

Tortuously Nanostructured Ultrathin Graphene Oxide-based Encapsulation for Flexible Displays

Dongwook Lee¹, Chan-Soo Kim¹, Woo-Jin Lee¹, Seung-Yeol Yang¹, Yong-Seog Kim¹

yskim@hongik.ac.kr

¹Department of Materials Science and Engineering, Hongik University, Seoul 04066, Republic of Korea

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ABSTRACT

We exemplify an effective design principle for mass-producible 2D material-based super-barriers for flexible displays: fabrication by scalable layer-by-layer assembly process, low defect density, tortuous nanostructure, 100 % surface coverage, hydrophobization, and van der Waals gap narrowing. These design principles consistently stem from one simple rule: blocking all possible diffusion pathways.

1 Introduction

OLED (Organic Light Emitting Diode) is a display that uses a light emitting layer as a multilayer stack structure of organic materials, and the thickness of the light emitting layer is very thin compared to conventional displays such as LCD and PDP. In addition, since it has its own light emitting characteristics, it has structural characteristics that do not require external light, so the form factor is very high. Thanks to these advantages, OLED has been studied as the next flexible display material, and recently rollable and foldable display are being released as commercial products. However, at the downside, the organic emitting layer that gives flexibility by using organic light emitting materials simultaneously enforces tradeoffs in stability and lifespan.

Organic materials are easily oxidized by moisture and oxygen and have the disadvantage of easily losing their properties. This characteristic was not a big problem in the initial rigid OLED display because glass was used as a material for the substrate and encapsulation membrane. Glass has a very high barrier performance of 10^{-6} g/m²-day or more, since frit glass seals the side of the device, the encapsulation performance of oxygen and water could be easily satisfied for OLED devices encapsulated using glass. However, since glass is an unbendable material, it became one of the materials that needs change for the flexible OLED. Although the encapsulation method by ultra-thin glass (UTG) has also been explored, UTG is very expensive and easily broken due to low bending radius.

To solve this problem, the encapsulation method currently used in flexible display is the composite thin film encapsulation. Thin film encapsulation is

formed by alternately and repeatedly laminating an organic layer and an inorganic layer. The inorganic layer serves as a substantial oxygen/molecular barrier since the diffusion flux through this layer is very low, while the organic layer grants flexibility and hampers defect propagation through the stacking.

In this thin film encapsulation structure, the key features to prevent permeation of oxygen and moisture are (i) tortuous path to maximize diffusion length and (ii) material defect suppression. Theoretically, the WVTR value of the inorganic layer can be low, so that even single layer of the inorganic layer can sufficiently preempt degradation of the OLED. In reality, WVTR falls far below the theoretical estimation, because of the defect generated during the process. The defect sites can greatly deteriorate the barrier performance because oxygen and water can easily pass through.

With current materials kept in the barrier, it is restricted to maneuver for more tortuosity. The simplest way to increase the tortuous path within the barrier is to introduce an additional layer. However, this design greatly compromises the flexibility of the device. Currently, the thickness of the organic layer is known to be about 7 μ m, while future flexible displays require to lower the bending radius below 1 mm. In addition, the organic material layer also functioning as the planarization layer during the OLED process cannot be thinned down beyond certain limit due to its multiple functions. Therefore, there is a need for a method capable of effectively increasing the tortuous path while limiting its thickness.

2 dimensional materials (2D materials) with suppressed defect concentration can serve as ideal building blocks for encapsulation layer, because of their innately large aspect ratio (few-layered 2D material thickness to width ratio) often reaching $10^3 - 10^5$. The morphology of 2D materials resemble large sheet of papers in the aspect ratio sense. This implies they can naturally lead to tortuously structured film when their sheets are stacked.

Amongst plethora of 2D materials, graphene-based materials are deemed best for practical demonstration of ultrathin flexible barrier. Since graphene-based materials have atomically thin, single layer of carbon atoms by definition, while imposed with no limit in lateral length scale. Along with the well-known mechanical flexibility, in-plane hexagonal atomic arrangement of carbon atoms has extremely narrow void within, of which size is only 0.064 nm. This void size is practically impermeable to all kinds of atoms in nature, including the smallest He. From this theoretical viewpoint, graphene-based materials have a very promising potential as encapsulation layer material, when combined with naturally emergent tortuosity and low defect density.

Despite the theoretical projection, the theoretically predicted encapsulation performance of graphene-based materials could not be met with actual experiments. In reality, defects tend to be generated in the graphene-based materials, and offers diffusion highways for foreign molecules, such as gaseous water and oxygen. The defect level suppression is especially difficult when they are produced by scalable methodologies, including wet chemistry-based Hummers' process. At the same time, the gifted tortuosity could not function due to those shortcuts. Controlling defect level is still possible when graphene-based materials are synthesized by state-of-art CVD. However, CVD process for high quality graphene synthesis results in very high unit price and requires high process temperature, it can be less practical even if its performance is satisfied. In addition, transfer process from the deposition substrate onto bare OLED device must be additionally performed, and the addition of such process may degrade the encapsulation performance.

In this research, we address (i) scalable production of graphene oxide by modified Hummers' method with suppressed defect level and $\sim 35\ \mu\text{m}$ average lateral width[1], and (ii) their scalable stacking into ultrathin ($< 15\ \text{nm}$) encapsulation layer with WVTR of $4.1 \times 10^{-5}\ \text{g/m}^2\cdot\text{day}$ and lag time of 1 month (730 hours)[8].

2 Experiment

All chemicals were analytical grade and used as received without further purification. The chemicals used were as follows: natural graphite (99 %, Alfa Aesar), potassium permanganate (KMnO_4 ; Sigma-Aldrich), hydrogen peroxide solution (H_2O_2 ; 30 %, Daejung Chem), concentrated sulfuric acid (H_2SO_4 ; 98 %, Daejung Chem), triethylamine (Et_3N , 99 %, Sigma-Aldrich), polyethylenimine (PEI, MW = 2000, 99 %, Sigma-Aldrich), 1,4-diazabicyclo[2.2.2]octane

(DABCO, 99 %, Sigma-Aldrich).

Detailed oxidation, hydrolysis, and exfoliation methodologies to produce negatively charged graphene oxide (nGO) can be found elsewhere[1]. Essentially, this nGO preparation protocol followed the well-known Hummers' method[2], while different in 2 main points: (i) oxidation reaction temperature below $10\ ^\circ\text{C}$, (ii) divided injection of KMnO_4 oxidants. The synthesis steps are purely based on wet-chemistry, and consist of intercalation of H_2SO_4 molecules, dose-by-dose input of KMnO_4 oxidizing agent, hydrolysis, and lastly additional carboxylation by EDC/NHS reaction.

Glycine-modified nGO (gly-nGO) was produced by reacting epoxide moieties on the basal plane of nGO sheets. The negative charge of nGO stems from carboxyl groups mostly concentrated along the periphery. Reaction with glycine imbues the same negative charge on the basal plane as well, further enhancing the static negative charge density[8].

Positively charged graphene oxide (pGO) is produced from nGO. pGO was prepared by ring-opening reaction at epoxide moiety, richly populating in the basal plane of nGO. 10 mL of water, 1 g of PEI, 5 g of Et_3N , and 2.5 g of DABCO were put into the reaction vessel with mechanical stirring (150 RPM) at $25\ ^\circ\text{C}$, for 30 minutes. Then 250 mL of 0.5 g/L nGO dispersion was added into the solution. After that, the entire reaction vessel was moved into $40\ ^\circ\text{C}$ -set oil bath and placed there for 6 hrs. After the reaction, the solution was centrifuged with water for purification. Right after the reaction, the solution exhibits a strong basic pH. Because such basic pH is detrimental for pGO dispersibility, the solution pH was lowered by adding 18 mL of 1 M HCl after the 1st centrifuge. The pGO-containing dispersion was washed repeatedly by water, until pH reached 5[8].

For the layer-by-layer (LbL) deposition of pGO and nGO on a substrate, first, PES film was treated by oxygen plasma system (50 W, Ar 30 sccm, O_2 10 sccm). The first layer of the encapsulation begins with pGO because the PES film surface becomes negatively charged after oxygen plasma treatment. The PES substrate was dipped into pGO coating bath. Then the pGO-coated PES film was carefully moved into a vacuum chamber set at $40\ ^\circ\text{C}$ for 20 minutes to remove trapped gas and residual water from coating process. Later, the PES film was placed into nGO or gly-nGO coating bath, followed by the same drying procedure. This set of alternating pGO/nGO or pGO/gly-nGO layers constitutes 1 dyad, and for best

encapsulation performance more dyads are needed[8].

Sequential reduction of the as-deposited film consisted of first vapor phase reduction by N_2H_4 and later thermal reduction under Ar[8].

Ca test was performed to obtain lag time and estimate WVTR[8]. Encapsulation layer covers the surface of Ca film, of which electrical resistance is monitored every hour. As soon as water vapor permeates, non-passivating Ca metal corrode to form electrically insulating hydroxide or oxide. The beginning of the electrical resistance rise was marked as lag time. Normalizing the lag time by the encapsulation film thickness estimates WVTR value. The Ca test was carried out at relative humidity (RH) of 85 % at 40 °C, which is remarkably harsher than most of previous WVTR test conditions[3]–[6].

3 Results and Discussion

First, the material defect generation during the synthesis of graphene oxide was exhaustively identified and suppressed. Main reasons for defect formation during graphene oxide synthesis from graphite raw material lies on excessive oxidation at the graphite particle surface and high power ultrasonication for exfoliation. Excessive oxidation only at the surface of graphite particles stems from consumption rate of oxidants is far quicker than even diffusion of oxidant toward the core of graphite particles. In order to cope with this issue, we lowered the oxidation temperature of graphite below 10 °C[1]. This unequally slows diffusion and the oxidant consumption, resulting in the former becomes more pronounced than the latter in effect. In the conventional Hummers' process without strict oxidation temperature control, KMnO_4 oxidant is consumed at the surface of graphite, before it diffuses through the galleries. Also, the high power ultrasonication became no longer needed as graphene oxide sheets exfoliate by themselves, if EDC/NHS reaction step finishes the entire synthesis. Another benefit from avoiding ultrasonication is preservation of large lateral size of the nGO sheets, whereas diminished lateral size is inevitable as a consequence of ultrasonication[1], [7]. This last step boosts yield of the exfoliated nGO, while thinning down each nGO sheet down to monolayer. EDC/NHS doubles the carboxyl group density in the basal plane of nGO, thereby doubling the Coulombic repulsion among otherwise stacked sheets[1]. To this extent, natural flake graphite was chosen as the starting raw material, as its defect density is lower than competing raw material, graphite nanoplatelets. Combined with above mentioned process condition engineering, this choice of raw material eventually

leads to sustained defect density, as can be confirmed from Raman spectroscopy. More detailed analysis can be found elsewhere[1].

Next, we stacked low defect, large size graphene oxide into an ultrathin barrier film, of which microstructure naturally bare tortuosity[8]. The remaining shortcuts for water vapor include (i) horizontal gap space between the adjacent graphene oxide sheets, (ii) vertical spacing between the loosely restacked graphene oxide sheets. Also, (iii) relative hydrophilicity of graphene oxide compared to graphene or graphite cannot inhibit adsorption of water vapor, which is the very first step for water vapor permeation. In order to close the (i) horizontal gap, wide open to water vapor, the surface coverage of graphene oxide coating was enhanced to ~100 % [8]. As the width of graphene oxide rises, Coulombic repulsion among the same charged sheets within the same layer become overpowered by attraction energy from the layer right below. For instance, when pGO is already deposited on oxygen plasma treated PES substrate, and gly-nGO is being coated on that, gly-nGO in the aqueous dispersion will repel each other while competing with Coulombic attraction from the sessile pGO. The physics of this competition strongly favors deposition over non-coating, as the lateral size of GO becomes larger. The ~100 % coverage is achieved when the mean lateral size exceeds 20 μm . Without glycine modification, the coverage of the $(\text{nGO/pGO})_n$ film saturates at ~90 % [8].

Sequential reduction of $(\text{gly-nGO/pGO})_n$ lead to (ii) vertical gap closure and (iii) inhibition of water adsorption[8]. The sequential reduction readily tightens the interlayer distance from 1.07 nm to 0.36 nm, so that there remains only very cramped space for water molecule to diffuse through, which in turn greatly downturns water diffusivity. Also, the liquid water contact angle evolves from 0° (or complete absorption of liquid water droplet into the film) to 93°, as a dramatic result of the sequential reduction[8]. The Ca test reveal that lag time of 6-dyad $(\text{pGO/gly-nGO})_6$ barrier film can reach up to 730 hrs (nearly 1 month), despite thickness below 15 nm. This lag time corresponds to WVTR of $4.1 \times 10^{-5} \text{ g/m}^2\cdot\text{day}$ [8]. Systematic suppression of all possible water vapor diffusion pathways, along with mechanistic inhibition actualized the super-barrier characteristic of the 15 nm-thin film.

4 Conclusions

We successfully reduced the concentration of defects and obtained ~35 μm -wide graphene oxide sheets by (i) keeping reaction temperature below

10 °C for slower oxidation, (ii) dose-by-dose oxidant injection for slower oxidation and (iii) natural flake graphite as low-defect raw material[1]. The graphene oxide sheets were coated on substrate by layer-by-layer deposition, of which surface coverage reached up to 100 % [8]. After the deposition, tortuosity within the graphene oxide barrier became actualized. Sequential reduction of the graphene oxide film by N_2H_4 vapor and then heat annealing under Ar shifts the surface hydrophobic and narrows down the interlayer spacing [8]. Hydrophobic surface now deters water vapor adsorption, while closer interlayer distance hampers water vapor diffusion along the galleries [8]. Combined with suppression of shortcuts by defects and uncovered area and naturally occurring tortuosity, this research exemplifies the well-known wisdoms for encapsulation design, by painstakingly exploiting the 2D material advantages. This result also emphasizes that the encapsulation layer can become ultrathin for future flexible displays, without need to sacrifice super-barrier performance for mechanical flexibility.

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