ROLL-TO-ROLL GRAPHEINE TRANSFER AS AN EFFECTIVE TOOL FOR THE PROTECTION OF ARTWORKS

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ABSTRACT
All art materials are generally prone to degradation. In particular, the 20th century artworks exhibit short lifetime expectancy due to the introduction of new materials and techniques that are more sensitive to environmental conditions. The exposure of contemporary artworks to UV and visible light, also in addition to oxidizing agents and humidity, trigger certain degradation effects, such as fading, yellowing and discoloration. The result of these degradation mechanisms is the severe and irreversible alteration of the artworks, which is an inestimable legacy of mankind.

Graphene-related materials have been found to provide considerable ultraviolet shielding as coatings, while a single layer CVD graphene absorbs up to 3 times more in the UV region (190-400 nm), than in the visible range. Additionally, chemical molecules such as water or oxygen cannot penetrate a continuous graphene membrane providing ultimate shielding against degradation. In short, an invisible veil of graphene could provide protection for old and contemporary paintings against all these factors.

The most effective way of large-scale CVD graphene transfer is the roll-to-roll method. The basic parameters which define the success of the transfer process are the transfer rate, the temperature and pressure. It has been shown earlier that the slower the transfer rate, the more effective is the graphene transfer. Additionally, based on preliminary experiments that have been performed during the micro-rolling procedure, it was observed that mild heating has positive effect on the transfer quality. Regarding the transfer pressure, it has been found that application of high pressure between the rollers results in a homogeneous transferred graphene film.

In this research project, we covered artworks with graphene using the roll-to-roll method for dry graphene transfer, while an environmental chamber has been built for accelerated environmental aging measurements. The results obtained thus far show that graphene films can provide effective protection to artworks and pave that way for developing this technique as a novel non-destructive and reversible method for artwork protection.

INTRODUCTION
Graphene was first isolated by Geim and Novoselov in 2004 by mechanical cleavage of graphite using the so-called scotch tape method. It consists of a single layer arrangement of carbon atoms in a honeycomb structure and has been found to possess outstanding properties which include high optical transparency, UV light absorption, oxygen and chemical molecules impermeability, chemical stability and remarkable mechanical behavior1,2. In order to meet the need for mass fabrication of large-area and high-quality graphene the Chemical Vapor Deposition (CVD) method is now routinely used3. The synthesis of CVD graphene takes place in a low-pressure furnace at high temperature. A metallic foil is used as the catalytic substrate for graphene growth. Afterwards the graphene layer must be transferred on the desirable substrate according to the application it will be utilized. The reported transfer methods can be classified as wet or dry processes. The wet graphene transfers involve stamping of a polymethylmethacrylate (PMMA) or polydimethyl-siloxane (PDMS) film onto graphene to act as a support, then etching of the metallic foil and finally graphene transfer onto the desired substrate. However, these transfers may induce wrinkles and defects in the transferred...
graphene, altering its properties\textsuperscript{4,5}. On the other hand, the dry transfer is employed for direct graphene transfer using an intermediate supporting substrate\textsuperscript{6}. The latter method is suitable for graphene transfer onto delicate substrates such as paper and artworks without affecting their quality and will be described below.

**ROLL-TO-ROLL GRAPHENE TRANSFER**

There are three essential steps in the roll-to-roll graphene transfer (figure 1): deposition of a suitable polymer onto the graphene grown on copper, etching of the copper layers, and release of the graphene layers and transfer onto a target substrate\textsuperscript{7}. For the roll-to-roll dry transfer the following procedure was pursued: Firstly, the prepared from the CVD reactor specimen carrying graphene is attached to a commercial adhesive membrane by employing the roll-to-roll apparatus. Afterwards, a water solution of Ammonium Persulfate is used to etch the copper, and finally, deionized water to clean any remaining dirt or residue of the Ammonium Persulfate. After the adhesive membrane with the graphene remains inside a vacuum chamber in order to be de-hydrated, it is ready to be transferred. For the transfer process, the graphene/adhesive film is attached to the target substrate and by employing the roll-to-roll machine with the appropriate parameters of temperature, pressure and rolling speed the graphene is deposited on the surface of the target substrate.

*Figure 1. Illustration of the roll-to-roll Graphene transfer.*

The basic parameters which define the success of the roll-to-roll graphene transfer process are the transfer rate, temperature and pressure, as well as the surface energy and the roughness of the target substrate. It is highlighted elsewhere\textsuperscript{7,8} that the slower the transfer rate, the more effective is the graphene transfer. We conducted some contact angle measurements, as well as profilometry measurements, in order to examine which paper substrate is more appropriate to host graphene. Based on these measurements (*table 1*), the best substrate for graphene deposition is the glossy paper because of its higher surface energy and lower surface roughness compared to the other paper substrates. Additionally, based on preliminary experiments that has been done on the micro-rolling procedure, it was observed that mild heating has positive effect on the transfer quality. This indicates that the transfer process must be done in slow rate to ensure the homogeneous heating of the graphene and the substrates to the desirable temperature by the laminator’s rollers, where the transfer takes place. Regarding the transfer pressure, it is noticed that application of high pressure between the rollers results in homogeneous transferred graphene film.

*Table 1. Contact angle and profilometry measurements of various paper substrates.*

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Contact angle with glycerol (°)</th>
<th>Surface energy (mN/m or mJ/m(^2)) or dyn/cm</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardboard paper</td>
<td>52.5 ± 5</td>
<td>44.7 ± 2.7</td>
<td>1485</td>
</tr>
<tr>
<td>Glossy paper</td>
<td>77.3 ± 0.4</td>
<td>30.7 ± 0.2</td>
<td>34</td>
</tr>
<tr>
<td>Canvas paper</td>
<td>89.6</td>
<td>23.7</td>
<td>3950</td>
</tr>
</tbody>
</table>
ROLL-TO-ROLL LAMINATOR CONSTRUCTION

In order to standardize and optimize the graphene transfer process, a roll-to-roll machine was designed and constructed based on a commercial laminator. The system operates up to 180°C and the operating motor’s rotational velocity varies from 0.05 to 5 rpm. A stepper motor was used at the laminator machine because it can be controlled to a high degree of accuracy without any feedback mechanisms and could maintain a smooth rotation at very low speed. At its maximum current the output shaft of the motor’s gearbox produces a continuous torque higher than that required to preserve continuous and stable rotation when high pressure was applied between the rollers. The distance between the rollers is slightly variable.

*Figure 2. Final laminator’s configuration.*

ROLL-TO-ROLL GRAPHENE TRANSFER ON ARTWORK

Using the above rolling machine, we examined its efficiency by trying to cover with monolayer graphene a real artwork, prepared by a professional Greek painter Ms Matina Stayropoulou, as shown in *figure 3*. Several spots were chosen to perform colorimetric measurements using a portable instrument from x-rite. The artwork was then kept in a chamber for several weeks for accelerated aging. A portion of the artwork was covered using a cardboard screen, to have a non-aged reference. Thanks to the area that was protected, the changes in color are clearly manifested (*figure 4*).

*Figure 3. The artwork, during (left) and after treated with monolayer graphene (right).*

*Figure 4. The artwork, before (left) and after aging/ fading of the colors for one month(right).*
CHARACTERIZATION METHODS AND RESULTS

RAMAN SPECTROSCOPY MEASUREMENTS
A typical Raman spectrum of graphene is shown in figure 5 (left), and the three characteristic peaks of graphene are shown to be present. The G and 2D peaks at the spectrum indicate the presence of good quality monolayer graphene, and the D peak is evidence of the presence of graphene defects. The quality of graphene and the level of coverage of a commercially purchased painting by monolayer graphene using the presented above rolling machine were examined with Raman Spectroscopy. As shown in figure 5 (right) the contour of the intensity of the 2D peak within an area of 40x40 μm² appears to be uniform with small fluctuations of the intensity that is possibly due to slight rippling of graphene caused by the transfer procedure.

COLORIMETRIC MEASUREMENTS
In colorimetry, the quantification of color is based on the three-component theory of color vision which states that the human eye possesses receptors for three primary colors (red, green and blue) and all the colors are seen as mixtures of these primaries. These components are referred to as L*a*b coordinates. In the L*a*b diagram, L* indicates lightness, and a* and b* are the chromaticity coordinates. So, using the initial and final L*a*b coordinates of a color the Delta E, the color’s change, can be calculated using the equation 1. The higher the Delta E, the more significant the chromatic difference between the initial and final state of the color. The protective action of monolayer graphene over several colors of the real artwork was examined during the accelerated aging. The colorimetric measurements indicate that the graphene protection is quite good, and especially over pink is excellent, as it is shown in the colorimetric diagram in figure 6 (right). The protection factor of graphene for pink color reaches 50%.

\[
\Delta E = \sqrt{(L_f - L_0)^2 + (a_f - a_0)^2 + (b_f - b_0)^2}
\]

(1)

Figure 5. Raman spectrum of graphene (left) and contour diagram of the intensity of the characteristic peak 2D of graphene for the commercial painting (right).

Figure 6. Portable colorimeter, the L*a*b diagram appears on the screen (left) and colorimetric measurements after 1 month of accelerated aging for pink color (right) of the real artwork.
CONCLUSIONS
The main conclusions of this research are the following:

➢ The construction of a handmade roll-to-roll machine for successful dry graphene transfers.
➢ The successful graphene transfers on paper substrates despite their roughness, as it is evident from the Raman measurements.
➢ Based on the colorimetric results, just one graphene layer seems to offer great protection for colored paper substrates.
➢ The protection factor of monolayer graphene is different for each color.

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*The as-presented above research results are protected by patent filing to Hellenic Industrial Organization with application number 20180100579, and entitled “Art protection with the use of 2D-materials such as graphene”, “Προστασία έργων τέχνης με τη χρήση δισδιάστατων υλικών όπως το γραφένιο”.

REFERENCES