Degradation Protection of Color Dyes Encapsulated by Graphene Barrier Films

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S *Supporting Information*

ABSTRACT: The decolorization of paintings, photographs, and artworks is a common phenomenon related to the oxidative degradation of color dyes reacting with oxygen or water molecules, which also causes a critical problem in organic light-emitting diodes (OLEDs). It is expected that the gas-impermeable property of graphene and h-BN can be utilized to protect the color dyes from degradation. However, the transfer method has been limited to a polymer with high glass transition temperature (T_g) or a glass substrate due to hot or wet transfer conditions. Here, we report the dry transfer coating of the graphene barrier films on flexible substrates at room temperature using a roll-to-roll process to prevent the bleaching of color dyes, which can be widely used to protect various colorization and light-emitting materials for sustainable printing and display technologies in the future.

Graphene-Coated Color-Printing Paper & OLED
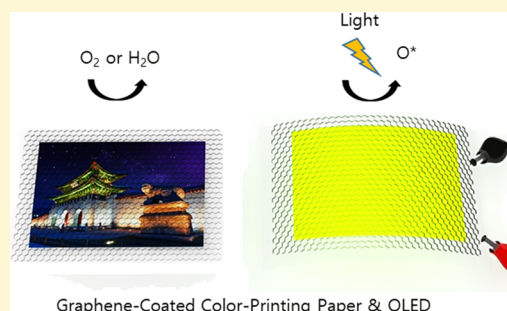
Graphene[1−3] prohibits the penetration of gases and liquids owing to its closely packed lattice structures smaller than any atomic or molecular radii,[4−7] which can be utilized as high-performance barrier films for various optoelectronics device applications.[8−11] On the other hand, organic color dyes commonly used for light-emitting devices or color-printing technology are very sensitive to moisture or oxygen, leading to photodegradation and decolorization even under ambient light.[12] Preventing oxidative degradation[13,14] by using graphene nanosheet, graphene oxide, CVD graphene, and other composite materials[15−17] have been proposed. However, most of the graphene oxide or reduced graphene oxide-based films described in literature entail difficulties to be employed as an encapsulation material for dyes or electroluminescent polymers since they either do not meet the transmittance requirement or are inflexible. In addition, the coating of the gas-impermeable CVD graphene layer has not been available on printer papers or on electroluminescent dyes/polymers because of hot lamination temperatures or wet transfer conditions. Here, we report the dry transfer coating of CVD graphene films on an inkjet-printed paper and an OLED device at room temperature, which efficiently prevents the degradation of color dyes. The protective graphene coating can be continuously done using a roll-to-roll method similar to a conventional printing process.[18,19] Thus, we expect the present method can be widely used to protect various color-printed materials as well as light-emitting materials that need to be preserved for prolonged display and device operation in flexible and printed electronics in the future.[20]

RESULTS AND DISCUSSION

First, the large-area graphene has been synthesized by a roll-to-roll chemical vapor deposition (CVD) method on a roll of Cu foil at 1000 °C with flowing 10 sccm H_2 and 75 sccm CH_4 for 4 min[3,21,22] (Figure S1).The pressure sensitive adhesive film (PSAF) is laminated on the graphene grown on the Cu surface, followed by etching of Cu by aqueous 0.1 M ammonium persulfate (APS) (Figure 1a).[23] The resulting graphene on PSAF, showing an excellent barrier property with low water vapor transmission rate (WVTR) (Figure S2) is laminated on a photo-printing paper (Figure 1b). The liquid-like behavior of the PSAF adhesive allows a complete wetting of graphene on the surface of the color-printed paper, which maximizes the van der Waals interaction with the target surface.[7] During the
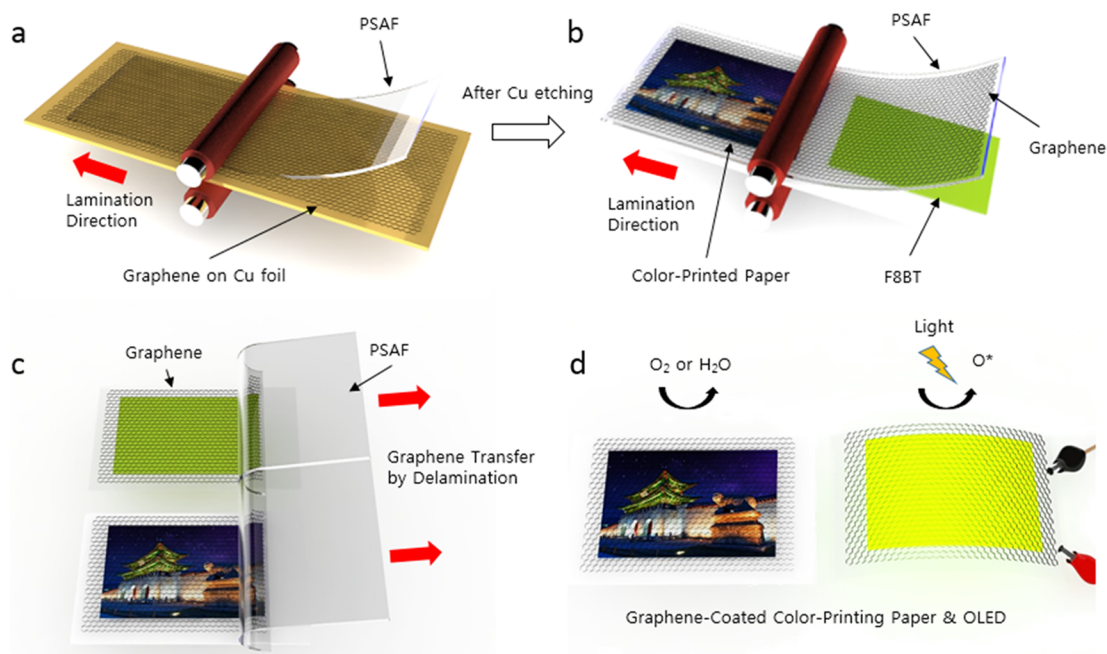
Figure 1. Schematic illustration on the transfer coating process of graphene on a color-printed photo paper. (a) PSAF laminated on graphene grown on Cu. (b) Attaching graphene on PSAF to a target photo-printed paper and F8BT-coated film by lamination at room temperature. (c) Detaching the PASF from the photo-printed paper and F8BT-coated film, where the graphene layer stays due to the stronger adhesion with the substrate surface. (d) Concept of preventing gas-permeation and photo-induced degradation of dye-coated substrates with graphene coating.
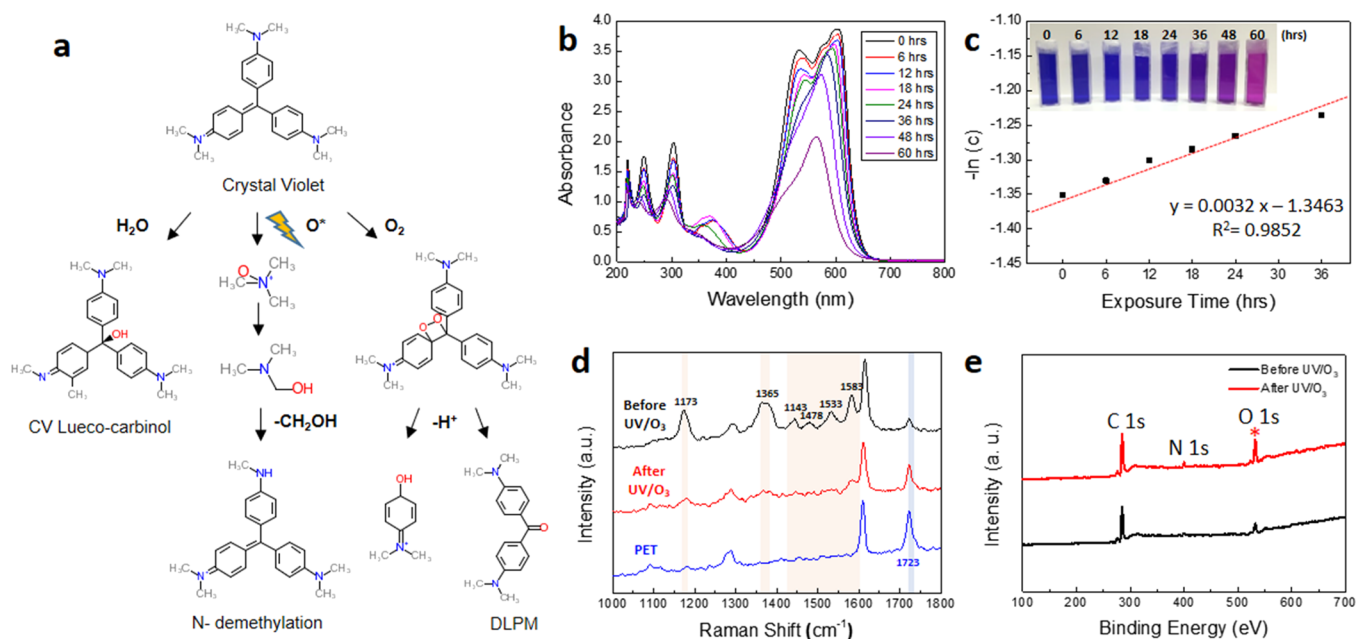

Figure 2. Photodegradation pathway of crystal violet (CV) and its spectroscopic analyses. (a) Suggested photolysis mechanism of CV by hydroxyl addition, N-demethylation, and photo-oxidation. (b) Absorbance spectra of CV after exposure to a halogen lamp (AM 1.5 G solar spectrum: 100 mW cm^{-2}) for 0, 6, 12, 18, 24, 36, 48, and 60 h, respectively. (c) Plot showing the reaction kinetics of CV degradation. (d, e) Raman and XPS analyses of CV corresponding to before and after degradation by UV/ozone treatment, respectively.

delamination of PSAF, the graphene stays on the surface of the color-printed paper because of the stronger adhesion between graphene and paper (Figure 1c).[7] The color-printed paper covered with graphene can be protected from decolorization reaction with oxygen or water molecules or with singlet oxygen species generated by ultraviolet and visible light (Figure 1d). CV, one of the most common blue dyes used in printer inks, was used to monitor the degradation effect with and without

graphene coating against the oxidative environment. Various oxidation methods (i.e., halogen lamp (Figure 2b,c and Figure S3), UV/ozone treatment ($\lambda = 254$ nm, 50 W; Figures 2d,e and 3), and heat treatment (Figure 4b))[24] were attempted to monitor the degradation of CV.

It is well known that the main decolorization pathway of CV involves photolysis process via hydroxyl addition, N-demethylation, and photo-oxidation reactions[25,26] (Figure
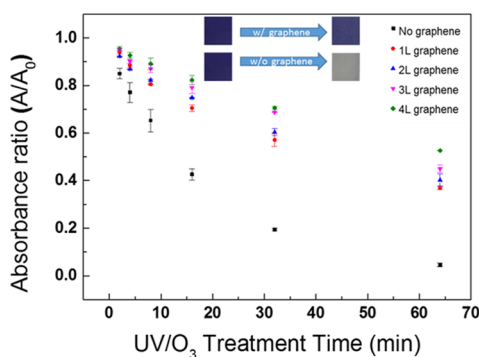
Figure 3. UV/ozone-induced absorbance ratio (A/A0) change. The absorbance of UV/ozone-treated crystal violet (CV) on PET substrates with and without graphene coating with respect to increasing time and the different number of graphene layers at room temperature.

2a). During the degradation of CV structures, the major peaks around 600 nm in the UV−vis spectra decreases as shown in Figure 2b, resulting in clear decolorization in a liquid phase (Figure 2c, inset). The increasing absorbance peaks near 360 nm also indicate the decomposition of CV into DLPM (4,4′-bis(dimethylamino)benzophenone) and DLBP (4-(dimethylamino)benzophenone), and the peaks decrease after 18 h as DLPM and DLBP are decomposed into smaller molecules such as carboxylic acids, amines, and alcohol species (Figure 2b). The decreasing rate at the highest absorption intensity indicates that the decomposition of CV by light is the first order reaction (Figure 2c), implying that the decoloriza-

tion reaction can be efficiently prevented by blocking H_2O or O_2 molecules.

The main cause of decolorization is the dissociation of C−C and C−N bonds and the formation of C−O and C=O bonds, which occurs when the CV is attacked by reactive oxygen radicals formed by the photoexcitation.[24,27] In particular, the dissociation of C−C bonds disturbs the resonance between the aromatic rings of CV, leading to the bleaching of blue colors as the charge delocalization energy is shifted to a transparent range.[24] We further investigated the origin of the color change using Raman and XPS spectroscopy as shown in (Figure 2d,e), which indicates that the covalent bonds in CV are altered by light-induced oxidation reaction with O_2 or H_2O. The Raman spectra exhibit that the characteristic peaks of CV disappeared after UV/ozone treatment for 64 min, implying that CV is decomposed by oxidation. The XPS spectra with increased O 1s related to the oxidation also show the oxidative color degradation of CV.[28] Thus, we conclude that the absorbance change is relevant to the changes in Raman and XPS for the oxidation degree of CV, which is used in further experiments to verify the antidecolorization effect of graphene coating.

To monitor the change in UV−vis absorbance, a PET film is dip-coated with 1 mM CV solution and exposed to UV/ozone condition. The UV−vis absorbance of CV decreases with increasing time and decreasing number of graphene layers (Figure 3), which clearly shows that the decolorization by UV/ozone treatment can be efficiently prevented by coating a graphene layer on color dyes. After 64 min of UV/ozone treatment, the changes in absorbance ratio were 95.4% for no graphene, 63.1% for one-layer graphene, 60.8% for two-layer graphene, 65.0% for three-layer graphene, and 47.4% for four-
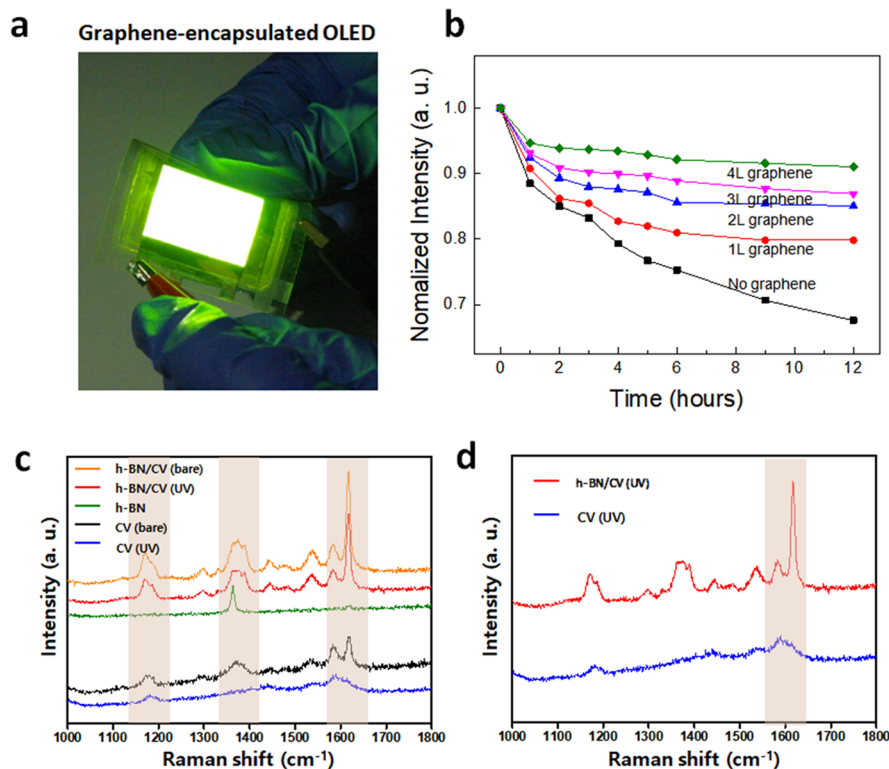
Figure 4. Degradation protection properties of graphene and h-BN layers. (a) OLED device encapsulated by transferred graphene layers. (b) PL intensities of EL polymer (F8BT) coated with a varying number of graphene layers. (c, d) Raman spectra of CV w/ and w/o h-BN encapsulation after 5 min UV/ozone treatment, corresponding to the red and blue lines, respectively. The structural damage of CV molecules results in the disappearance and broadening of the Raman peaks.

layer graphene. We also found that this effect can be further enhanced by adding more layers of graphene because the graphene layer physically blocks the O_2 and H_2O in ambient conditions as well as prevents photo-induced oxygen radicals. As a result, the color of CV can be prolonged even under harsh oxidative conditions.

Finally, the photoluminescence(PL) spectra of electroluminescent (EL) polymer dyes, F8BT (poly(9,9-dioctylfluorene-alt-benzothiadiazole) and poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl), coated with varying number of graphene layers also clearly show that the degradation can be efficiently suppressed by graphene (Figure 4b). In addition, the graphene-coated F8BT exhibits more stability as the number of graphene layers increases. After 12 h of heat treatment at 85 °C, the decrease in normalized PL intensities were 32.5% for no graphene, 20.2% for one-layer graphene, 15.0% for two-layer graphene, 13.1% for three-layer graphene, and 9.0% for four-layer graphene, respectively.

We also tested the decolorization protection of color dyes by h-BN layers, using similar approaches and confirmed that the transfer of h-BN multilayers (5−6 layers) also successfully prevents the degradation of CVs. There was almost no change in Raman spectra in h-BN protected CVs before and after UV/ozone treatment (orange and red lines in Figure 4c, respectively), while the nonprotected CVs exhibited the disappearance and broadening of the Raman peaks due to structural damages on their sp^2 bonds (the blue line in Figure 4d).

CONCLUSIONS

The dry transfer technique using PSAF does not require hot lamination or wet cleaning steps, allowing the coating of photo-printing papers. Using the PSAF transfer technique, we demonstrated that the coating of graphene films on a color-printed paper at room temperature using a roll-to-roll process prevents the bleaching of color and EL polymer. A common blue dye, crystal violet (CV), is used to monitor the time-dependent color degradation caused by photolysis reactions, evidenced by UV−vis spectroscopy, Raman spectroscopy, XPS, and color histogram analyses. The comparison between the actual photo images with and without graphene coating clearly shows that the decolorization of dyes can be efficiently prevented. Thus, we expect that the proposed graphene-encapsulation method can be widely used to protect various colorization and light-emitting materials for sustainable printing and display technologies in the future.

EXPERIMENTAL SECTION

Preparation of Monolayer Graphene on PSAF. Monolayer graphene was synthesized under 4.2×10^{-1} Torr by roll-to-roll CVD method on a high-purity copper foil (Newone Global, 99.99%) with flowing 10 sccm H_2 and 75 sccm CH_4 for 4 mins. PSAF laminated on graphene grown on Cu and back-side graphene was etched by oxygen plasma (100 W RF power) with flowing 20 sccm O_2 for 20 s under 150 mTorr. The PSAF with graphene was transferred using conventional dry-transfer method on a target photo-printed paper after removing Cu foil by 0.1 M ammonium persulfate solution.

Decolorization and Optical Characterization Methods. UV/ozone-oxidation experiment was carried out in UV Ozone Cleaner chamber at room temperature. Heat-oxidation experiment was performed in ambient condition at 85 °C. Raman spectroscopy (Renishaw Co.) was performed using 514 nm and 633 nm laser at room temperature. Atomic analysis was carried out using X-ray

photoelectron spectroscopy (XPS, AXIS-HSi). Absorbance spectrum was measured by Genesis 10S equipment from 200 to 800 nm.

ASSOCIATED CONTENT

ⓢ Supporting Information

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Additional experimental details and figures (PDF)

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Notes
The authors declare no competing financial interest.

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