

REDUCED GRAPHITE OXIDE-INDIUM TIN OXIDE COMPOSITES FOR TRANSPARENT ELECTRODE USING SOLUTION PROCESS

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1. Introduction

Indium tin oxide (ITO) is a frequently used material because of its unique characteristics including good conductivity, high optical transmittance over the visible wavelength region, and excellent adhesion to substrates. ITO thin films have been prepared by various deposition techniques such as spray pyrolysis, magnetron sputtering, ion-plating, electron beam evaporation, and sol-gel processing. Among these methods, the sol-gel method has the advantages of using low-cost metal salts and organic solvents as raw materials and providing high surface texture at lower crystallizing temperatures. However, the high sheet resistance of ITO produced by the sol-gel method compared to ITO fabricated by other methods is a significant disadvantage.¹

Graphene, i.e., atomically thin two-dimensional sheets of carbon, has emerged as a subject of enormous interest because of its exceptional micromechanical and electron transport properties. Graphene has high values for Young's modulus (~1,100 GPa), fracture strength (125 GPa), thermal conductivity (~5,000 W/m K), mobility of charge carriers (200,000 cm²/V s) and specific surface area (calculated value, 2,630 m²/g), plus it exhibits fascinating transport phenomena such as the quantum Hall effect.² Graphene can be derived by mechanical cleavage, chemical vapor deposition, epitaxial graphitization, synthesis from solid carbon sources, or the mass production of graphene-like layers from graphite oxide (GO), which is prepared by oxidation of graphite through protocols based on the Hummers method. Among these preparation methods, GO is inexpensive to prepare, chemically flexible, and can be spun cast to form large area films.³ The hydroxyl, carboxyl, carbonyl, and epoxide functional groups present on the basal surface or edge of graphene make it hydrophilic. So,

it can even be dispersed in water instead of in harsh solvents. However, the presence of oxygen (or other functional groups) on the graphene sheets reduces electron mobility such that a reduction process is needed to recover electron mobility. The reduction of GO has been carried out using wet chemistry approaches in hydrazine hydrate (HYD), sodium borohydride, p-phenylene diamine (PPD), or hydriodic acid.⁴

In this report, we use a simple sol-gel method to directly coat an electrically conductive film onto a transparent glass substrate. As GO sheets can be rendered electrically conductive by chemical deoxygenation, their subsequent reduction inside the matrix would lead to more electrically conductive inorganic materials. Therefore, it is expected that highly conductive reduced GO (rGO) will increase the conductivity of ITO produced by the sol-gel method, rendering a low cost, highly transparent, and low resistance ITO film.

2. Experiments

Preparation of GO

GO was produced by a modified Hummers method. Briefly, a small amount of graphite powder was stirred with NaNO₃ and H₂SO₄ while being cooled in an ice water bath for 4h. KMnO₄ was gradually added, and the mixture was stirred at 25 °C until a highly viscous liquid was obtained. After adding pure water, the suspension was heated in a water bath at 98 °C for 15 min. Then, the suspension was further treated with warm water and H₂O₂ in sequence. The mixture was centrifuged at 4000 rpm and washed with HCl and water. Finally, GO was dried at 50 °C for 24 h.

Reduction of GO

HYD was used as a reducing reagent to change GO to rGO. GO powder in an aqueous solution was

mixed with HYD (50 ~ 60 % aqueous solution) at a concentration ratio of GO : HYD = 1 mg : 1 mmol. The reaction was performed under a water cooled condenser. After vacuum filtration and washing with acetone, rGO was obtained (HYD-rGO). PPD was also used as a reducing reagent. In this case, GO powder in water was sonicated and PPD was dissolved in N,N-dimethylformamide. The colloid and the solution were mixed and refluxed in a water bath at 90 °C for 24 h. After vacuum filtration and washing with acetone, rGO was obtained (PPD-rGO).

Preparation of rGO-ITO hybrid materials

ITO films were prepared according to the conventional sol-gel procedure. $\text{In}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ and SnCl_2 (9:1) were used as starting materials, and were dissolved in a mixture of ethanol and acetylacetone. To make more homogenous solutions, the solution was stirred at 25 °C for 3 h. Four types of samples were prepared to be used as anodes for organic light emitting diode (OLED): three consisting of a sol-gel ITO mixture combined with either GO, PPD-rGO, or HYD-rGO, while ITO made by the sol-gel method as a reference. The ratio of rGO compared to sol-gel ITO was 0.5 mg/mL, which corresponds to 0.66 wt % with respect to the ITO solution. All hybrid materials were heat treated 500 °C for 1 hr under air ambient.

Fabrication of OLED

Four types of samples were cleaned with acetone, isopropyl alcohol, and de-ionized water in sequence, and were then dried with high purity nitrogen gas. Then, the samples were treated with O_2 plasma for 1 min with a power of 150 W in order to optimize the work-function of the anode. After the samples were loaded into a thermal evaporator, a hole transport layer of 4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (70 nm), an emitting layer of 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-10-(2-benzothiazolyl) quinolizino-[9,9a,1gh] coumarin (0.1 %) doped Alq3 (40 nm), a hole blocking layer of bathocuproine (5 nm), an electron transport layer of tris(8-hydroxyquinoline) aluminum (20 nm), an electron injection layer of LiF (1 nm), and a cathode of Al (100 nm) were deposited in sequence. The active area of the device was $3 \times 3 \text{ mm}^2$. The current density-voltage and luminance-

current density were measured. All measurements were performed in a glove box under a N_2 ambient.

3. Results and discussion

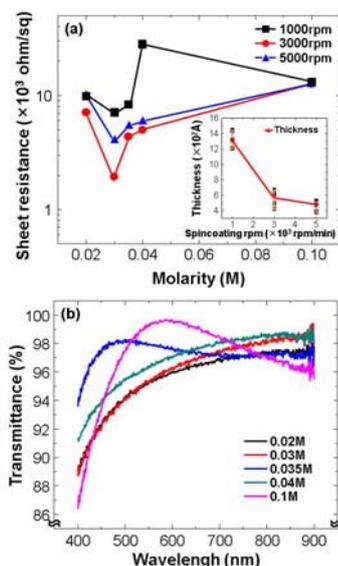


Figure 1. (a) Change in sheet resistance of sol-gel ITO as a function of molarity of SnCl_2 . All samples were annealed at 500 °C under air ambient for 1 hr. The average thickness as a function of spin coating speed is shown in inset of Figure 1. (b) Transmittance spectra with the concentration of SnCl_2 . All samples were prepared by spin coating at 3000 rpm, followed by heat treatment at 500 °C under air ambient for 1 h.

Optimization of sol-gel ITO

Figure 1(a) shows the change in sheet resistance for sol-gel ITO as a function of SnCl_2 molarity. The samples were prepared by spin coating with speeds of 1000, 3000, or 5000 rpm, followed by heat treatment at 500 °C under an air ambient for 1 hr. The sheet resistance of ITO decreased until the molarity of SnCl_2 reached 0.03 M regardless of the spin coating speed. The sheet resistances of ITO using 0.03 M SnCl_2 were the lowest and were 6×10^3 , 2×10^3 , and $4 \times 10^3 \text{ } \Omega/\text{sq}$ for speeds of 1000, 3000, and 5000 rpm, respectively. It was found that the film became rough and the sheet resistance increased again as the molarity of SnCl_2 increased. Therefore, fabrication conditions for sol-gel ITO were optimized by using 0.03 M SnCl_2 at 3000 rpm. The average thickness as a function of spin coating speed is shown in the inset of Figure 1. As shown, the thickness decreased from 1300 to 500 Å as spin

coating speed increased from 1000 to 5000 rpm. Transmittance spectra as a function of SnCl_2 concentration are shown in Fig. 1(b). All samples were prepared by spin coating at 3000 rpm, followed by heat treatment at 500 °C under air ambient for 1 h. The transmittances of all samples are higher than 90 % regardless of the concentration of SnCl_2 . The case of 0.1 M SnCl_2 looks to have the highest transmittance. However, this coating is not uniform such that spots of bare glass occur in some places. Therefore, it is concluded that the optimum condition for the fabrication of sol-gel ITO is to use 0.03 M SnCl_2 with $\text{In}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (1:9), and to spin coat on glass at 3000 rpm.

GO and rGO

Figure 2(a) shows an optical microscope image of GO. A GO solution (3 mg/mL) in water was spin-coated on SiO_2 (300 nm)/Si substrate at 300 rpm. It is shown that some flakes seemed to exist in a few layers. The typical size of a GO particle is a few micrometers. An AFM image of a GO sheet is shown in Fig. 2(b). Although the size of the GO sheets is inhomogeneous, the average height of GO was found to be ~ 1.5 nm. Figure 2(c) shows the Raman spectra of GO, PPD-rGO, and HYD-rGO. The peak for G-O (1599 cm^{-1}) at the G-band was up-shifted compared with that of graphite (1580 cm^{-1}). This was attributed to the presence of isolated double bonds that resonate at frequencies higher than that of the G-band of graphite. The G-band of PPD-rGO or HYD-rGO occurred at 1583 cm^{-1} , which corresponds to the recovery of the hexagonal network of carbon atoms with defects. The intensity ratios of the D-band (I_D) to the G-band (I_G) in GO, PPD-rGO, and HYD-rGO were calculated to be 0.67, 0.91, and 0.83, respectively. Therefore, the reduction process altered the structure of GO resulting in high quality sheets with few defects. Elemental analysis was also performed to confirm that PPD-rGO and HYD-rGO were deoxygenated well, as shown in Table I. After GO was treated with PPD or HYD, the carbon ratio increased from 51.80 to 68.29 or 71.53, but the oxygen ratio decreased from 44.34 to 19.58 or 18.30 indicating that GO was successfully reduced by PPD or HYD.

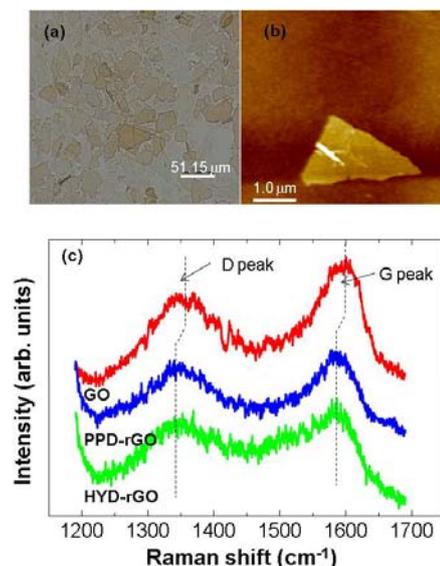


Figure 2. (a) Optical microscope image of GO spin-coated on SiO_2 (300 nm)/Si substrate, (b) AFM image of GO, and (c) Raman spectra of GO, PPD-rGO, and HYD-rGO.

Synthesis and characterization of rGO-ITO hybrid materials

Figure 3(a) illustrates the change in sheet resistance in ITO intercalated with rGO as a function of annealing temperature. The ratio of additives to sol-gel ITO was fixed at 0.66 wt % and heat treatment was performed for 1 hr under an air ambient. The sheet resistance decreased with annealing temperature. After the samples were heated at 500 °C for 1 h, and the sheet resistance decreased to 2.0×10^3 , 1.5×10^3 , 1.0×10^3 , and $0.7 \times 10^3 \text{ } \Omega/\text{sq}$ for ITO, ITO with GO, ITO with PPD-rGO, and ITO with HYD-rGO, respectively. Based on these results, conductive rGO was distributed in less conductive sol-gel ITO, thereby reducing the sheet resistance. Transmittance spectra of ITO with rGO after heat treatment at 500 °C for 1 hr are shown in Fig. 3(b). The transmittance values of all samples are greater than 85 % even though the transmittance of ITO with the additive is lower than that of ITO. It is possible that some flakes of GO or rGO overlapped with each other, decreasing the transmittance of the samples.

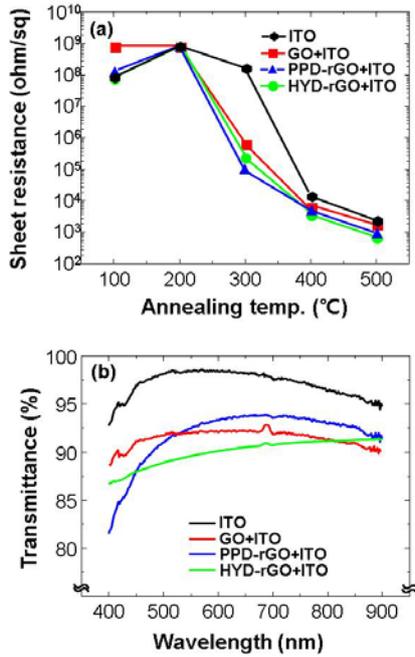


Figure 3. (a) Change in sheet resistance for ITO intercalated with rGO as a function of annealing temperature. The ratio of additives compared to sol-gel ITO is fixed to 0.66 wt % and heat treatment was performed for 1 hr under air ambient. (b) Transmittance spectra of ITO with 0.66 wt % rGO after heat treatment at 500 °C for 1 hr.

rGO-ITO hybrid materials as a transparent electrode

Figure 4(a) shows the current density-voltage curve of OLED fabricated using ITO, ITO with GO, ITO with PPD-rGO, or ITO with HYD-rGO as anodes. The operating voltage at a current density of 30 mA/cm² was 23.8, 20.0, 21.7, and 14.2 V for ITO, ITO with GO, ITO with PPD-rGO, and ITO with HYD-rGO, respectively. Current density-voltage curves of OLED using ITO with GO or ITO with PPD-rGO as anodes look like linear, suggesting that the anode induced significant leakage current. The luminance-current density behavior is shown in Fig. 4(b). As shown, the luminance value at a current density of 90 mA/cm² is 7500, 2100, 4700, and 11000 cd/m² for OLED using ITO, ITO with GO, ITO with PPD-rGO, or ITO with HYD-rGO as anodes, respectively. Even though the device performance is very poor compared to the OLED using sputtered ITO as anodes, it is thought that HYD-rGO in the sol-gel ITO effectively decreases operating voltage and increases luminance in OLED.

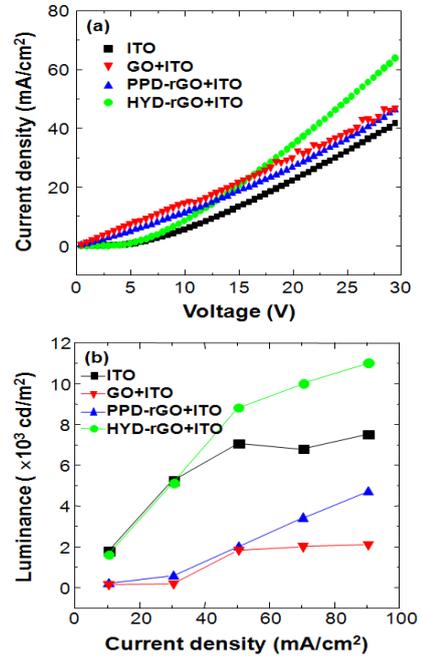


Figure 4. (a) The current density-voltage curve and (b) luminance-current density characteristic of OLED using ITO, ITO with GO, ITO with PPD-rGO, or ITO with HYD-rGO as an anode.

4. Conclusion

We investigated the effect of sol-gel ITO intercalated with rGO on the electrical and optical properties of OLED. Raman spectra showed that the G-band of PPD-rGO or HYD-rGO down-shifted from 1599 to 1583 cm⁻¹ and the I_D/I_G ratio increased from 0.67 to 0.91 or 0.83, indicating the recovery of the hexagonal network of carbon atoms with defects. Elemental analysis data showed that oxygen content decreased from 44.34 to 19.58 and 18.30 after GO was treated by PPD or HYD, indicating that PPD or HYD effectively deoxygenates GO. After adding 0.66 wt % PPD-rGO or HYD-rGO into sol-gel ITO, the sheet resistance of the film decreased from 2×10^3 to 1.0×10^3 or 0.7×10^3 Ω/sq, respectively. However, the transmittance value was still maintained as high as 87 %. Operation voltage at a current density of 30 mA/cm² in OLED using HYD-rGO+ITO hybrid material as anodes decreased from 23.8 to 14.2 V. Simultaneously, the luminance value at a current density of 90 mA/cm² also increased from 7500 to 11000 cd/m². Therefore, rGO is

effective in reducing the sheet resistance of sol-gel ITO.

Acknowledgements

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