Supporting Information

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Extraordinary Protective Efficacy of Graphene Oxide over the Stone-Based Cultural Heritage

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**Table S1.** Set of samples, with weather assays, nomenclature and characterization techniques.

| Size                  | Assay                      | Coating       | Name  | Techniques                                      |
|----------------------|----------------------------|---------------|-------|------------------------------------------------|
| 18 large samples     | Rainfall                   | Graphene oxide| NG10  |                                               |
|                      |                            |               | NG20  |                                               |
|                      |                            |               | NG30  |                                               |
|                      |                            | None          | N10   |                                               |
|                      |                            |               | N20   |                                               |
|                      |                            |               | N30   |                                               |
|                      | Thermal Changes           | Graphene oxide| RG10  | Photogrammetry, hydraulic press, biofouling |
|                      |                            |               | RG20  | observation                                    |
|                      |                            |               | RG30  |                                               |
|                      |                            | None          | R10   |                                               |
|                      |                            |               | R20   |                                               |
|                      |                            |               | R30   |                                               |
|                      | Thermal changes + Rainfall| Graphene oxide| AG10  |                                               |
|                      |                            |               | AG20  |                                               |
|                      |                            |               | AG30  |                                               |
|                      |                            | None          | A10   |                                               |
|                      |                            |               | A20   |                                               |
|                      |                            |               | A30   |                                               |
| 15 Medium samples    | Rainfall                   | Graphene oxide| NG1   | Surface color and optical microscopy (x10)    |
|                      |                            |               | NG2   |                                               |
|                      |                            | None          | N1    |                                               |
|                      |                            |               | N2    |                                               |
|                      |                            |               | N3    |                                               |
|                      | Thermal Changes           | Graphene oxide| RG1   |                                               |
|                      |                            |               | RG2   |                                               |
|                      |                            | None          | R1    |                                               |
|                      |                            |               | R2    |                                               |
|                      |                            |               | R3    |                                               |
|                      | Thermal changes + Rainfall| Graphene oxide| AG1   |                                               |
|                      |                            |               | AG2   |                                               |
|                      |                            | None          | A1    |                                               |
|                      |                            |               | A2    |                                               |
|                      |                            |               | A3    |                                               |
| 12 small samples     | None                       | Graphene oxide| N/A   | X-Ray Photoelectron Spectroscopy (XPS)        |
|                      |                            |               |       |                                               |
|                      |                            |               |       |                                               |
Figure S1. Concentration screening over time in aqueous medium by UV-Vis spectroscopy of GO (upper plot), and, for comparison, non-oxidized graphene (lower plot). Initial concentration of both nanomaterials = 0.05 mg/mL

On the one hand, it is clear how GO is much more water dispersible than any of its non-oxidized relatives. It remains unaltered in suspension at least during the first 8h of settlement. On the other hand, non-oxidized graphene seems to de-stabilize in aqueous environments very rapidly, in a matter of few minutes. At 8h, the latter loses around 50% of its initial concentration by precipitation, while GO will still stand. Right after 8h have elapsed, GO starts to precipitate, relatively slowly, ending up in a loss of about the 25% of its initial concentration. It is worth noting that, at least in the timespan of 24h, this GO precipitation is easily reversible by vigorous shaking and/or mild ultrasounds application. So the stability of GO in aqueous dispersion is good enough to work with, as for the requirements of our coating protocol.
Figure S2. XPS spectra (C1s core level) for GO-coated dolomite (center) and its separate constituents. The carbonates band at 289 eV end up depleted by the coverage of GO, pointing to the successful immobilization of such nanostructure over the stone surface.
Table S2. Additional core level binding energies (eV).

| Sample               | C 1s  | O 1s  | Ca 2p_{3/2} | Mg 2p | Al 2p | Si 2p ** |
|----------------------|-------|-------|--------------|-------|-------|----------|
| Dolomite             | 284.8 | 289.4(14)* | 531.8       | 347.3 | 50.2  | 74.5     | 102.8    |
| GO-coated dolomite   | 284.8 | 286.2 | 289.4 (4)*   | 531.8 | 347.4 | 50.3     | 75.5     | 102.8    |
| GO                   | 284.8 | 286.2 | 531.8        |       |       |          |          |

* The carbonate percentage in the C 1s core level is shown in parenthesis.
** Dolomite contains, besides magnesium and calcium carbonates, aluminosilicates.

Table S3. Atomic composition (at. % ratio) of dolomite samples.

|                    | C_{carbonate}/Ca | Mg/Ca | Al/Ca | Si/Ca |
|--------------------|------------------|-------|-------|-------|
| Dolomite           | 1.311            | 0.728 | 0.852 | 1.985 |
| GO-coated dolomite | 1.356            | 0.019 | 0.950 | 1.745 |

Figure S3. XPS spectra (C1s core level) to show the differences between zero (left) and three (right) GO coating passages. The depletion of the carbonates band again serves as a means to spot the presence of GO on the stone surface. The random presence of potassium (dependent on the sample specimen) may also be used as such.
Table S4. Sample specimens (small size) used for the colorimetric measurements, along with the NCS codings and variations of blackness and tones after climatic assays (rainfall + abrupt thermal changes).

| GO coating passages | Sample number | Colour codes | Variation of blackness (%) | Tone |
|---------------------|---------------|--------------|----------------------------|------|
|                     |               | Before erosion | After erosion | NCS |                     |
| 0                   | 1             | S 1010-Y30R   | S 1510-Y30R   | 5   | Same                |
|                     | 2             | S 2020-Y20R   | S 1510-Y30R   | -5  | Redder              |
|                     | 3             | S 1510-Y20R   | S 1510-Y30R   | 0   | Redder              |
| 1                   | 4             | S 1510-Y20R   | S 1510-Y30R   | 0   | Redder              |
|                     | 5             | S 1510-Y30R   | S 1510-Y30R   | 0   | Same                |
|                     | 6             | S 2010-Y20R   | S 2010-Y10R   | 0   | Yellower            |
| 2                   | 7             | S 1510-Y30R   | S 2010-Y30R   | 5   | Same                |
|                     | 8             | S 1010-Y30R   | S 2010-Y20R   | 10  | Yellower            |
|                     | 9             | S 1505-Y30R   | S 2010-Y20R   | 5   | Yellower            |
|                     | 10            | S 1510-Y20R   | S 2010-Y20R   | 5   | Same                |
| 3                   | 11            | S 1510-Y20R   | S 2010-Y20R   | 5   | Same                |
|                     | 12            | S 1510-Y20R   | S 2010-Y40R   | 5   | Redder              |
|                     | 13            | S 1510-Y20R   | S 2010-Y40R   | 5   | Redder              |
|                     | 14            | S 2010-Y20R   | S 3010-Y30R   | 10  | Redder              |
| 4                   | 15            | S 2010-Y30R   | S 3010-Y20R   | 10  | Yellower            |
|                     | 16            | S 2010-Y10R   | S 3010-Y30R   | 10  | Redder              |
|                     | 17            | S 1505-Y30R   | S 2010-Y20R   | 5   | Yellower            |
|                     | 18            | S 1505-Y30R   | S 3010-Y30R   | 15  | Same                |
Figure S4. Different biofouling events encountered after the rainfall simulation on big-size (20x10x30 cm$^3$ in average) dolomite stones: (a) green algae; (b) Lecidea fuscoatra lichen; (c) thalli of verrucaria (Heliotropium europaeum); (d) Aspicilia cinerea lichen (white shades). All these are very common biofouling microorganisms present on ornamental stones exposed in the open. In some lichens, sexual reproduction structures were found (indicating that the lichen was alive and proliferating). However, all of these were exclusively found on non-coated stones, while the GO-coated ones did not exhibit biofouling in any case.
Figure S5. Methodology for the climatic thermal changes simulations, shown for big size samples: (a) setup for the heating step; (b) setup for the cooling step; (c) control of the ambient temperature with a household thermometer; (d, e) control of the stones superficial temperature with an IR thermometer.
Figure S6. Temperature deviation study on different large stone samples (see table S1 for nomenclature) subjected to thermal changes with (blue lines) or without (red lines) associated
cycles of rainfall simulation. GO-coated samples are denoted with “G” in their names (dashed lines). Black vertical lines indicate the change from cooling to heating or vice versa.

The temperature assay was first performed at 25 min (Figure S6, top), to two sets of samples which started from a warm (“R” samples) or cold (“A” samples) temperature, and subjected to cooling or heating, respectively, followed by the reverse process. The temperature evolution (always measured on the stone surface) was not linear and exhibited variable thermal rates, but with no significant differences among samples with or without the GO coating. In only 25 min the samples experienced a thermal contrast of about 20ºC (in absolute value).

Then, a similar assay was carried out at a 30 min interval of heating/cooling (or vice versa), adding up a total processing time of 1h (Figure S6, center). In this case, similar observations could be made, again with no appreciable differences in the temperature readings when GO is present. In this case, the thermal contrast is smoother, as a difference of only 10ºC (in absolute value) is reached in 30 min.

Finally, a last assay was performed on a set of samples which were previously stabilized at -20ºC for 24h (Figure S6, bottom). These samples were heated, and after a first interval of high thermal change rate for the first 20 min, the behavior was quite linear until reaching room temperature. The longest linear section in this progressive change was found for an interval of 40 min (between 30 and 70 min), so it was eventually decided that each thermal cycle on stone samples had a duration of 40 min.
Figure S7. Geometry and distribution of the photographs of the sample and the model in Agisoft Metashape.