene can be successfully transferred over different substrates (that is, glossy paper, cardboard and canvas), as demonstrated by Raman spectroscopy. In fact, the presence of the graphene Raman graphitic (G) and second order (2D) peaks²³ is evidence of the successful deposition of a graphene veil onto artworks (Fig. 1b). More specifically, the clearly observed 2D peak is strong and symmetrical; however, the identification of G and defect-sensitive D peaks is not straightforward due to the superimposing spectral background of the substrates and requires peak deconvolution (Methods). Following this, the G peak has been found to be located at $\sim 1,585 \text{ cm}^{-1}$ for all the systems, thus revealing a slight residual compression of graphene

after transfer. Finally, a very small D peak is discerned for graphene transferred on glossy paper and cardboard, thus demonstrating that the defect density is low after transfer on moderately rough papers. On the contrary, for canvas, which is the substrate with the highest root-mean-squared roughness ($R_q \approx 3.9 \mu\text{m}$), a notable D peak is observed by the deconvolution analysis, and this indicates a higher defect density for substrates with higher roughness (Supplementary Fig. 4). Moreover, the homogeneous distribution of intensity of the 2D peak presented in the Raman mapping shown in Fig. 1c confirms that graphene can be successfully transferred over large surfaces with high coverage using the roll-to-roll process employed here. Furthermore, scanning electron microscopy images of paper with and without graphene also prove the presence of graphene, highlighting its typical wrinkled and folded morphology (Supplementary Fig. 5).

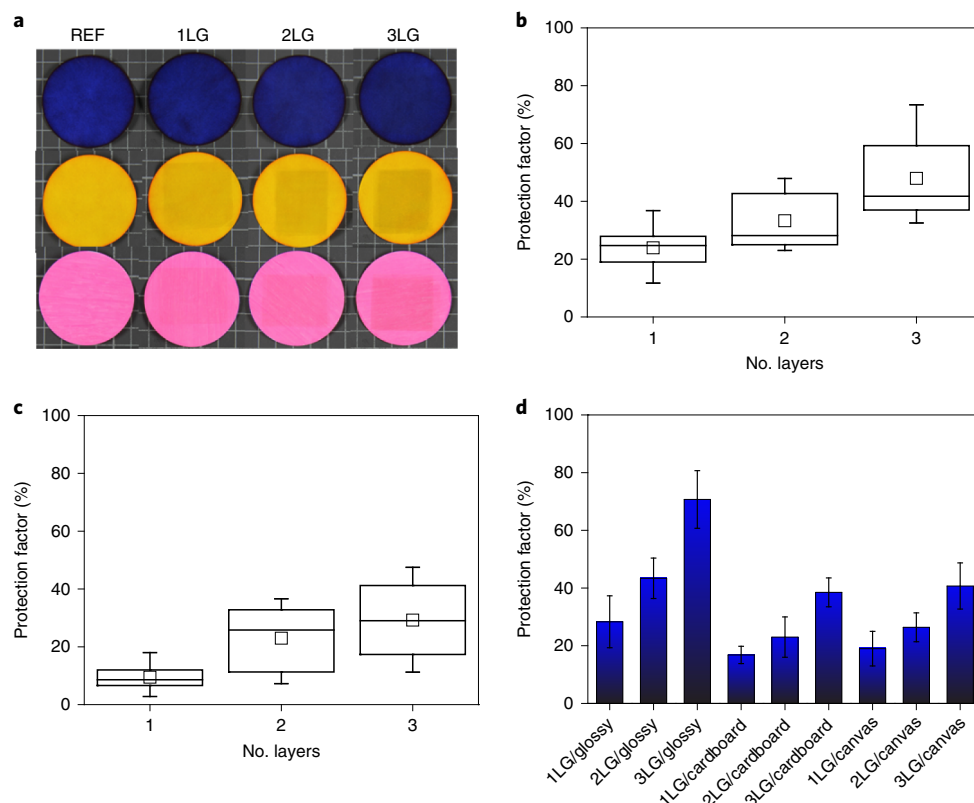


Fig. 2 | Ageing of mock-ups with graphene veils. **a**, Pictures of coloured mock-ups, without and with mono-, bi- and trilayers of graphene (respectively, REF, 1LG, 2LG, 3LG). **b**, Protection factor as a function of N layers for different mock-ups upon ageing with UV light. **c**, PF as a function of N layers for different mock-ups upon ageing with visible light. **d**, Protection factor for different substrates featuring blue colour upon ageing with UV light. In **b** and **c**, box plots show mean (\square), median, quartiles (boxes) and range (whiskers) of PF values. In **d**, error bars represent s.d.

By repeating the roll-to-roll procedure on the same substrate (meaning on the PSAF and not the final target substrate, which is the art object), multilayered graphene films can be deposited. Preliminary tests on the use of graphene to protect artworks were conducted on paper mock-ups featuring several light-sensitive dyes and inks, and covered with mono-, bi- and trilayer graphene (Fig. 2a). In all cases, the visual appearance of the graphene-coated mock-ups was investigated and the colour difference after deposition has been expressed in terms of the ΔE^* (colour difference) index (Supplementary Table 3). For samples covered with a monolayer graphene veil (number of layers, $N=1$), the measured ΔE^* values range from 1.9 to 8.9, depending on the type of colour. Generally, the presence of graphene is only perceptible under close observation when deposited on dark colours (such as blue), whereas it is perceptible at a glance when deposited on light colours (such as pink)²⁴. For $N > 1$, higher ΔE^* values are measured as a result of the gradual darkening of the covered surfaces (each layer absorbs 2.3% of visible light). It is worth noting that these values are still lower than those measured on the same set of samples covered using commercial products for the prevention of colour fading (Extended Data Fig. 1). On such samples, the ΔE^* values range from 17 to 20, which in our opinion cannot be considered acceptable for artwork conservation, in spite of the effective anti-fading protection that they provide. Furthermore, the tested commercial products are not easily removable from the artwork surface, in contrast to the graphene veils, which can easily be removed (see also below).

The experimental samples covered with mono-, bi- and trilayer graphene were artificially aged under different lighting conditions (neon and white/visible light lamps, UV radiation; Methods and

Supplementary Fig. 6) to induce the fading of the colours. To compare the colorimetric coordinates after ageing of bare samples versus samples covered with graphene, we have calculated a protection factor (PF), according to:

$$\text{PF (\%)} = \left(\frac{\Delta E^*_{\text{colour without graphene}} - \Delta E^*_{\text{colour with graphene}}}{\Delta E^*_{\text{colour without graphene}}} \right) \times 100 \quad (1)$$

As shown in Fig. 2b,c and Extended Data Fig. 2, monolayer graphene veils demonstrate an average PF of 23.8% after 5 days of exposure to UV light and 9.6% after 4 weeks exposure to visible light. Protection factor has been found to increase almost linearly with the number of graphene layers, regardless of the type of light used for the ageing of samples. More specifically, graphene veils have been found to provide protection factors as high as 73% upon ageing with UV light for $N=3$ but higher values are envisaged for $N > 3$. It is important to note here that PF offered by monolayer graphene has been found to vary with substrate type. In particular, the PF values are higher for glossy paper, while lower values are measured on quite rough surfaces such as canvas (Fig. 2d). This is in line with the better quality of deposited graphene obtained on nanometre-smooth substrates as shown by Raman spectroscopy (Fig. 1b); however, it is important to underline that even in the case of substrates with a microroughness, such as canvas (Fig. 2d), graphene veils still provide protection against colour fading.

Degradation of dyes is usually due to photolytic processes, which can involve reactions with oxygen (or singlet oxygen species generated

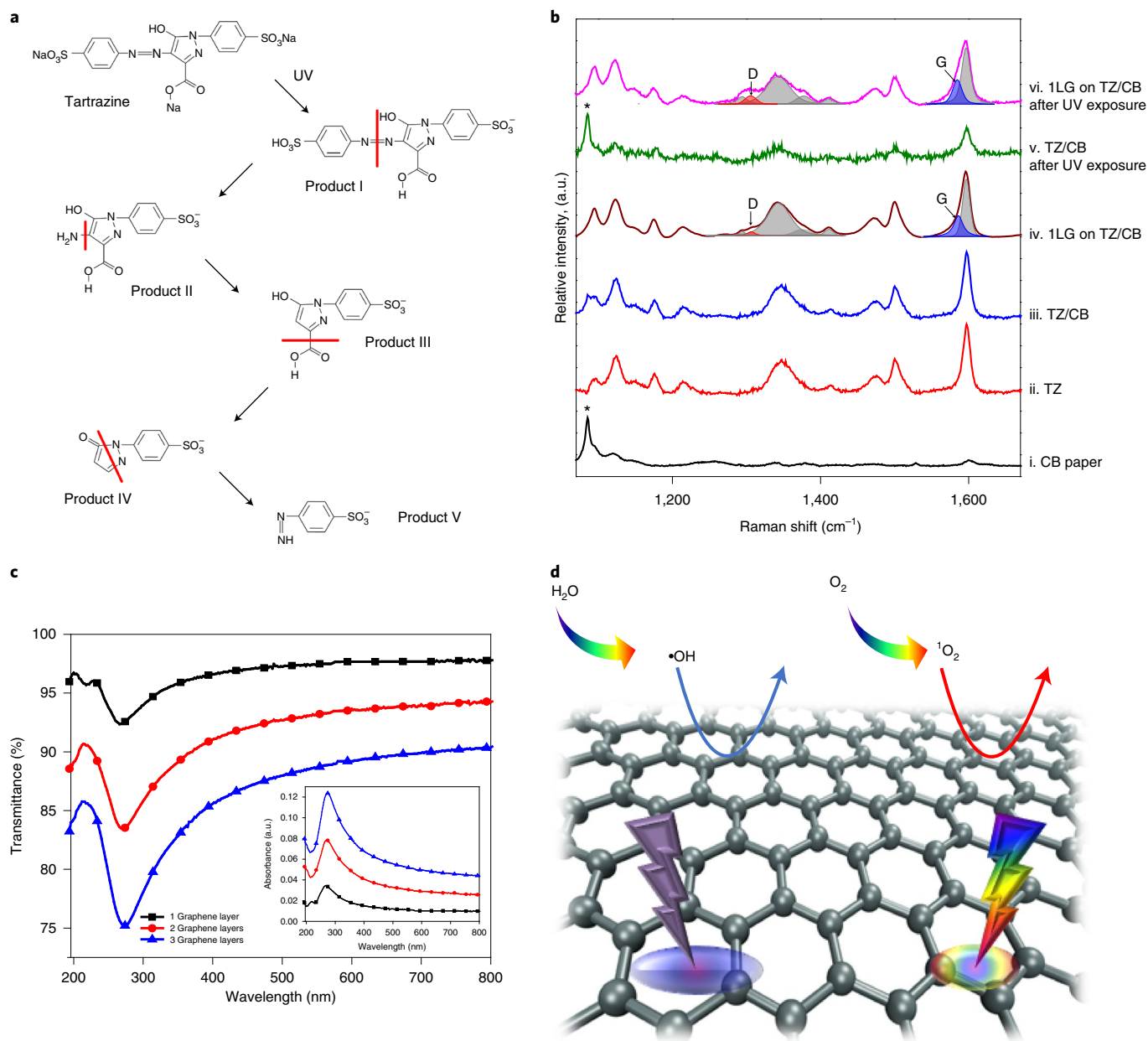


Fig. 3 | Mechanism of protection against photo-fading of colours. **a**, Mechanism of the degradation of tartrazine²⁶. **b**, Representative Raman spectra of cardboard (CB), tartrazine (TZ), tartrazine-coloured cardboard (TZ/CB) before and after ageing with UV light, single-layer graphene-coated tartrazine-coloured cardboard (1LG on TZ/CB) before and after ageing with UV light. Lorentzian fits (represented by the coloured peaks) are superimposed on the experimental data. **c**, Transmittance spectra of a graphene veil with increasing number of layers, synthesized with the CVD method. Inset: the corresponding absorption spectra in absorbance units. **d**, Sketch of protection mechanism provided by graphene veils against colours fading. a.u., arbitrary units.

by UV light) or water molecules^{25–29}. Tartrazine, a yellow azo dye, was used to monitor the protective effect of graphene coating against the colour fading in an oxidative environment. It is well known that tartrazine undergoes photolytic degradation under UV and visible radiation. Its complete discoloration is due to azo bond cleavage and subsequent rupture of the five-membered ring (Fig. 3a)²⁶. As shown in Fig. 3b, after exposure to UV light for 5 days, the characteristic Raman peaks of tartrazine weaken, compared with the cardboard peak located at $1,094\text{ cm}^{-1}$, as a result of the decomposition of the dye. However, when monolayer graphene is deposited onto tartrazine, its Raman spectrum remains unaltered after exposure to UV light. This provides a spectroscopic proof of the effectiveness of graphene against colour degradation. It is also important

to note here that in this process, the spectral features of graphene are still evident, although the small increase in the D/G ratio indicates a slight increase in defect density (shown in Fig. 3b(iv) and in Supplementary Fig. 7 for the other substrates). This is an important manifestation of the durability of graphene as a long-term protective layer of artworks. In addition to that, it is important to note that the graphene coating remains intact when the graphene/substrate system is subjected to a bending fatigue test (Supplementary Fig. 8), which simulates practical conditions of possible mechanical loading during the lifetime of the art object.

The protection against dye photodegradation provided by graphene can mainly be attributed to two of its most characteristic features, that is, its capability of absorbing UV light²⁷ and its

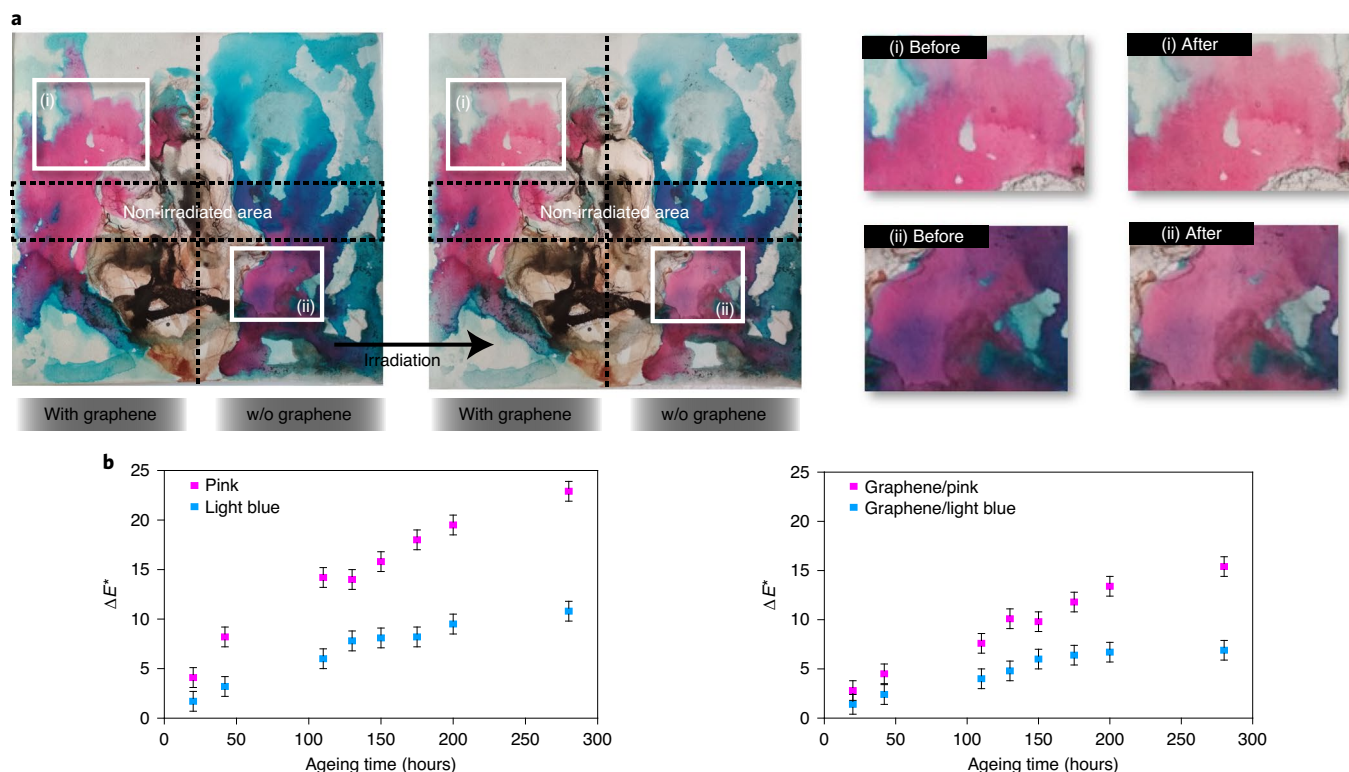


Fig. 4 | Ageing of an artwork with graphene. **a**, The painting entitled ‘Triton and Nereid’ before and after 130 hours of accelerated ageing under visible light. A central area was covered during ageing to be used as a reference. The difference induced in the pink areas (i, unprotected (w/o, without) and ii, protected by (with) graphene) is shown after 130 hours of artificial ageing, equivalent to about 65 years of museum exhibition. **b**, Colorimetric data acquired on pink and light blue dyes upon ageing, on unprotected areas (left) and areas protected with graphene (right).

impermeability to oxygen and water molecules^{30–33}. In Fig. 3c, the UV–visible transmittance and absorbance spectra for dry graphene transfer for one, two and three layers are shown. Graphene shows an asymmetric broad absorption peak at 270 nm, and its overall absorbance increases almost proportionally with increasing number of layers (Fig. 3c inset). In fact, taking into consideration that the reflectance of graphene is negligible, the UV absorbance at 270 nm for monolayer graphene reaches 8% and can reach 25% in the case of trilayer graphene. In the visible range, monolayer graphene absorbs about 2.3% of incident light allowing for the transmission of the remaining 97.7%. The application of an increasing number of graphene layers lead to a substantial increase in the absorbance within the visible range³². This is mainly due to the random (incommensurate) stacking of the hexagonal lattices of the upper and lower layers, which results in much weaker interlayer interaction compared with exfoliated (Bernal stacked) multi-layer graphene²¹. The explanation for this behaviour has already been presented in previous publications^{14,23} and has also been reproduced in Supplementary Fig. 9. Although graphene sheets of large dimensions produced by the CVD process are not free of defects (such as wrinkles, gaps and tears), it has been demonstrated (Supplementary Fig. 10) that they can still provide impressive shielding against diffusion of oxygen, moisture and other species (for example volatile organic compounds, VOCs) to the underlying substrate^{33–36}. The stacking of additional layers further improves the barrier effect since any discontinuities (gaps or tears) on a given graphene layer are covered/remedied by the subsequent overlying veils^{35,36}. The anti-fading function of graphene veils is therefore based on the synergetic mechanism involving the reduction of the harmful radiation transmitted to the artwork and the effective blockage of the diffusion of oxidizing agents (Fig. 3d).

Graphene is known to be impermeable to several corrosive gases^{37–39}. This point may represent a key factor in art conservation because environmental factors such as air pollutants, human emissions and VOCs, which are emitted from surrounding materials and from objects themselves, are known to represent a further source of damage for artworks in display or storage. In this regard, we have performed several tests on the fading of a green dye in the presence of acetic acid, which is one of the most common VOCs. As reported in the Supplementary Information, when a graphene layer is deposited on the coloured surface, the fading of the dye is impeded considerably (Supplementary Fig. 11). In addition to that, as depicted in Supplementary Figs. 12 and 13, the presence of graphene layers increases the hydrophobicity of the treated surface and prevents the penetration of oils on porous substrates (Supplementary Figs. 12 and 13). Overall, we can conclude that graphene veils have been found not only to protect colours from photo-fading but also from degradation induced by other harmful substances.

Having proven the effectiveness of graphene veils in reducing the fading of colours on mock-ups, further tests were then conducted on a series of real artworks that features highly light-sensitive inks. Here, artworks were artificially aged under lighting that is commonly used in museums and galleries (for example, neon and white light lamps). For instance, the artwork entitled ‘Triton and Nereid’, shown in Fig. 4a, was half covered with a single layer of CVD graphene, prior to being subjected to prolonged, accelerated ageing under white light (1,050 hours, which is equivalent to $\gg 200$ years of continuous exhibition of the artwork in museum lighting conditions, as estimated based on refs. ^{40,41}). The colour changes of light blue and pink dyes in the protected and unprotected areas were monitored over time and are reported in Fig. 4b. An overall protection

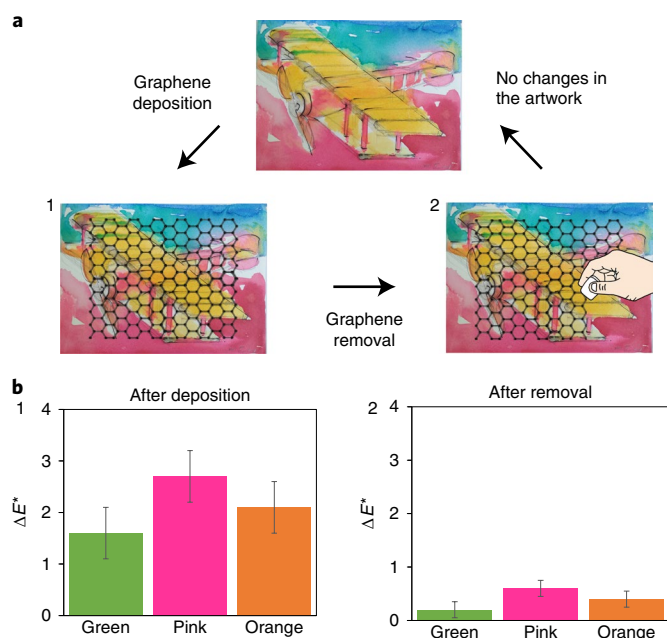


Fig. 5 | The removal of the graphene membrane from an artwork. **a**, A scheme showing the deposition and subsequent removal of graphene from 'Biplane, Handley Page H. P. 42' using a soft rubber eraser. **b**, Colorimetric data acquired during the process of graphene deposition and removal clearly show that the veil is almost invisible or only just noticeable on different colours ($\Delta E^*_{\text{Green}} = 0.2$, $\Delta E^*_{\text{Pink}} = 0.6$ and $\Delta E^*_{\text{Orange}} = 0.4$) and that it can be removed without damaging the optical integrity of the artwork.

factor (PF) for the light blue dye of ~38.5% and for the pink dye of 27.5% were obtained after 130 hours of exposure (equivalent to ~65 years^{40,41}). The different fading of the two spots can be ascribed to the different light-fastness of the dyes used by the artist. When aged under visible light for 1,050 hours, the light blue dye shows a PF of ~35%. Similar data were obtained for another artwork belonging to the same series, entitled 'Resistance' (Supplementary Table 4). This clearly demonstrates the effectiveness of monolayer graphene in the protection of highly light-sensitive dyes from fading providing a proof of concept on its potential use in art conservation.

Even if it is not always feasible, the reversibility of the treatment, especially in the case of paintings and graphic artworks, is a desired feature. As indicated above, graphene adheres to surfaces via weak bonds and this should favour its removability¹². Therefore, to verify our hypothesis, we deposited on 'Biplane, Handley Page H. P. 42' a single layer of CVD graphene, and then removed the protective coating, by means of a soft rubber eraser (Fig. 5a). To assess the effect of removal, colorimetric coordinates (ΔE^*) were recorded on three coloured spots before and after graphene deposition, and after the removal of the veil (Fig. 5b). The colour differences measured before deposition and after the removal of the graphene layer are within experimental error. This proves that the process is reversible and that the graphene veil can easily be removed without damaging the optical integrity of the artwork, as verified also by SEM inspection (Supplementary Fig. 14).

A final test was carried out on paper mock-ups featuring the pink ink used in real artworks, to check the condition of the colour underneath the graphene layer after ageing. To this aim, colorimetric coordinates were recorded (i) before and after graphene deposition; (ii) before and after ageing; and (iii) at the end of the ageing process after the removal of graphene. The results of the experiments are summarized in Fig. 6 and in Supplementary Table 5. As

shown, the colour that was not protected by graphene displayed a ΔE^* of ~10.2 (Sketch 1) after 70 hours. When graphene is present, the ΔE^* at the end of the ageing is ~4.6 (Sketch 2). Just after the removal of graphene using a rubber eraser (Fig. 5), a similar ΔE^* of 5.4 was recorded, which clearly demonstrates that the presence of graphene ensures the protection of the colour underneath (Sketch 3). Similar results were obtained after shorter ageing times, as reported in Supplementary Table 5.

Overall, we have demonstrated the successful roll-to-roll transfer of graphene on glossy paper, cardboard and canvas, and the effectiveness of graphene veils against colour fading upon exposure to radiation, oxidizing agents, and other harmful agents, such as VOCs and oils. It is clear that the roughness of the substrates, which in graphic artworks generally ranges from several nanometres to a few micrometres (Supplementary Fig. 4 and refs. ^{42,43}), can be a critical issue in the deposition of a monoatomic veil such as graphene and, consequently, on its protective action. For substrates with higher roughness, it is generally recognized that graphene can homogeneously cover only very small areas because the presence of asperities may result in cracks and tearing²⁰. Therefore, the direct deposition of graphene veils may not be envisaged for artworks with extremely rough surface or even embossed patterns, such as brushstroke-laden paintings, and for historical fragile artworks. Hence, we have explored a complementary, contactless graphene-based route for colour protection, which is based on the deposition of CVD graphene on picture framing glass. As reported in the supplementary information, the addition of monolayer graphene on a commercial museum glass can improve its protection factor without affecting its transparency (Supplementary Discussion and Extended Data Fig. 3), proving that, if the surface coverage of artworks is not feasible, a different, thus still effective, alternative solution based on graphene can still be available.

In conclusion, with graphene being a bidimensional barrier, not only to light, but also to oxygen, moisture and other harmful agents, this proof of concept could pave the way for developing ground-breaking solutions for the full protection of paintings and

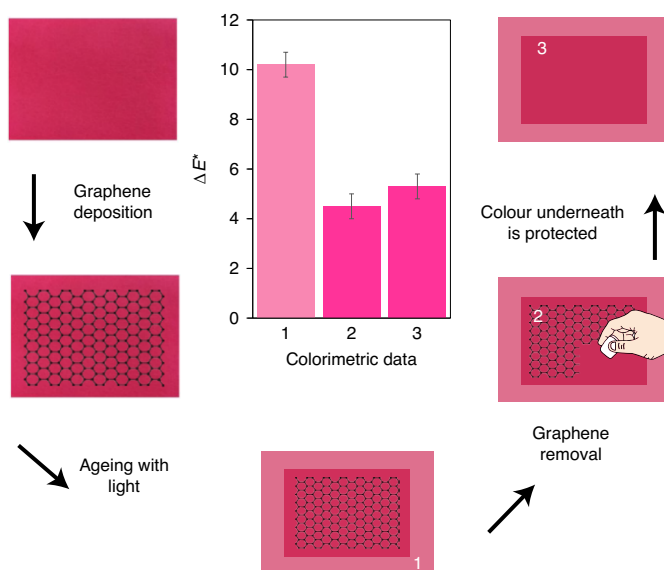


Fig. 6 | The protection of colour underneath the graphene layer. Diagram showing paper mock-ups featuring a pink dye, which were protected with graphene and then aged under visible light. At the end of ageing, the graphene layer was removed using a soft rubber eraser. Colorimetric data reported in the histogram were acquired during the process and clearly showed the effectiveness of graphene in protecting the pink dye from fading.

graphic artefacts, which would be useful both for display and during storage or transportation, common operations for museums, galleries and art collections (Supplementary Video).

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41565-021-00934-z>.

Received: 11 December 2019; Accepted: 20 May 2021;

Published online: 01 July 2021

References

- Dümcke, C. & M. Gnedovsky. *The Social and Economic Value of Cultural Heritage: Literature Review* (European Expert Network on Culture, 2013).
- Jablonski, E., Learner, T., Hayes, J. & Golden, M. Conservation concerns for acrylic emulsion paints: a literature review. *Tate Papers* 2 <https://www.tate.org.uk/research/publications/tate-papers/02/conservation-concerns-for-acrylic-emulsion-paints-literature-review> (2004).
- Sterflinger, K. & Pinzari, F. The revenge of time: fungal deterioration of cultural heritage with particular reference to books, paper and parchment. *Environ. Microbiol.* 14, 559–566 (2012).
- Vanmeert, F., Van Der Snickt, G. & Janssens, K. Plumbonacrite identified by X-ray powder diffraction tomography as a missing link during degradation of red lead in a Van Gogh painting. *Angew. Chem. Int. Ed. Engl.* 1889, 3607–3610 (2015).
- Baglioni, P., Carretti, E. & Chelazzi, D. Nanomaterials in art conservation. *Nat. Nanotechnol.* 10, 287–290 (2015).
- Tsoukleri, G. et al. Subjecting a graphene monolayer to tension and compression. *Small* 5, 2397–2402 (2009).
- Androulidakis, C. et al. Graphene flakes under controlled biaxial deformation. *Sci. Rep.* 5, 18219 (2015).
- Berry, V. Impermeability of graphene and its applications. *Carbon N.Y.* 62, 1–10 (2013).
- Su, Y. et al. Impermeable barrier films and protective coatings based on reduced graphene oxide. *Nat. Commun.* <https://doi.org/10.1038/ncomms5843> (2014).
- Spitz Steinberg, R., Cruz, M., Mahfouz, N. G. A., Qiu, Y. & Hurt, R. H. Breathable vapor toxicant barriers based on multilayer graphene oxide. *ACS Nano* 11, 5670–5679 (2017).
- Reina, A. et al. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano Lett.* 9, 30–35 (2009).
- Cho, D. H. et al. Effect of surface morphology on friction of graphene on various substrates. *Nanoscale* 5, 3063–3069 (2013).
- Taherian, F., Marcon, V., Van Der Vegt, N. F. A. & Leroy, F. What is the contact angle of water on graphene? *Langmuir* 29, 1457–1465 (2013).
- Mak, K. F., Ju, L., Wang, F. & Heinz, T. F. Optical spectroscopy of graphene: from the far infrared to the ultraviolet. *Solid State Commun.* 152, 1341–1349 (2012).
- Zhong, G. et al. Growth of continuous graphene by open roll-to-roll chemical vapor deposition. *Appl. Phys. Lett.* 109, 193103 (2016).
- Lee, W. H. et al. Simultaneous transfer and doping of CVD-grown graphene by fluoropolymer for transparent conductive films on plastic. *ACS Nano* 6, 1284–1290 (2012).
- Chandrashekar, B. N. et al. Roll-to-roll green transfer of CVD graphene onto plastic for a transparent and flexible triboelectric nanogenerator. *Adv. Mater.* 27, 5210–5216 (2015).
- Chen, X. D. et al. High-quality and efficient transfer of large-area graphene films onto different substrates. *Carbon N.Y.* 56, 271–278 (2013).
- Martins, L. G. P. et al. Direct transfer of graphene onto flexible substrates. *Proc. Natl Acad. Sci. USA* 110, 17762–17767 (2013).
- Kumar, S., Kaushik, S., Pratap, R. & Raghavan, S. Graphene on paper: a simple, low-cost chemical sensing platform. *ACS Appl. Mater. Interfaces* 7, 2189–2194 (2015).
- Bae, S. et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat. Nanotechnol.* 5, 574–578 (2010).
- Kim, S. J. et al. Ultraclean patterned transfer of single-layer graphene by recyclable pressure sensitive adhesive films. *Nano Lett.* 15, 3236–3240 (2015).
- Malard, L. M., Pimenta, M. A., Dresselhaus, G. & Dresselhaus, M. S. Raman spectroscopy in graphene. *Phys. Rep.* 473, 51–87 (2009).
- Schuessler, Z. Delta E. 101. [zschuessler.github.io/DeltaE/](https://github.io/DeltaE/) (2020).
- Keuch, P. *Kinetics: Fading of Triphenylmethanes Dyes—Pseudo First Order Reaction* (Univ. Regensburg, Institute of Organic Chemistry, 2004).
- Dos Santos, T. C. et al. Assessment of the breakdown products of solar/UV induced photolytic degradation of food dye tartrazine. *Food Chem. Toxicol.* 68, 307–315 (2014).
- Das, S. R. et al. Single-layer graphene as a barrier layer for intense UV laser-induced damages for silver nanowire network. *ACS Nano* 9, 11121–11133 (2015).
- Sarno, M., Rossi, G., Cirillo, C. & Incarnato, L. Cold wall chemical vapor deposition graphene-based conductive tunable film barrier. *Ind. Eng. Chem. Res.* 57, 4895–4906 (2018).
- Wang, M. et al. Graphene-draped semiconductors for enhanced photocorrosion resistance and photocatalytic properties. *J. Am. Chem. Soc.* 139, 4144–4151 (2017).
- Choi, K. et al. Reduced water vapor transmission rate of graphene gas barrier films for flexible organic field-effect transistors. *ACS Nano* 9, 5818–5824 (2015).
- Nam, T. et al. A composite layer of atomic-layer-deposited Al₂O₃ and graphene for flexible moisture barrier. *Carbon N.Y.* 116, 553–561 (2017).
- Nair, R. R. et al. Fine structure constant defines visual transparency of graphene. *Science* 320, 1308 (2008).
- Kim, D. J. et al. Degradation protection of color dyes encapsulated by graphene barrier films. *Chem. Mater.* 31, 7173–7177 (2019).
- Seethamraju, S. et al. Million-fold decrease in polymer moisture permeability by a graphene monolayer. *ACS Nano* 10, 6501–6509 (2016).
- Seo, H. K. et al. Laminated graphene films for flexible transparent thin film encapsulation. *ACS Appl. Mater. Interfaces* 8, 14725–14731 (2016).
- Kim, H. W. et al. Selective gas transport through few-layered graphene and graphene oxide membranes. *Science* 342, 91–95 (2013).
- Guo, F. et al. Graphene-based environmental barriers. *Environ. Sci. Technol.* 46, 7717–7724 (2012).
- Paranse, M. O., da Cunha, T. H. R., Ferlauto, A. S. & de Souza Figueiredo, A. S. Monolayer and bilayer graphene on polydimethylsiloxane as a composite membrane for gas-barrier applications. *J. Appl. Polym. Sci.* 134, <https://doi.org/10.1002/app.45521> (2017).
- Kidambi, P. R. et al. Assessment and control of the impermeability of graphene for atomically thin membranes and barriers. *Nanoscale* 9, 8496–8507 (2017).
- Calculating the Energy from Sunlight over a 12-Hour Period* (NASA, 2012); https://www.grc.nasa.gov/www/k-12/Numbers/Math/Mathematical_Thinking/sun12.htm
- National Optical Astronomy Observatory (NOAO). Recommended light levels. NOAO. https://www.noao.edu/education/QLTkit/ACTIVITY_Documents/Safety/LightLevels_outdoor+indoor.pdf (2015).
- Singh, S. P. A comparison of different methods of paper surface smoothness evaluation. *BioResources* 3, 503–516 (2008).
- Goyal, H. Physical properties. *Properties of Paper* <https://paperonweb.com/paperpro.htm#PhysicalProperties> (2015).
- Han, G. H. et al. Poly(ethylene co-vinyl acetate)-assisted one-step transfer of ultra-large graphene. *Nano* 6, 59–65 (2011).

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s), under exclusive licence to Springer Nature Limited 2021

Methods

Production of graphene veils. Graphene monolayers were synthesized on copper foils in an Aixtron BM Pro CVD chamber. The copper foils were supplied by Halcor (Viohalco) and used as the catalyst substrate. For graphene production, the foil was cut into $7 \times 7 \text{ cm}^2$, cleaned using isopropanol to remove any organic contamination and introduced into the CVD chamber. After closure, the pressure of the chamber was immediately pumped down to 0.1 mbar and then a mixture of argon/hydrogen (Ar/H_2) gases was introduced (250 SCCM/50 SCCM) with a pressure below 25 mbar. The foil was heated to $1,000^\circ\text{C}$ for 5 min for annealing. Afterwards, the sample was cooled down to 925°C while methane (CH_4) was introduced into the chamber (10 SCCM) as carbon feedstock to initiate the graphene growth on copper foil surface. After 5 min, the H_2 flow was terminated, the chamber was cooled down to 650°C and the CH_4 flow was also terminated. Then, the chamber was cooled down to room temperature under an argon atmosphere.

Graphene transfer method. The roll-to-roll method²², with no use of solvents or chemicals, is ideal for deposition of graphene without damaging the artworks. For that reason, a tailor-made roll-to-roll machine based on a commercial laminator was designed and built. The whole procedure is shown in Fig. 1a. Firstly CVD graphene is cleaned of dust, dirt and/or water molecules by purging with nitrogen gas on its surface. The specimen is then attached to one side of a commercial flexible polyester (PET)/silicone membrane by employing the roll-to-roll machine (Supplementary Fig. 1), at a rolling speed of $0.195\text{--}0.325 \text{ mm s}^{-1}$ and pressure of $0.1\text{--}0.5 \text{ MPa}$. The PET/silicone film was chosen as a backing substrate because it adheres well to the copper sheet with the graphene on top of it and is transparent and flexible. It is also resistant to the aggravating agents of subsequent processing steps (oxygen plasma, etching and pressure-transfer temperature). The graphene deposited on the other side of the membrane is then removed using oxygen plasma. Subsequently, a water solution of 0.1 M ammonium persulfate is used to etch the copper and, afterwards, deionized water is used to clean off any remaining dirt or ammonium persulfate residue. The PET/silicone/graphene membrane is left for at least 8 hours inside a vacuum chamber in order to be dehydrated. Afterwards, the membrane is ready to be transferred onto a paper substrate. For the graphene transfer, the reverse procedure of rolling, that is unrolling (or delamination) (Fig. 1a), is performed, using the same parameters indicated above, at a temperature of $50\text{--}55^\circ\text{C}$. For the deposition of bi-, tri- or multilayered membranes, we repeated the same procedure so as to have non-Bernal stacked multilayers.

The dry transfer method is based on the use of PSAF, such as the PET/silicone membrane adopted herein as a supporting layer. It takes advantage of the difference in wettability and adhesion energy of graphene with respect to PSAF and the target substrate. The PSAF layer is then simply peeled off from the target substrate, thus leaving the graphene membrane on the substrate. The basic parameters that define the success of the transfer process are estimated to be the transfer rate, temperature and pressure. Empirically, we have observed that the lower the transfer rate, the more effective is the graphene transfer. Finally, it was observed that mild heating to $50\text{--}55^\circ\text{C}$ has a positive effect on the transfer quality. Such an effect is attributed to the change of surface properties of PET/silicone since its surface energy is decreased by the thermal treatment. For the graphene membranes, the transfer process must be performed at a slow rate to ensure the homogeneous heating of graphene and the substrates to the desirable temperature by the laminator rollers. Regarding the transfer pressure, it was noticed that application of high pressure between the rollers results in a homogeneously transferred graphene film. Hence, the design of the laminator was based on the above parameters and findings. A commercial cold/hot laminator FJK 320 was modified to be used as the roll-to-roll transfer system. The system could operate up to 180°C and the initial motor speed was 3.5 r.p.m. , which corresponds to a linear velocity of 9.2 mm s^{-1} , since the roller diameter is 2.5 cm . The measured speed was much higher than that required for the given application, so the initial motor was replaced by the NEMA-17 stepper motor with an integrated planetary gearbox with a 99.51/1 drive ratio. The final configuration of the modified laminator is presented in Supplementary Fig. 1.

General information about colorimetric measurements. Colorimetric coordinates are extracted from reflectance spectra using standard illuminant D65 and a standard observer at 10° (CIE 1964). The colour difference between samples can be expressed in terms of the ΔE^* parameter, calculated from the colorimetric coordinates L^* , a^* and b^* which represent luminosity, red–green and blue–yellow parameters, respectively, as follows:¹⁵

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (2)$$

To compare the colorimetric coordinates after the ageing of unprotected and samples protected with graphene, we use the PF as described in the main text. Details about the preparation, characterization and ageing of mock-ups and real artworks are reported below.

Paper mock-up featuring a blue and a yellow dye: preparation, characterization and ageing. Filter paper disks (Whatman no. 1, 99% made with cotton fibres, paper density = 88 g m^{-2} ; diameter = 55 mm) and commercial cardboard disks (paper

density = 250 g m^{-2} ; diameter = 55 mm) were used to prepare paper mock-ups. On each filter paper disk, $600 \mu\text{l}$ of Methyl blue (Sigma-Aldrich, product number: M6900) and tartrazine (Sigma-Aldrich, product number: T0388) (2.5% (w/w) aqueous solution) were applied using a micropipette. On cardboard samples, 2 ml of each dye was applied using the same procedure reported above. Samples were left to dry under the hood for 48 hours. On each sample, graphene veils of one, two and three layers ($3.5 \times 3.5 \text{ cm}^2$) were deposited, using the roll-to-roll method described in the section Graphene transfer method. Graphene appears to follow the pattern of the surface with no apparent gaps or cracks. On some samples, two commercial protective products were applied using a brush: (1) Lascaux – UV Protect 1 (archival varnish with UV protection, Gloss 2072, 400 ml) and (2) Lukas spruh film (Spray Film with UV protection, Matt 2322, 400 ml). An unprotected sample was used as a reference. Before and after deposition, reflectance spectra were acquired using a Cary 100 UV–VIS spectrophotometer, working in a wavelength (λ) range of $400\text{--}700 \text{ nm}$ (with 1-nm resolution), equipped with an integrating sphere with a circular sampling spot (diameter = 1.5 cm). The error related to ΔE^* values obtained using this instrument was ± 0.5 .

All the samples were then artificially aged in an in-house-built ageing chamber, equipped with three Neon Light Colour 765 Basic Daylight Beghelli neon lamps. The average illuminance was $11,000 \text{ lx}$, relative humidity was 40% and temperature was 36°C . The ageing lasted 4 weeks. A portion of each sample was covered during the ageing, to be used as a reference. Every week, reflectance spectra were acquired as indicated above. Colorimetric coordinates were obtained as described in the section General information about colorimetric measurements. Data obtained in these sets of samples are reported in Supplementary Table 3 and Extended Data Figs. 1 and 2.

Paper mock-up featuring commercial artistic paints: preparation, characterization and ageing. A plethora of paper mock-ups featuring commercial artistic paints was also purchased and prepared. Specifically, commercial colours like yellow, red, blue and green (Genuine Epson inks) were inkjet-printed onto the three under-investigation paper substrates: glossy (photo-printed paper), cardboard and canvas. Additionally, some filter paper disks were painted with a commercial pink marker (Pink Neon Stabilo) like those shown in Fig. 2a. On each sample, graphene veils of one, two and three layers ($2 \times 2 \text{ cm}^2$) were deposited using the roll-to-roll method described earlier. For the case of the pink filter paper disks only, the graphene veils measured $3.5 \times 3.5 \text{ cm}^2$. Graphene appears to be following the pattern of the surface with no apparent gaps or cracks. A bare sample was used as a reference. Before and after deposition, reflectance spectra for the pink-painted samples were acquired using a Cary 100 UV–VIS spectrophotometer, working in a λ range of $400\text{--}700 \text{ nm}$, while for all the other samples, the colorimetric coordinates were recorded using an FRU WR-10 portable colorimeter. The error related to ΔE^* values obtained using this instrument was ± 0.5 .

The pink-painted samples were then artificially aged for 4 weeks in the same ageing chamber that was previously described. A portion of each sample was covered during the ageing, to be used as a reference. Every week, reflectance spectra were acquired as indicated above. The other samples were artificially aged in an in-house-built ageing chamber equipped with a panel of seven lights emitting white/visible light and under intense UV-C (254 nm) light. The ageing lasted 5 days under the intense UV-C light and 4 weeks under the white/visible light. After ageing, the transferred graphene did not show any macroscopic defects such as cracks or wrinkles. All these samples are reported in Supplementary Table 3.

Raman spectroscopy. Raman spectroscopy was adopted for spectroscopic characterization of the materials at different stages of this study, namely the material preparation, the investigation of the degradation mechanism and the durability of graphene upon exposure to UV light. In all experiments, spectra were recorded at several points on each specimen using a Renishaw InVia Raman Spectrometer with a $1,200 \text{ grooves mm}^{-1}$ grating for the 785-nm laser excitation and a $\times 100$ lens. The power of the laser beam was kept below 1 mW to avoid heating of the specimen. Furthermore, regarding the effectiveness of graphene transfer, large-scale Raman mapping on glossy paper after graphene deposition was performed on a $1 \times 1 \text{ mm}^2$ area using a $\times 20$ lens at steps of $10\text{-}\mu\text{m}$. Raman spectra were baseline corrected and graphene peaks were fitted to Lorentzian functions. When graphene peaks were superimposed onto the peaks of the substrates, the necessary deconvolution process was applied. In this analysis, the Lorentzian components assigned to the substrates were held fixed, having had their parameters (position, full-width at half-maximum) evaluated from the spectra of the bare substrates.

‘Resistance’: characterization and ageing. The artwork ‘Resistance’ was donated by the artist. It is a painting in Indian inks on glossy paper placed over a canvas support. It measures approximately $20 \times 20 \text{ cm}^2$. To perform our experiments, half of the artwork was protected with monolayer graphene using the roll-to-roll method described in the section Graphene transfer method. Graphene appeared to follow the pattern of the painting surface with no apparent gaps or cracks. The artwork was then artificially aged in an in-house-built ageing chamber, equipped with three Neon Light Colour 765 Basic Daylight Beghelli neon lamps. The average illuminance was $11,000 \text{ lx}$, relative humidity was 40% and average temperature was

36 °C. The ageing lasted 16 weeks. A portion of the artwork was covered during ageing, to be used as a reference. Every 2 weeks, colorimetric coordinates on different spots were recorded using a X-Rite SP60 VIS portable spectrophotometer, with an integrating sphere with a circular sampling spot (diameter = 1.5 cm). The error related to ΔE values obtained using this instrument was ± 0.75 . After ageing, the transferred graphene did not show any macroscopic defects such as cracks or wrinkles. In Supplementary Table 4, data from the experiments conducted on this artwork are shown.

'Triton and Nereid': characterization and ageing. The artwork 'Triton and Nereid' was donated by the artist. It is a painting in Indian inks on glossy paper placed over a canvas support. It measures approximately $20 \times 20 \text{ cm}^2$. To perform our experiments, half of the artwork was protected with monolayer graphene using the roll-to-roll method described in the section Graphene transfer method. Graphene appeared to follow the pattern of the painting surface with no apparent gaps or cracks. The artwork was then artificially aged in an in-house-built ageing chamber, equipped with a panel of seven lights emitting white light. The ageing lasted a total of 1,050 hours. A portion of the artwork was covered during ageing, to be used as a reference. After ageing, the transferred graphene did not show any macroscopic defects such as cracks or wrinkles. Reflectance spectra were acquired using FRU WR-10 portable colorimeter. Colorimetric coordinates were obtained from reflectance spectra as described in the section General information about colorimetric measurements. The error related to ΔE values obtained using this instrument was ± 0.5 . In Fig. 4, pictures and data from the experiments conducted on this artwork are shown.

'Biplane, Handley Page H. P. 42': investigation of the removability of graphene. The painting 'Biplane, Handley Page H. P. 42' was donated by the artist. It is a painting in Indian inks on glossy paper placed over a canvas support. It measures approximately $20 \times 20 \text{ cm}^2$. This artwork was used to test the removability of monolayer graphene from the surface of the artefact. To do so, a graphene veil was placed using the roll-to-roll method described in section Graphene transfer method ($7 \times 7 \text{ cm}^2$). A soft rubber eraser (grey putty rubber) was used to remove the graphene layer after deposition. Before and after deposition, and after graphene removal, reflectance spectra were acquired using an FRU WR-10 portable colorimeter. Colorimetric coordinates were obtained from reflectance spectra as described in the section General information about colorimetric measurements. The error related to ΔE values obtained using this instrument was ± 0.5 . In Fig. 5, pictures and data from the experiments conducted on this artwork are shown.

Paper mock-ups featuring a pink dye: preparation, characterization and ageing. Cardboard (Bristol type) was used to prepare paper mock-ups. A pink ink (Carmine Red, Pelikan drawing ink) was applied on the samples using a paintbrush. Samples were left to dry under the fume hood for 24 hours. On each sample, a monolayer graphene veil ($7 \times 7 \text{ cm}^2$) was deposited, using the roll-to-roll method described in the section Graphene transfer method. Some samples were not protected with graphene and were used as references. The samples were then artificially aged in an in-house-built ageing chamber, equipped with a panel of seven lights emitting white light. The ageing lasted 70 hours. The bottom part of each sample was covered during ageing. At the end of ageing, the graphene was removed from the samples using the procedure described in the main text and in the section 'Biplane, Handley Page H. P. 42': investigation of the removability of graphene. Before and after deposition, upon ageing and after the removal of graphene, reflectance spectra were acquired using an FRU WR-10 portable

colorimeter. Colorimetric coordinates were obtained from reflectance spectra as described in the section General information about colorimetric measurements. The error related to ΔE values obtained using this instrument was ± 0.5 . In Fig. 6 and Supplementary Table 5, pictures and data from the experiments conducted on these mock-ups are shown.

Data availability

The data that supports the findings of this study are available from the corresponding authors on reasonable request.

References

45. Wyszecki, G. & Stiles, W. S. *Color Science: Concepts and Methods, Quantitative Data and Formulae* 2nd edn (Wiley Classics Library, 2000).

Acknowledgements

We acknowledge support from the European Research Council (ERC) through the GraphenART (779985) Proof-of-Concept project, and the APACHE (814496) project funded from the European Union's Horizon 2020 research and innovation programme. The painter M. Stavropoulou is sincerely thanked for donating original artworks for our experiments. C. Malliaris (FORTH/ICEHT) is thanked for designing and developing the roll-to-roll transfer system. G. A. Voyiatzis and G. Mathioudakis (FORTH/ICEHT) are thanked for performing the water vapour permeability measurements. D. Vroulias, V. Dracopoulos and T. Ioannides (FORTH/ICEHT) are thanked for performing the oxygen permeability measurements. Finally, the Laser, Non-Linear and Quantum Optics Laboratory of the Physics Department, University of Patras is acknowledged for the surface roughness measurements and the Plasma Technology Laboratory of the Chemical Engineering Department, University of Patras for the contact angle measurements.

Author contributions

M.K., G.G., M.G.P.C., G. Pa., G. Po. and G.T. designed and performed the experiments. M.K., G.A. and A.M. interpreted the data. M.G.P.C., G.G. and G. Po. drafted the manuscript. C.G. and P.B. conceived the work, participated in its design and coordination, supervised all experimental procedures and revised the manuscript.

Competing interests

A patent has been granted from the Hellenic Industrial Property Organisation (No. 1009757) while two applications (Nos. PCT/EP2019/085993 and EP21155800) have been submitted to the European Patent Office (EPO). The following authors are involved in the patents: M.K., G.G., M.G.P.C., G.A., G.Pa., G.Po., P.B. and C.G. The remaining authors (A.M. and G.T.) declare no competing interests.

Additional information

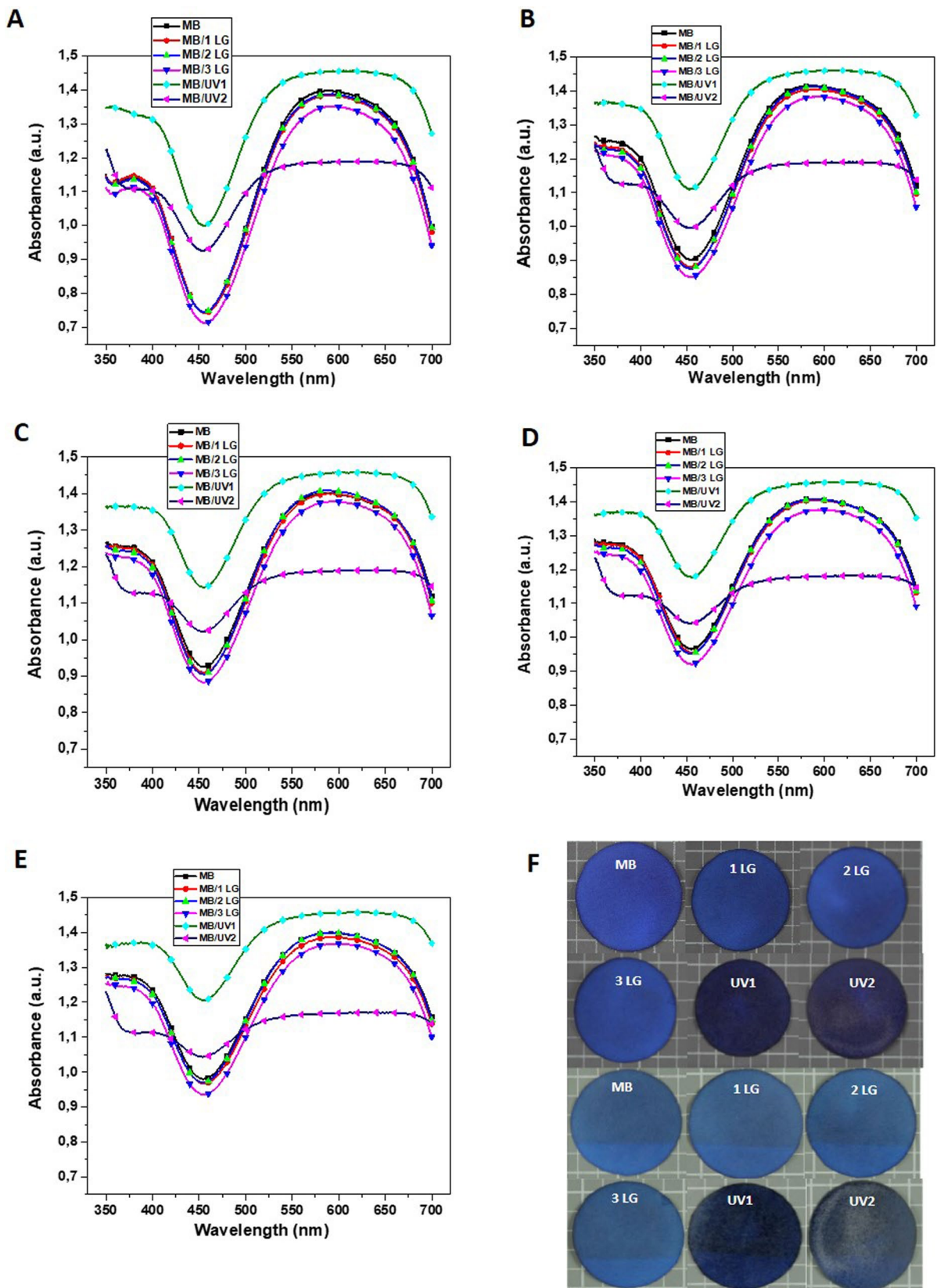
Extended data is available for this paper at <https://doi.org/10.1038/s41565-021-00934-z>.

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41565-021-00934-z>.

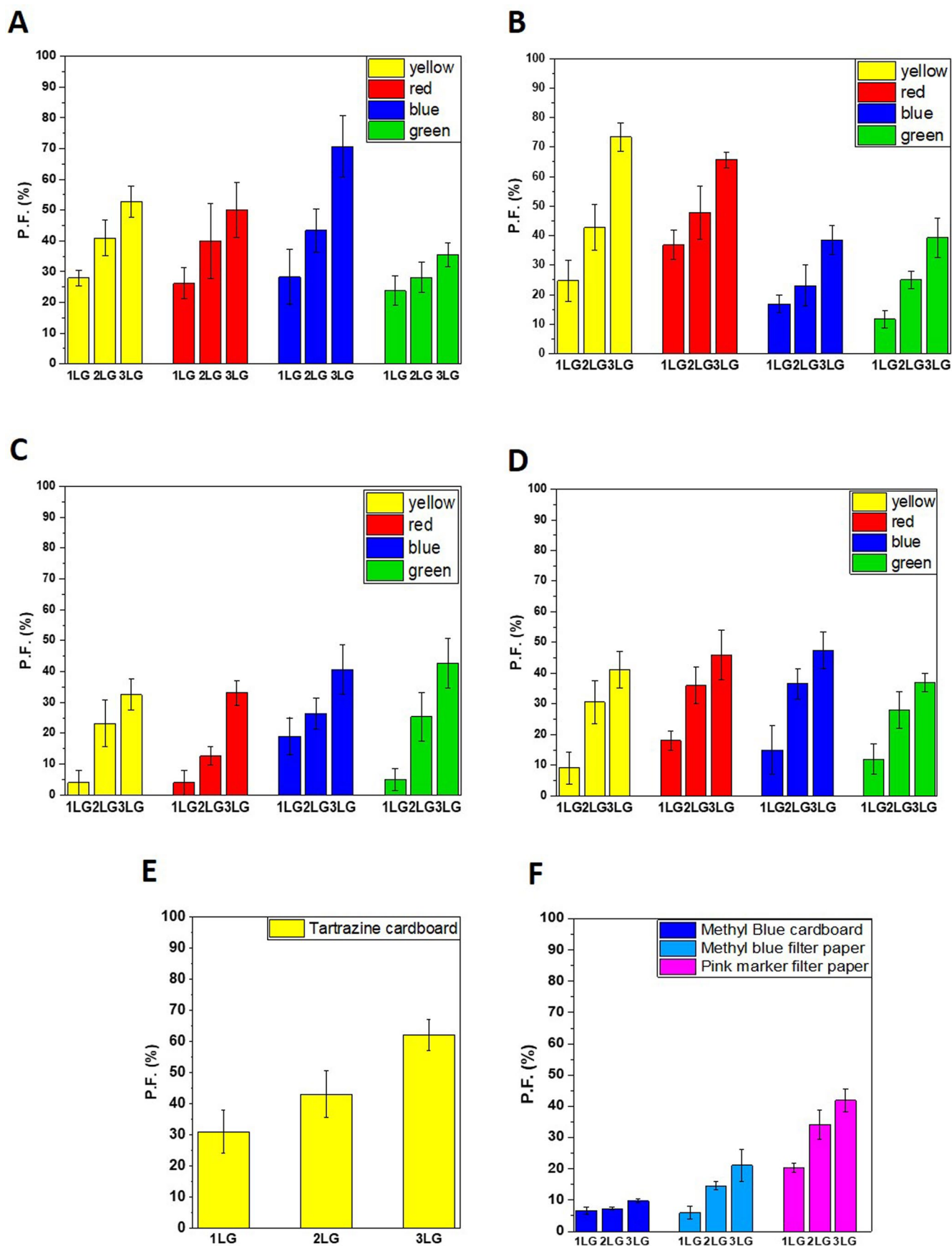
Correspondence and requests for materials should be addressed to C.G.

Peer review information *Nature Nanotechnology* thanks Gary Cheng, Jun Zhang and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permissions information is available at www.nature.com/reprints.

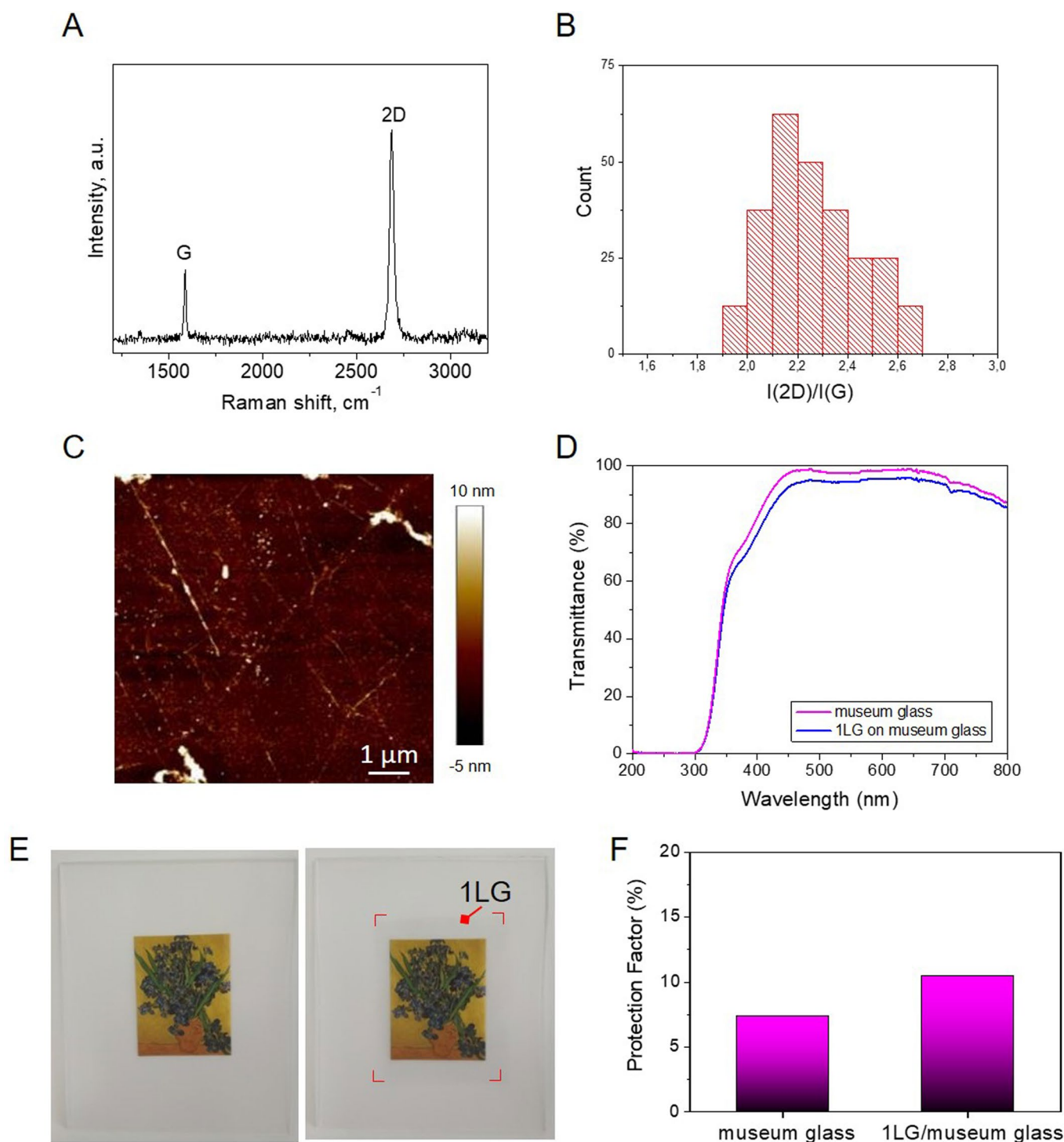


Extended Data Fig. 1 | Comparison of graphene veils with commercial products adopted in prevention of colour fading. Reflectance spectra before (a) and during ageing for 4 weeks (b to e) with Neon Light for mockups dyed with methyl blue (MB), coated with mono-, bi- and tri-layer graphene (1LG, 2LG and 3LG) and coated with commercial spray (UV1) and commercial varnish (UV2). Pictures of the specimens before (i) and after ageing (ii) are shown in F. PF for UV1 and UV2 after ageing are, respectively, 25.7% and 46.6%.



Extended Data Fig. 2 | See next page for caption.

Extended Data Fig. 2 | Protection factors (%) for all the investigated coloured mockups. Glossy paper (**a**), cardboard (**b**) and canvas paper (**c**) upon UV light exposure; glossy paper upon white/visible light exposure (**d**); Tartrazine on cardboard paper upon UV light exposure (**e**); cardboard/filter paper upon neon light exposure (**f**).



Extended Data Fig. 3 | Graphene-enhanced picture framing glasses. **a**, Typical Raman spectra of graphene transferred on “museum” glass. **b**, Statistical analysis of 2D/G intensity ratio from analysis of Raman mapping. **c**, Representative AFM topography of monolayer CVD graphene transferred on glass. **d**, Ultraviolet and visible transmittance spectra for “museum” glass with and without monolayer graphene. **e**, Pictures of commercial glass (FLABEG ARTControl UV60) and of the same glass coated in the central area with a single graphene layer. As shown, graphene is imperceptible and the glass transparency is not lost after graphene deposition. **f**, Protection factors for the commercial museum glass and the same coated with single layer graphene. Graphene coating offers an enhancement by ca. 40%.