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Transparent conductive electrode based on LBL deposition of graphene oxide and copper nanowires

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ABSTRACT

In this work, Graphene/Copper Nanowire (G/CuNW) based transparent conducting electrodes (TCEs) were prepared via spin-assisted layer-by-layer (LBL) deposition. 3-aminopropyltriethoxysilane (ɣ-APS) functionalized glass substrates were sequentially spin-coated with graphene oxide (GO) and CuNWs. Then, to enhance the electrical conductivity, the multilayer films were subjected to chemical reduction and thermal annealing. The ultimate films were characterized by a scanning electron microscope, UV–Vis spectrometer, and sheet resistance using a four-point probe method. 3-bilayer G/CuNWs films exhibited sheet resistance of 9 Ω/sq and optical transmittance of 67% (at 550 nm), which is comparable to commercial ITO electrode in terms of mainly sheet resistance.

1. Introduction

Transparent conducting electrodes (TCEs) are the key component of many modern optoelectronic devices including solar cells, light-emitting diodes and touch screens. Owing to its low sheet resistance (~15 Ω/sq) and relatively high optical transmission (~85%), indium tin oxide (ITO) is the industrially accepted material. However, the scarcity of indium and the inherent brittleness coupled to complicated and energy-intensive coating process of ITO create a strong incentive to find alternative transparent conductors for above-mentioned devices [1].

In the last decade, various nanomaterials including conducting polymers, carbon nanotubes, graphene and silver nanowires have been introduced as novel TCE material [2]. Among them, silver nanowires (AgNWs) have been extensively utilized in organic solar cells, organic light emitting diodes and displays owing to their high electrical conductivity, mechanical flexibility, and high transparency [3,4]. On the other hand, copper nanowires (CuNWs) are a promising TCE candidate because of their high intrinsic conductivity as well as the abundancy and lower cost of copper compared to silver. However, the oxidation problem of the CuNWs deteriorates their electrical properties, which in turn limits their widespread use in the TCEs [5,6].

To overcome the oxidation problem of CuNWs, various protecting approaches have been developed, such as encapsulation of the nanowires with polymeric layer [7], passivating with special corrosion inhibitors [8], use of inorganic shells [9] or coating the nanowires with graphene/graphene oxide (G/GO) sheets [10–15]. Among all these routes, G/GO demonstrated best protection of the CuNWs from oxidation without sacrificing the electrical properties. Strategies to prepare G/GO and CuNWs composite films include spray coating of both GO and CuNWs [10], simultaneous vacuum filtration GO and CuNWs followed by transfer to a substrate [11,13–15] and spray/blade coating of CuNWs followed by chemical vapor deposition of graphene [12]. These approaches include common drawbacks such as reproducibility and poor adhesion of the CuNWs to the substrate. On the other hand, layer-by-layer (LBL) deposition is a very promising approach that can create thin films with tunable morphology, surface properties and good adhesion to any surface [16].

In this study, therefore, G/CuNW multilayer based TCEs were fabricated via spin-assisted LBL deposition technique. 3-aminopropyltriethoxysilane (ɣ-APS) functionalized glass substrates were sequentially spin coated with negatively charged graphene oxide (GO) and positively charged CuNWs. Then, to enhance the electrical conductivity, the multilayer films were subjected to chemical reduction and thermal annealing. The ultimate films were characterized by a scanning electron microscope, UV–Vis spectrometer, and sheet resistance using a four-point probe method.

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2. Materials and methods

2.1. Materials

Cysteamine hydrochloride (CA, BioXtra), sodium borohydride ($NaBH_4$), 3-Aminopropyl triethoxysilane (ɣ-APS), anhydrous ethanol, methanol and DMF were obtained from Sigma–Aldrich. Copper nanowires (CuNWs) dispersed in ethanol (10 mg/ml) with an average diameter of 100 nm and length of 30–50 μm were purchased from Novarials Co. Glass slides (15 × 15 mm^2) were provided by Menzel-Glaser GmbH & Co. Deionized (DI) water (18.2 MΩ) was obtained with a Millipore-Q system.

2.2. Functionalization of glass substrate

Prior to treating the glass substrates with piranha solution [16], they were subjected to sonication in acetone, ethanol and DI water for 5 min and dried under N_2 flow. Then, the glass substrates were dipped in 3% ɣ-APS solution for 3 h, followed by washing with excess methanol and drying under N_2 flow.

2.3. Surface modification of CuNWs

0.026 M CA in DMF was added to CuNW solution (1 mg/ml), followed by stirring for 24 h at RT. Then, to remove the unreacted CA, the solution was centrifuged, followed by washing with DMF and DI water sequentially, and the final concentration was adjusted to 0.5 mg/ml by re-dispersing in DI water.

2.4. Preparation of transparent conductive electrode

Graphene oxide (GO) was synthesized as reported previously [16]. The ɣ-APS modified substrate was coated with GO solution (1 mg/mL) via spinning (2.500 rpm, 30 sec) and rinsed excessively with DI water. Then, the substrates were spin-coated (2.500 rpm, 30 sec) with CuNWs solution, followed by vigorously rinsing with DI water. Multilayer films were acquired via repeating the mentioned processes. Finally, the films were subjected to chemical reduction and thermal annealing under inert gas atmosphere based on our previous report [16].

2.5. Characterization

Surface charges of CuNWs and GO were evaluated by zeta potential analyzer (Nano ZS, Malvern Instruments). The surface morphology of the TCEs were characterized by field emission scanning electron microscope (FIB-SEM Multibeam System, JIB 4601F) and sheet resistance of TCEs was measured by four-point probe technique (RM3000, Jandel), while the optical property was analyzed using UV–Vis spectrometer (Lambda 750, Perkin-Elmer).

3. Results and discussion

The CuNWs demonstrated a positive zeta potential (+32.0 mV), while the GO exhibited a negative value (−40.9 mV) (Fig. S1). These positive and negative charges resulted from protonation of $–NH_2$ and deprotonation of –COOH groups [16], respectively, which provide sufficient mutual attraction to ensure a stable LBL deposition.

Increasing the layer number provided a darkening red color (Fig. 1-a), which can be attributed to the increase in the number of GO and CuNWs. It is clearly shown that the film was still transparent even after four bilayer depositions. As shown in Fig. 1-b, the optical transmittance of films decreased with increasing number of bilayers. The strong bonding between the GO and CuNWs was derived from the ionic interactions between the negatively-charged hydroxyl groups of GO and the positively-charged amine groups of CuNWs [16]. Moreover, the film thickness measurement also supports the formation of successful

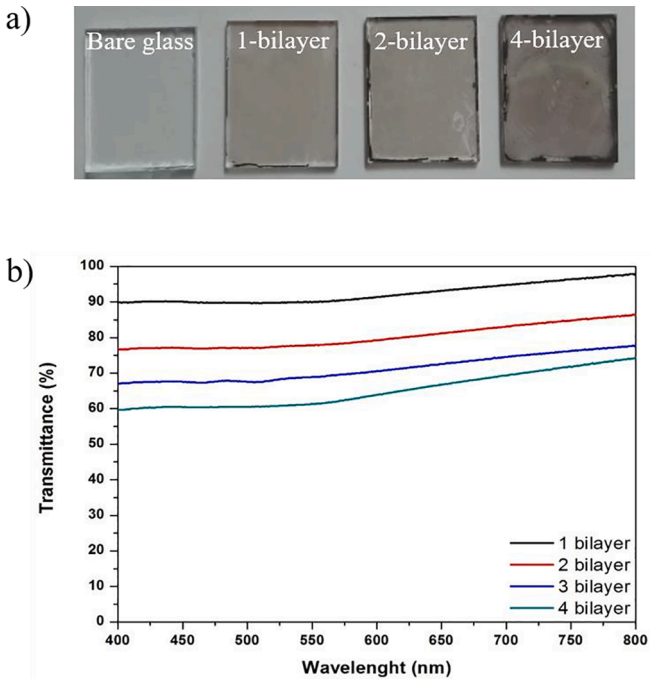

Fig. 1. (a) Macro images and (b) Optical transmittance of GO/CuNWs multilayer films.

multilayer, showing 72, 136, 256 and 551 nm with 1, 2, 3 and 4 bilayers, respectively. The 1 bilayer sample exhibited RMS value of 1.5 nm. As the number of bilayers increased, their RMS values increased, providing 3.2, 8.4 and 11.7 nm for 2, 3 and 4 bilayers, respectively (Fig S2).

As it could be seen in Fig. 2, number of the bilayers have strong influnce on the morphology of the multilayer films. It is noticeable that 1-bilayer film resulted in a low density of nanowires (Fig. 2-a). However, the density of the CuNWs on the surface was found to increase with the increased number of layers, which again demonstrates the successful LBL deposition. In addition, it is worthy to note that increasing the number of bilayers led to formation of more electron transport paths, and reduction in the size of voids which led to less optical transmission (Fig. 2 b-d).

After chemical reduction and thermal annealing, the sheet resistance of the multilayer films was evaluated as 50, 21, 9 and 7 Ω/sq for 1, 2, 3 and 4-bilayers, respectively. Moreover, the optical transmission at 550 nm was measured as 89, 77, 67 and 60% for 1, 2, 3 and 4-bilayers, respectively (Fig. 3-a). We believe that both graphene and CuNW network contributed to the conductivity of the multilayer film. The graphene acted as a conducting bridge between disconnected CuNWs, which in turn led to low sheet resistance. The 3-bilayer G/CuNWs films exhibited Figure of Merit (FOM) value of 94, which is comparable to that of ITO (T = 85%, R_S = 15 Ω/sq, FOM = 148.5).

Consequently, G/CuNW film performance was compared with the previous works in Fig. 3-b. The comparison reveals that our work has similar performance with the other coating techniqes. Moreover, the films obtained in this work have good adhesion to the substrate. The G/CuNW multilayer films in this work easily passed adhesion test with 3-M tapes without any change in sheet resistance and topology (not shown here). The strong adhesion could be explained by the strong ionic interaction between negatively charged GO and positively charged CuNWs (Fig. S3). Compared to other coating techniques, LBL deposition provides better results in terms of control over the morphology, tuning the optoelecronic properties, repeatibility and tailoring adhesion of the to the substrate.

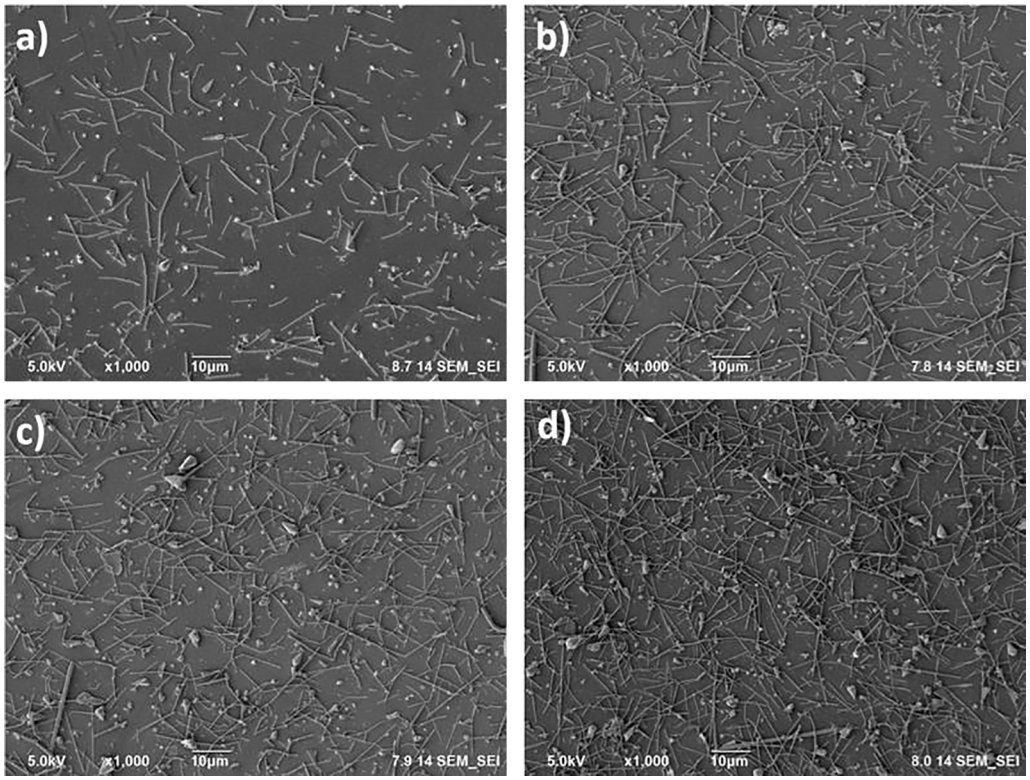

Fig. 2. a) SEM images of (a) 1, (b) 2, (c) 3 and (d) 4-bilayer GO/CuNWs films.

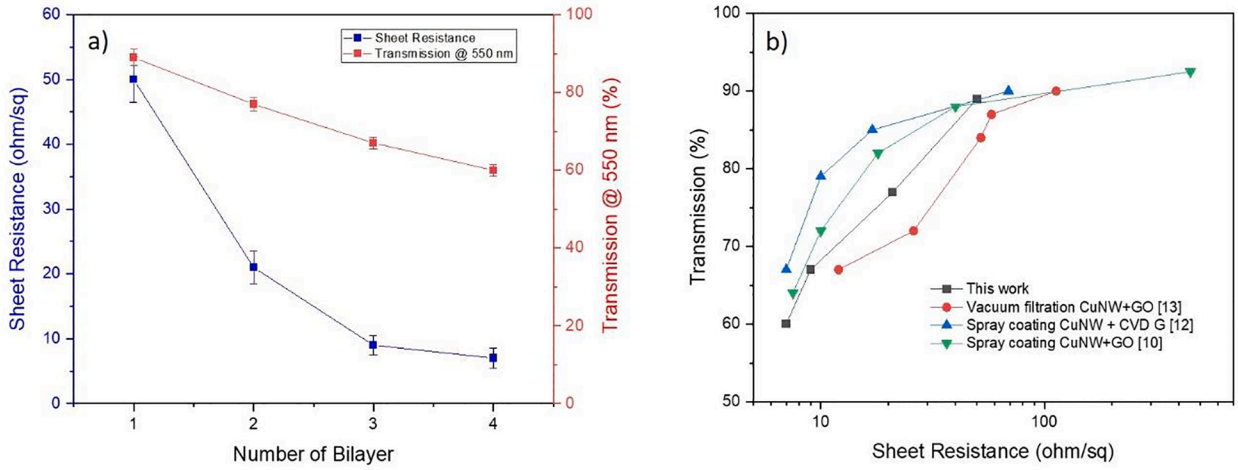

Fig. 3. (a) Sheet resistance and optical transmission at 550 nm of G/CuNW multilayer films and (b) Comparison of the sheet resistance and optical transmission values of this work with the references.

4. Conclusion

In this work, G/CuNWs based solution-processable transparent conducting electrode was successfully prepared via LBL coating method. The electrical and optical properties of G/CuNWs hybride electrodes were investigated by varying the number of bilayers. Optimum opto-electronic performance was obtained with 3-bilayer of G/CuNWs electrode, which provided sheet resistance of 9 Ω/sq, optical transmission at 550 nm of 67% and FOM value of 94. The demonstrated material system and coating technique has the potential to replace ITO where low-cost and flexible processability is preferred.

CRediT authorship contribution statement

B. Tugba Camic: Investigation, Writing – original draft. **Jaana Vapaavuori:** Writing – review & editing. **Fevzihan Basarir:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.131632.

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