Graphene nanoplatelets and other 2D-materials as protective means against the fading of coloured inks, dyes and paints

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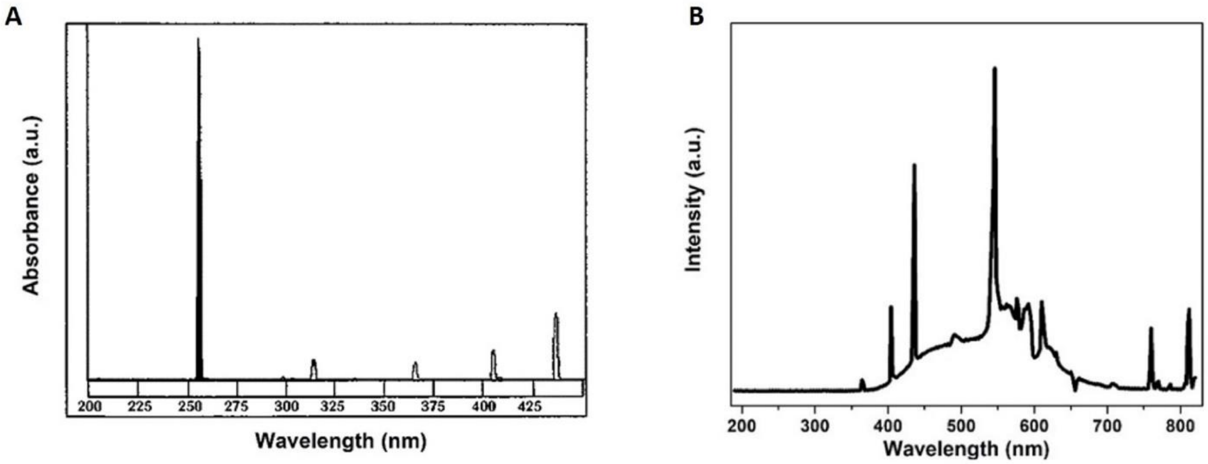
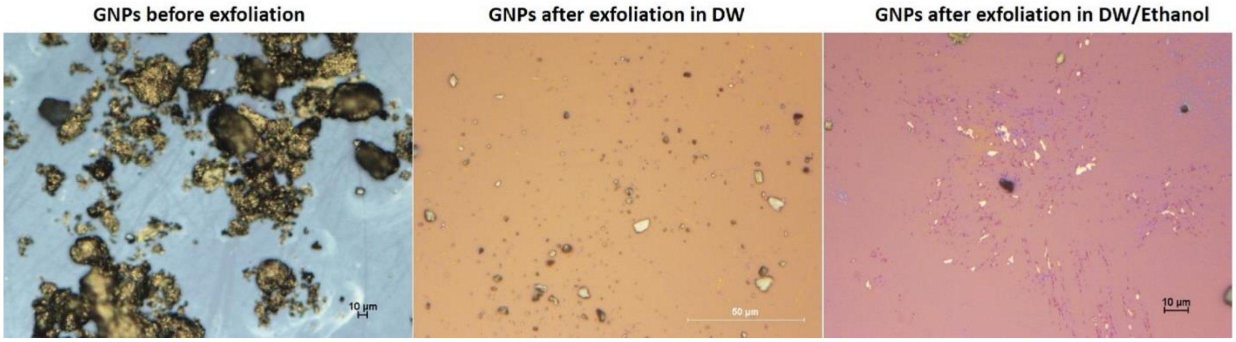


Figure S1: Emission spectra of lamps selected for the aging of mockups: 254 nm UV light without filter (A) and white light lamp (B).

Table S1: Power measured from the sensor for the UV-C lamp with a wavelength λ equal to 254 nm

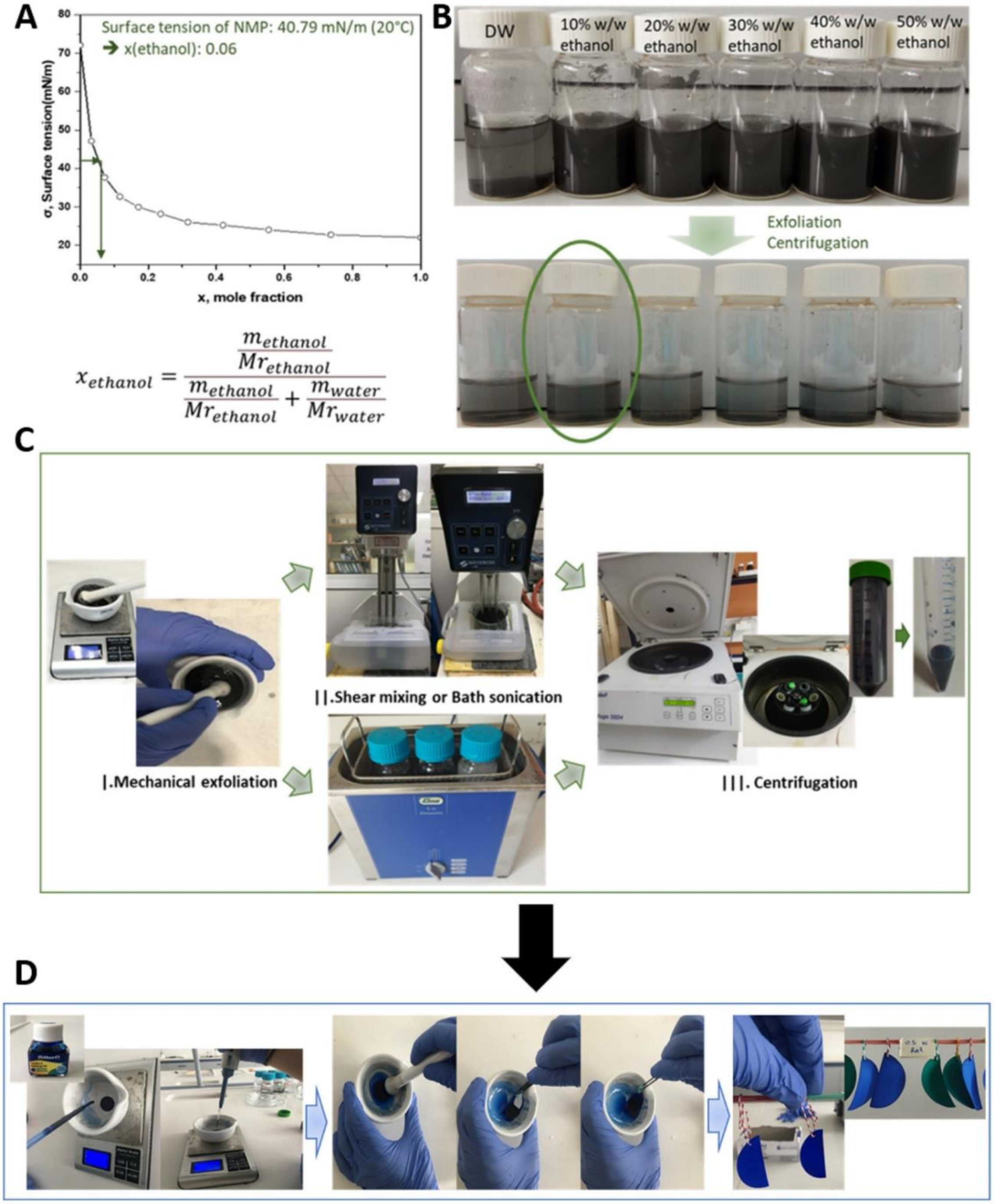
Distance from the sensor (cm)	Power (mWatts)
2	3-4
20	2-3


GNPs before exfoliation

GNPs after exfoliation in DW

GNPs after exfoliation in DW/Ethanol

Figure S2: From left to right: GNPs before the liquid phase exfoliation, after the exfoliation with distilled water and after the exfoliation with the binary mixture of distilled water/ethanol.



$$x_{ethanol} = \frac{\frac{m_{ethanol}}{Mr_{ethanol}}}{\frac{m_{ethanol}}{Mr_{ethanol}} + \frac{m_{water}}{Mr_{water}}}$$

Figure S3: A) Surface tension of water/ethanol solutions for various mole fractions of ethanol and the equation of calculation of the mole fraction of ethanol for a given amount of water. B) Samples of dispersions of GNPs in water/ethanol solvent for various ethanol content before (upper) and after (bottom) the exfoliation with shear mixing. The best dispersion of GNPs is highlighted. (C) Schematic of the followed steps for the preparation of dispersions of exfoliated GNPs with shear mixing exfoliation. D) Schematic of the process for the preparation of filter papers coloured with inks with GNPs.

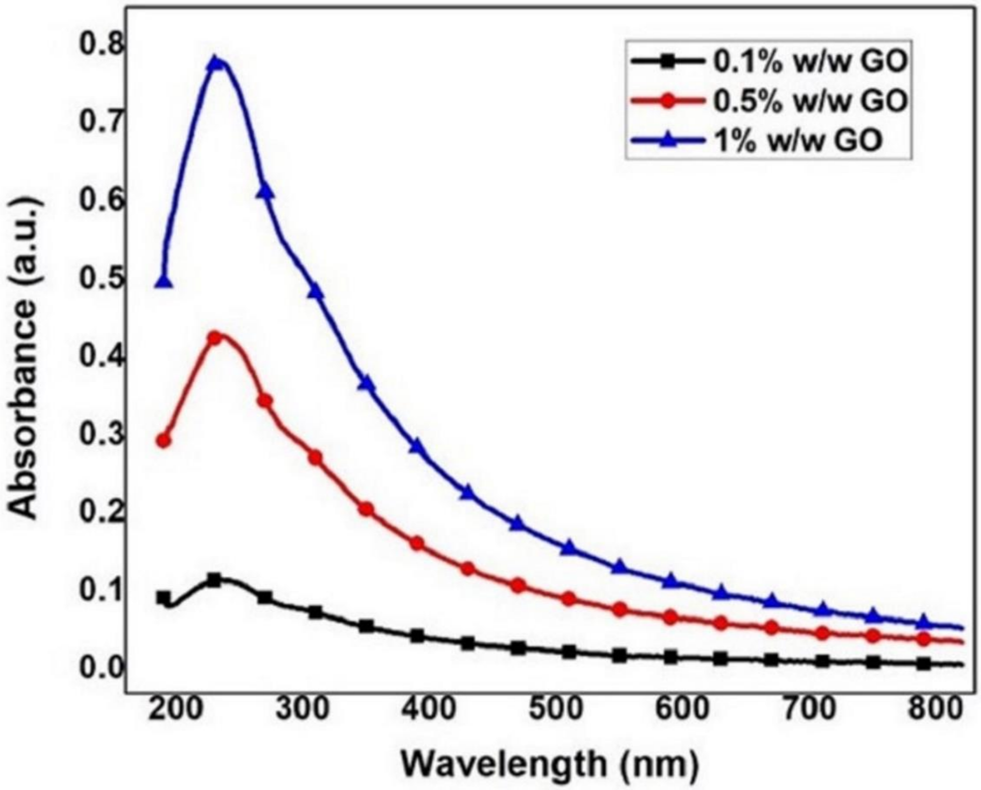
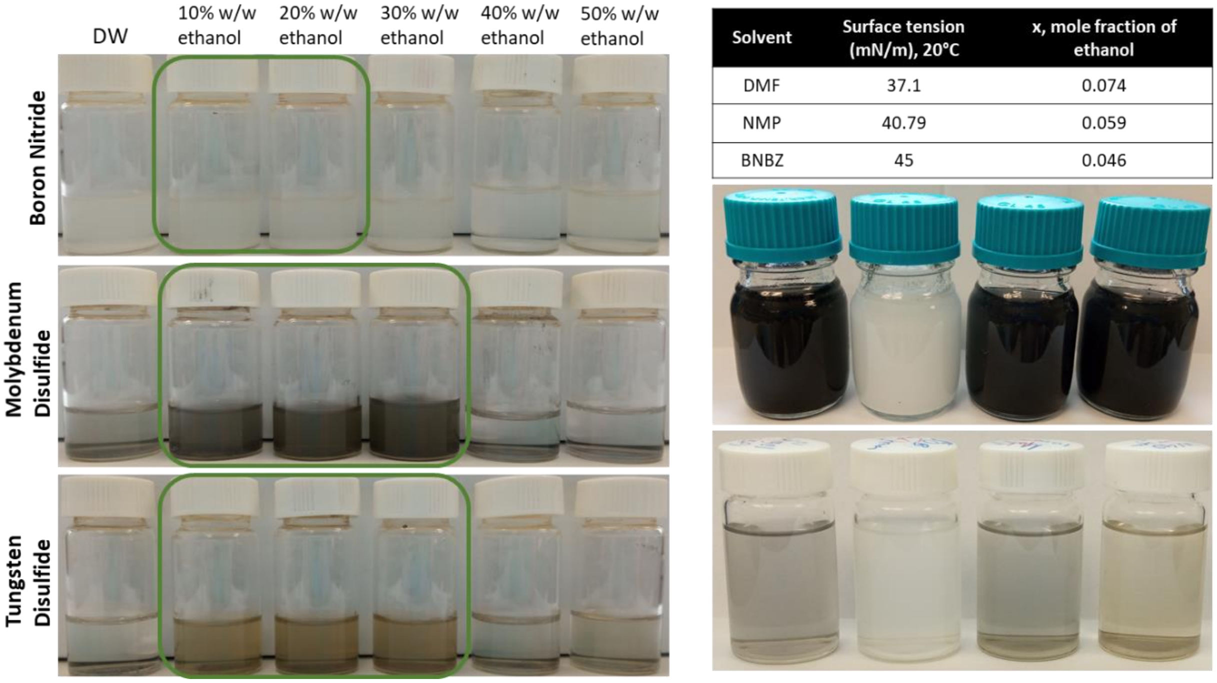


Figure S4: Absorbance spectra for dispersions of GO in water with concentrations equal to 0.1, 0.5 and 1% w/w.



Solvent	Surface tension (mN/m), 20°C	x, mole fraction of ethanol
DMF	37.1	0.074
NMP	40.79	0.059
BNBZ	45	0.046

Figure S5: On the left: Samples of dispersions of hBN, MoS_2, and WS_2 in water/ethanol solvent for various ethanol after the exfoliation with bath sonication. The best dispersions of 2D materials are highlighted. On the right, up: Mole fractions of ethanol in an aqueous solution to simulate common solvents for successful exfoliation. At the middle: Stable solutions of bulk 2D materials (from left to right): GNPs, hBN, MoS_2 and WS_2, dispersed in the suitable ethanol/water solution for each one. Bottom: Dispersions of exfoliated 2D materials (from left to right): GNPs, hBN, MoS_2 and WS_2 after bath sonication and centrifugation in the suitable ethanol/water solution for each one.

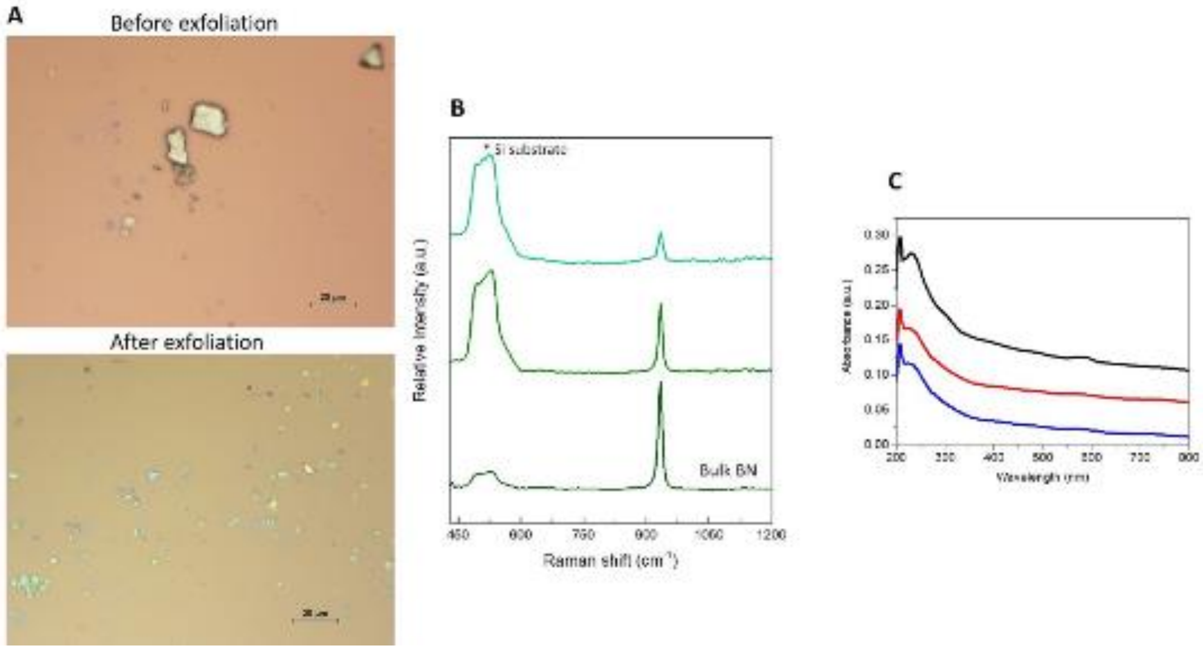


Figure S6: A) Representative Optical Microscopy images of hBN crystals before (top) and after (bottom) the applied exfoliation using a binary mixture of water/ethanol as solvent and ultrasonic sonication, B) Representative Raman spectra of hBN before (‘*Bulk*’) and after (top) the exfoliation. The relative intensity of the peak corresponding to the Si substrate is also shown for comparison reasons. C) Representative UV-Vis absorbance spectra for exfoliated hBN solution in water/ethanol with increasing concentration, heading from the bottom to the top.

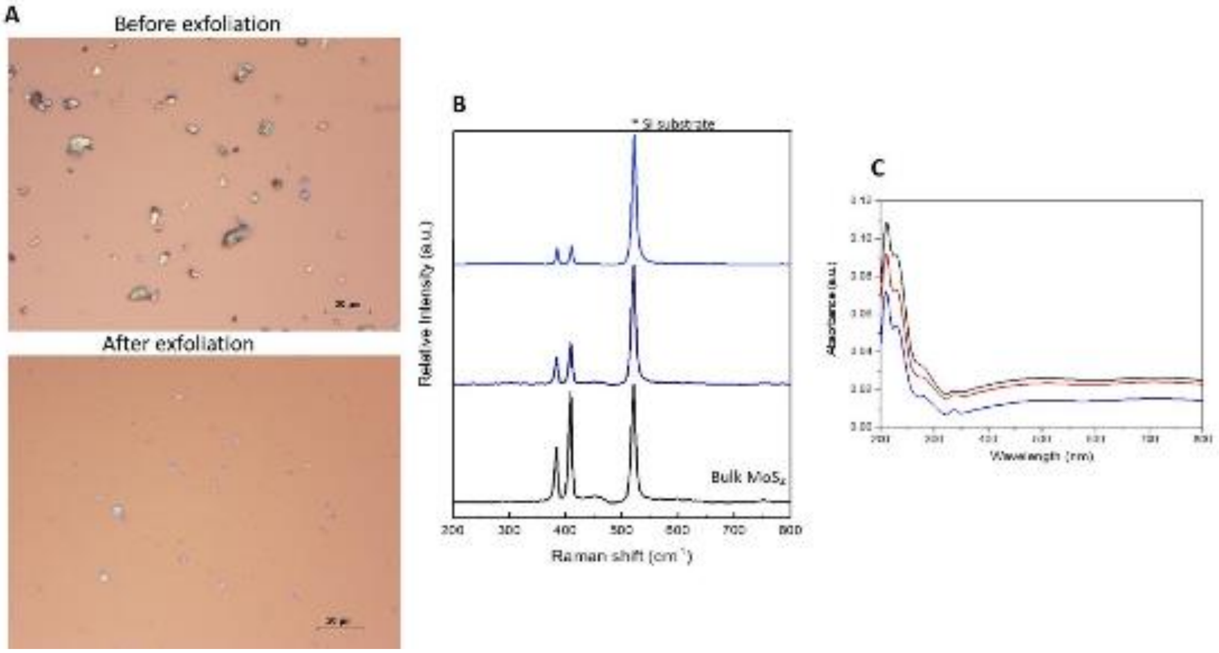


Figure S7: A) Optical microscopy images of MoS_2 crystals before (top) and after (bottom) the applied exfoliation using a binary mixture of water/ethanol as solvent and ultrasonic sonication, B) Raman spectra of MoS_2 before (‘*Bulk*’) and after (top) the exfoliation. The relative intensity of the peak corresponding to the Si substrate is also shown for comparison reasons. C) UV-Vis absorbance spectra for exfoliated MoS_2 solution in water/ethanol with increasing concentration, heading from the bottom to the top.

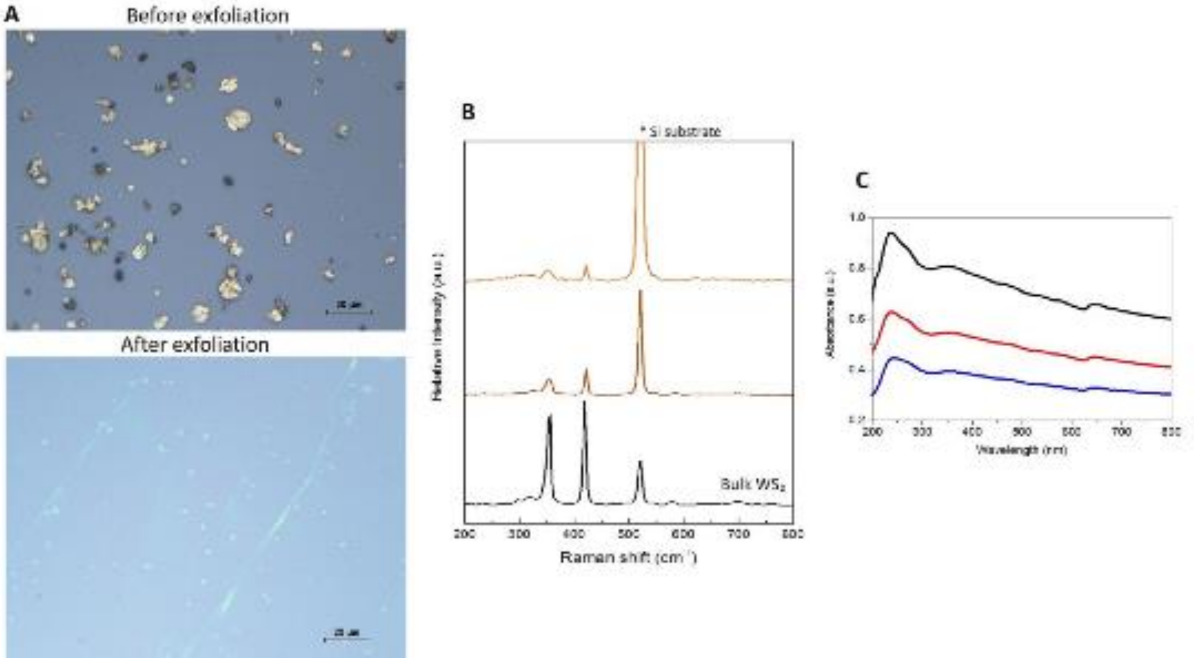


Figure S8: A) Representative Optical Microscopy images of WS_2 crystals before (top) and after (bottom) the applied exfoliation using a binary mixture of water/ethanol as solvent and ultrasonic sonication, B) Representative Raman spectra of WS_2 before ('*Bulk*') and after (top) the exfoliation. The relative intensity of the peak corresponding to the Si substrate is also shown for comparison. C) UV-Vis absorbance spectra for exfoliated WS_2 solution in water/ethanol with increasing concentration, heading from the bottom to the top.

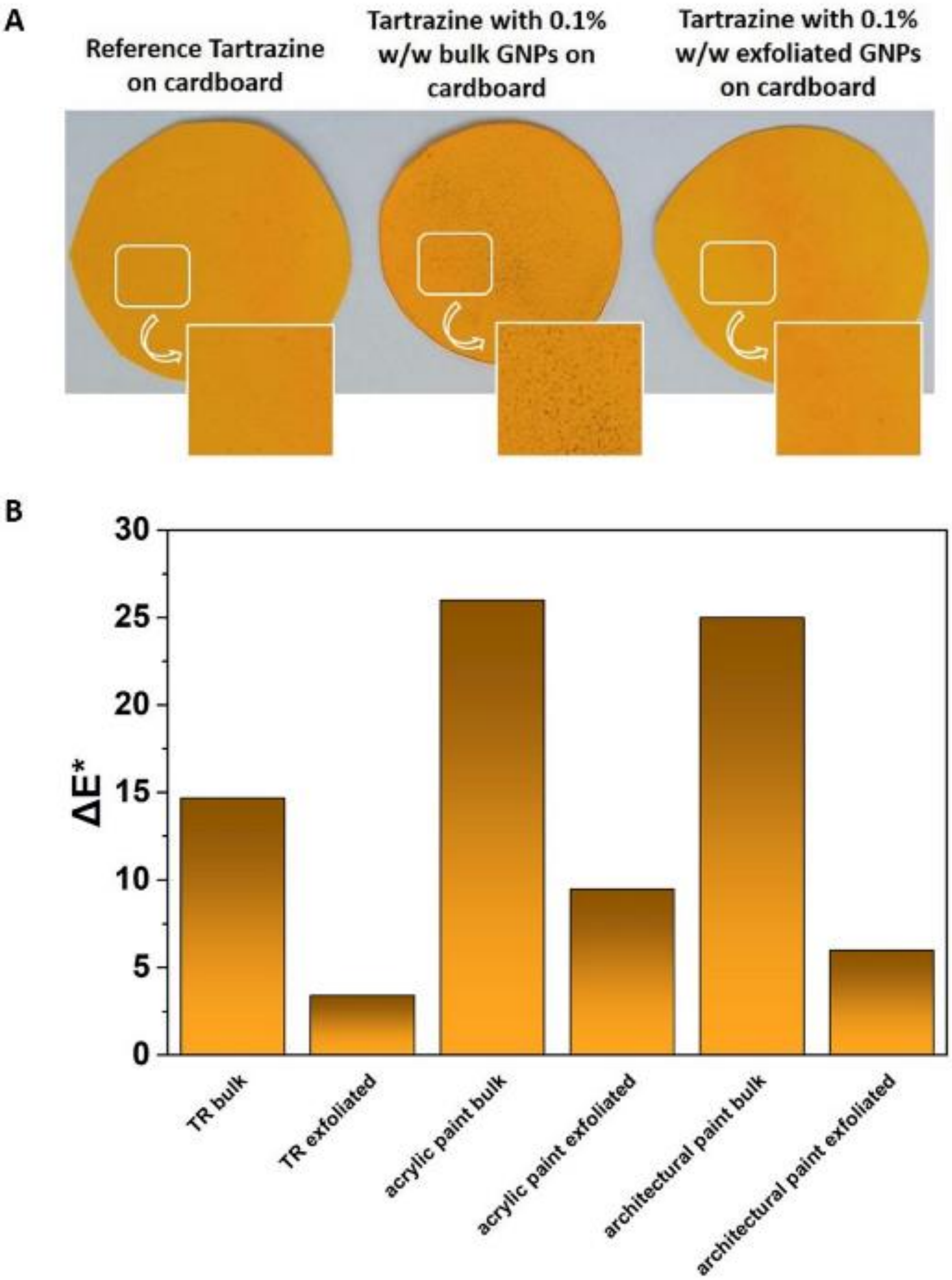


Figure S9: Yellow colour and GNPs. A) Three representative cardboards dyed with tartrazine. From left to right, a cardboard dyed only with tartrazine as reference, a sample dyed with a solution composed of tartrazine sol and 0.1% w/w GNPs water solution after ultrasonic sonication for 30 mins (coded here for simplicity as *bulk GNPs*) and finally a sample dyed with a solution composed of tartrazine sol and 0.1% w/w GNPs (GNPs-doped tartrazine solution) after the described exfoliation of the graphite powder. B) The colorimetric index ΔE* for several yellow colours used for this work, and, comparing the ultrasonic sonication (coded as *bulk*) technique to the described exfoliation (coded as *exfoliated*). From left to right, the first two columns regard tartrazine on cardboard, the following are about an acrylic paint (Royal Talens acrylic) again on cardboard and the last two describe yellow architectural paints.

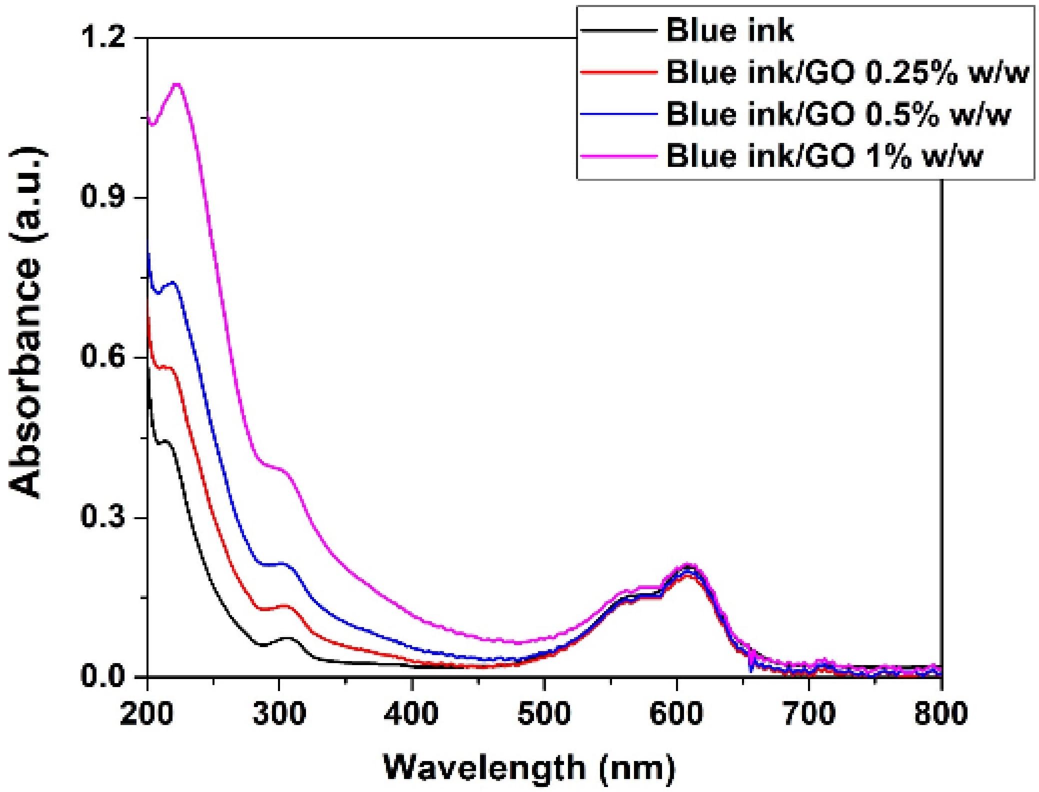


Figure S10: Representative absorbance spectra for commercial blue ink with the addition of GO diluted in water.

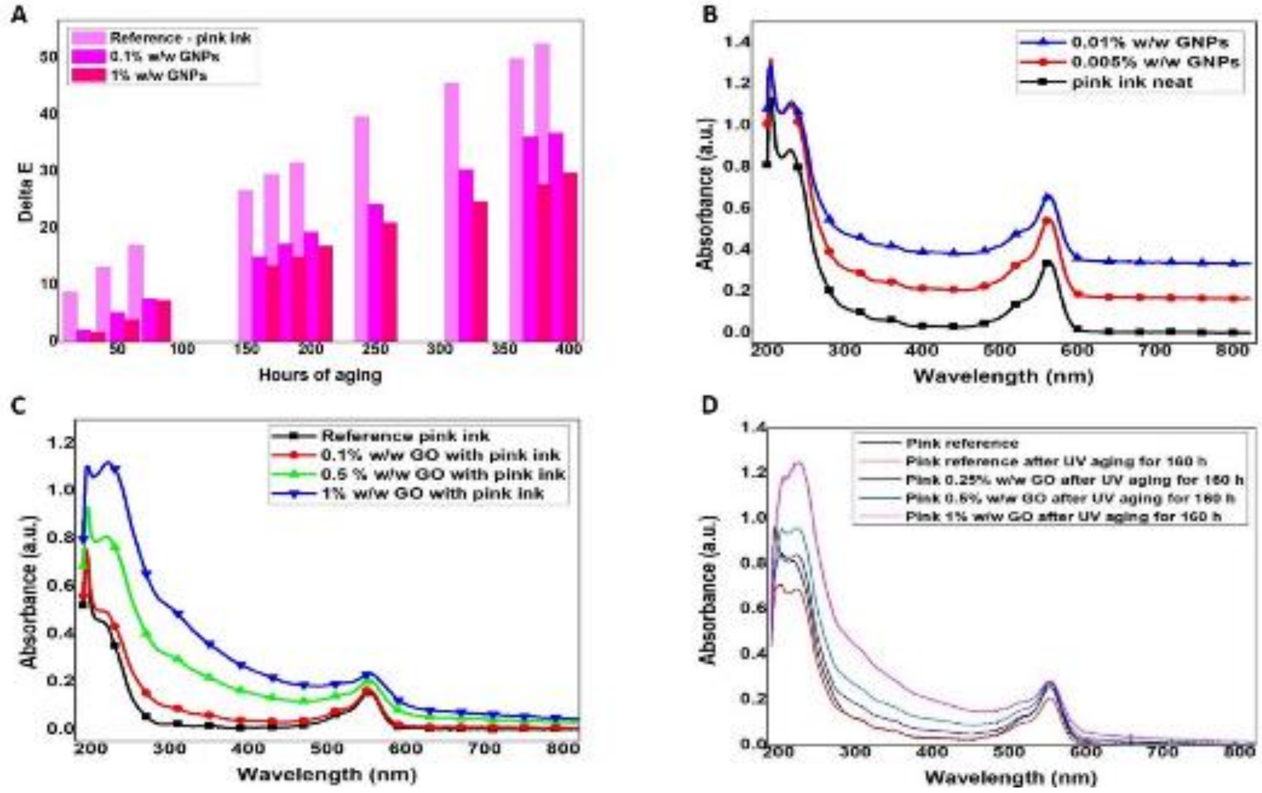


Figure S11: GNPs on pink colour. (A) The progress of Delta E index during aging for commercial pink ink with the addition of GNPs dispersed in water after the fading of the ink with visible light for 390 hours, (B) Absorbance spectra for commercial pink ink with the addition of GNPs dispersed in water, (C) Absorbance spectra for commercial pink ink with the addition of GO diluted in water, and, (D) Absorbance spectra for commercial pink ink with the addition of GO diluted in water after performing an aging/fading of the ink with UV light for 160 hours.

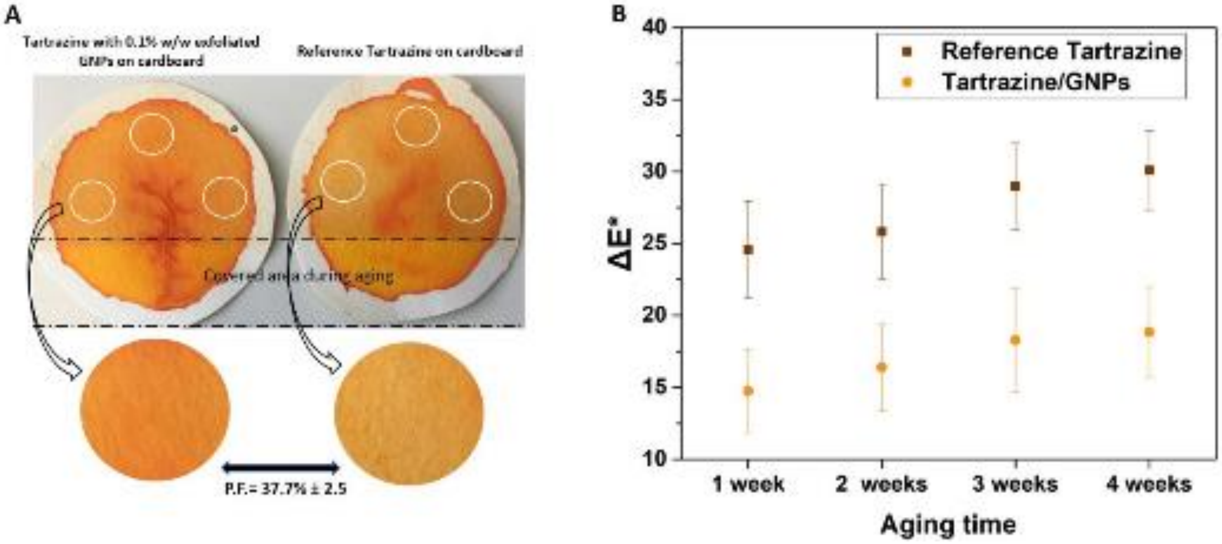


Figure S12: Aging of tartrazine doped with GNPs. (A) Two representative specimens of tartrazine doped with graphene after an aging with UVC light for 4 weeks (with dashed lines is the covered area during the aging, for comparison reasons), B) ΔE* versus aging time for these two specimens plus the calculated protection factor for the graphene-based colour.

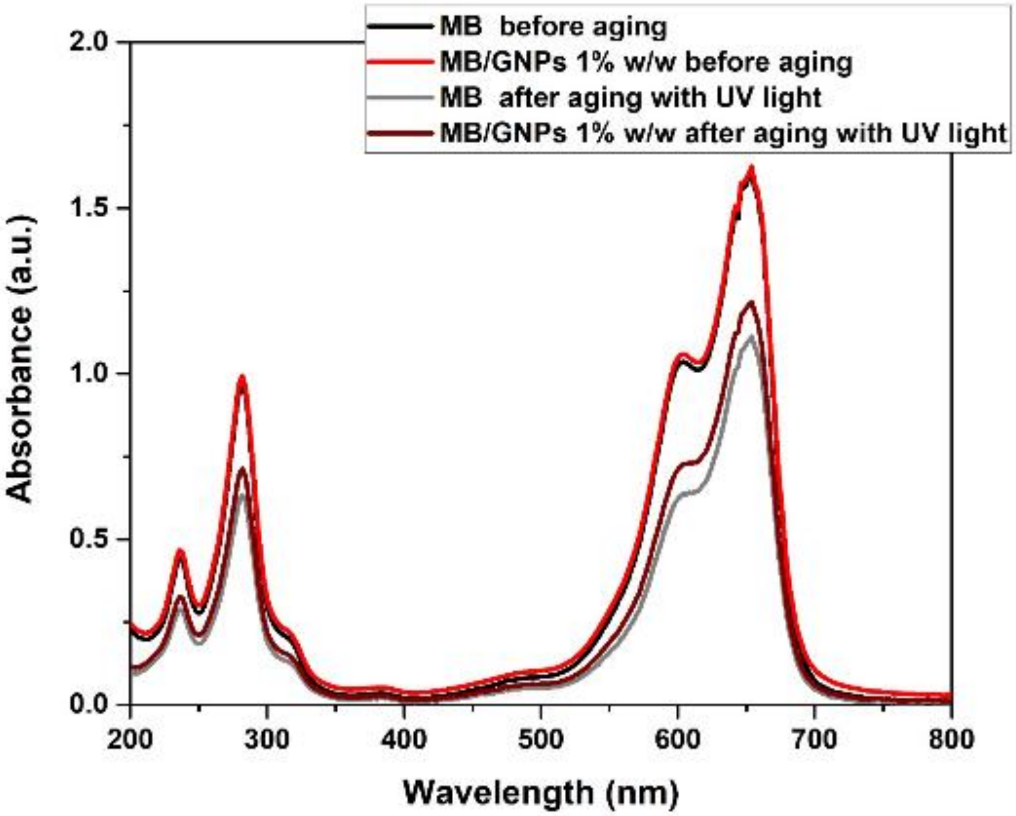


Figure S13: UV-vis absorption spectra of methylene blue solution in water, with and without the addition of graphene, before and after performing an aging with UV light for 250 hours.

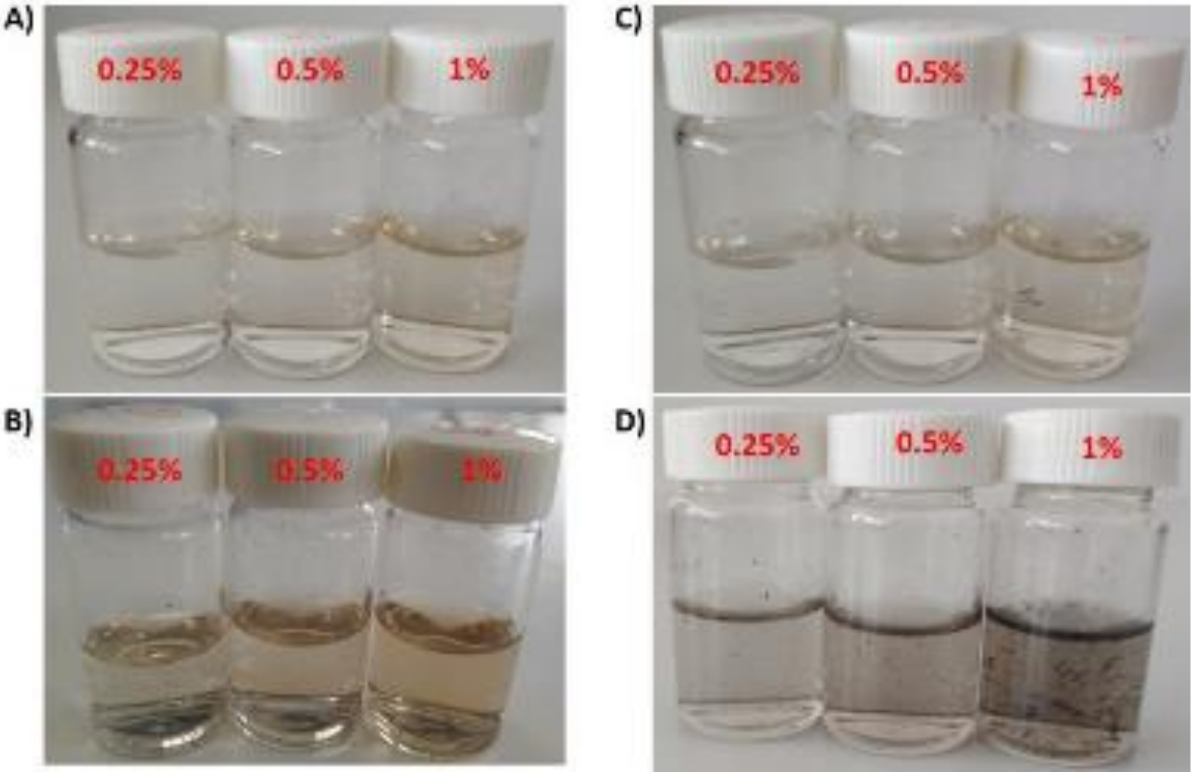


Figure S14: UV induced GO reduction. A) Pictures of diluted GO in deionized water before treatment with UV light. The GO concentrations were 0.25, 0.5 and 1% w/w, B) after 160 hours of UV irradiation, C) diluted GO before treatment with visible light. The GO concentrations were again 0.25, 0.5 and 1% w/w, and D) after 60 hours of visible irradiation.

Graphene Oxide Synthesis

GO synthesis was performed in tandem with quality control, where spectroscopic and morphological characterization techniques such as Raman, SEM and AFM were used, in order to achieve the desired quality. The Raman spectrum of GO (***Figure S15A***) comprises several frequency bands, each one assigned to a certain structural configuration [1]. The main Raman peak is the so-called G peak, located at 1580 cm^{-1} and is related to the E_{2g} mode and the in-plane stretching of C=C bonds. The most prominent "disorder' Raman spectrum is the so-called D peak, appearing at about 1360 cm^{-1}, is related to the breathing mode and its intensity is associated with the presence of either structural defects or crystal edges of the lattice [2]. The 2D peak at 2680 cm^{-1} is the second-order overtone of the D peak, which requires two-phonon scattering for activation, while the other two peaks at ~2950 cm^{-1} and ~3100 cm^{-1} are corresponding to the overtone of D + G peaks and G peak, respectively [3]. The two main Raman peaks of GO (G and D) are very sensitive to small changes of the sp^3/sp^2 ratio. Also, the intensity ratio of these two peaks, I_D/I_G, is correlated to the changes of the sp^3/sp^2 ratio and can be used for the characterization of GO. By analyzing a sufficient number of the Raman spectra, the intensity ratio I_D/I_G for the GO was found to be at 0.97 ± 0.01. Furthermore, both SEM and AFM photos indicated that GO was well exfoliated (***Figure S15B*** and ***C***). In particular, the maximum lateral size of the GO flakes was found up to 150 μm, with a larger number of smaller flakes, their smallest size not exceeding 1 μm. Moreover, from AFM measurements, the thickness of a single layer GO was estimated at ~1.2 nm. The increase of the thickness of GO, compared to a single layer of graphene (0.335 nm), is related to the presence of functional groups on the GO lattice. On the other hand, more structural defects such as holes, cracks and wrinkles are visible from AFM images. These defects are the result of the GO synthesis process, decorated by hydroxyl, carboxyl and carbonyl functional groups.

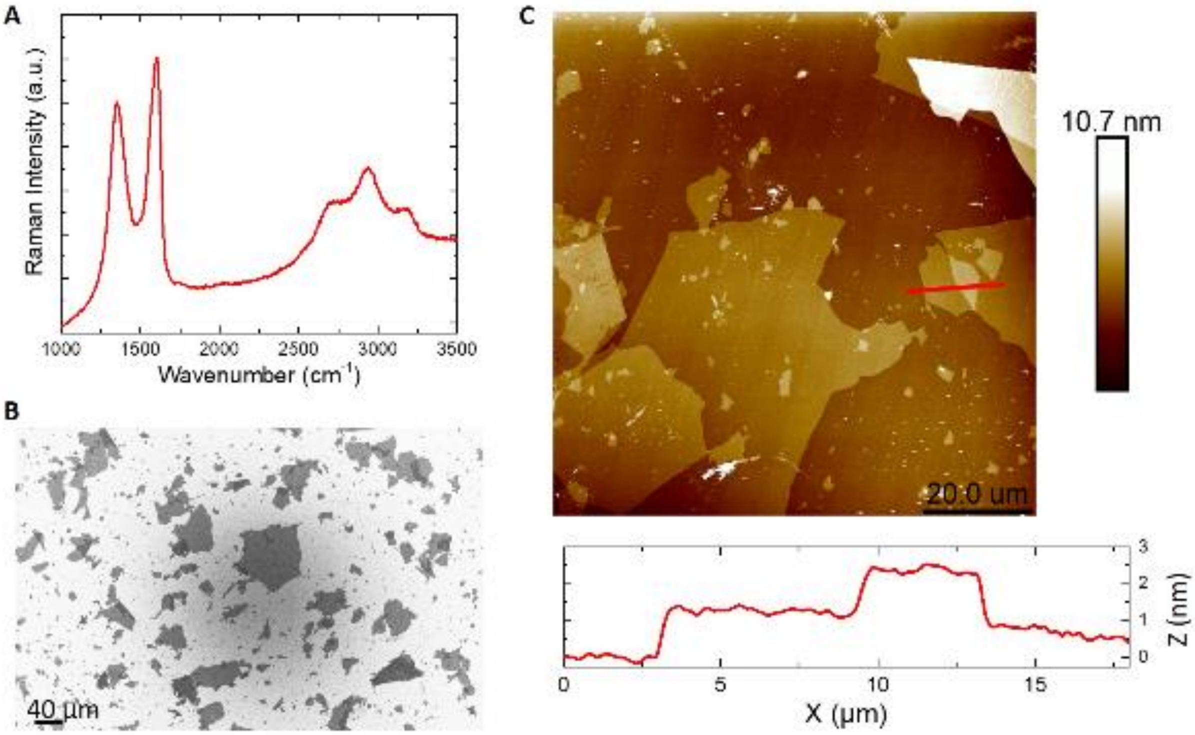


Figure S15: A) Raman spectrum of produced GO **B)** SEM photo for GO sheets, **C)** Atomic force microscopy (AFM) images of single layer GO flakes with thickness 1.25 nm.

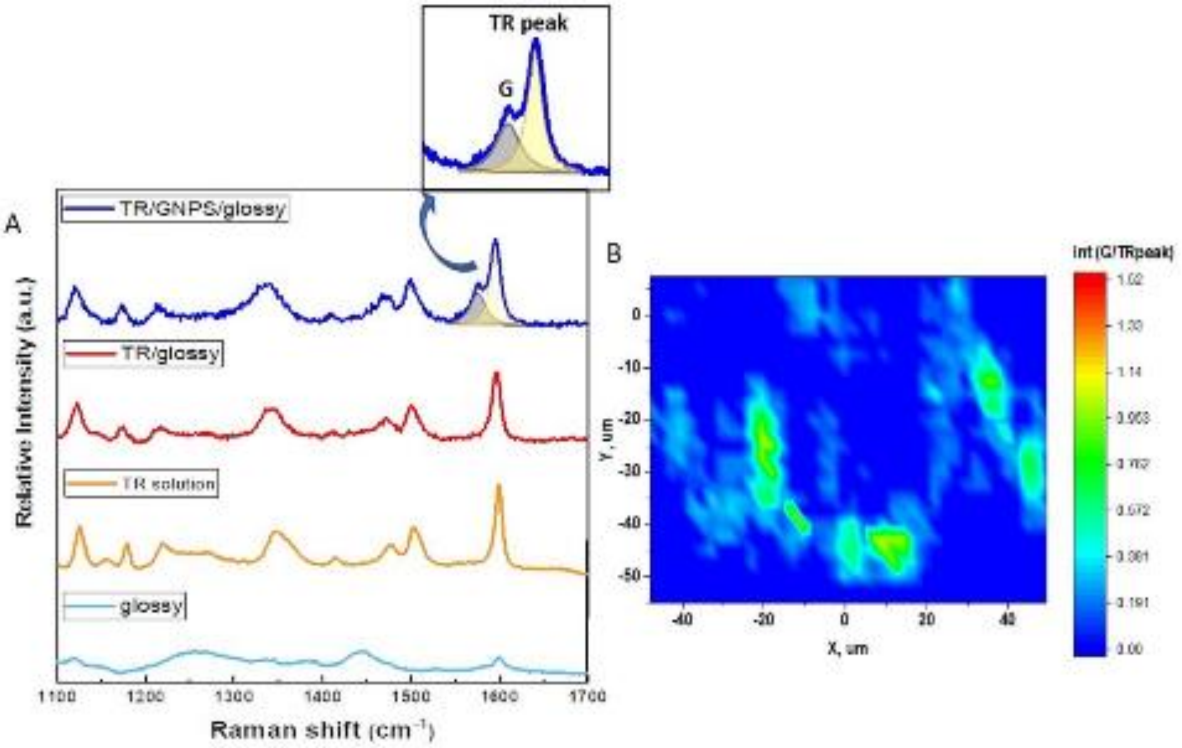


Figure S16: Raman mapping of the characteristic G peak of graphene after being added into tartrazine. The paper substrate used for this mapping which was dyed with graphene-doped tartrazine was glossy paper.

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