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Top-Emission Organic Light-Emitting Diode with a Novel Copper/Graphene Composite Anode

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The relatively high sheet resistance of graphene compared with indium tin oxide (ITO) blocks the applications of graphene as transparent electrodes in organic light-emitting diodes. A novel copper (Cu)/graphene composite electrode is presented and employed as the anode of a top-emission organic light-emitting diode with the structure of Cu/graphene/V_2O_5/NPB/Alq_3/Alq_3: C545T/Bphen: Cs_2CO_3/Sm/Au. The Cu/graphene composite electrodes are fabricated by growing graphene directly on Cu substrates via the chemical vapor deposition method without any transfer process. The maxima of current efficiency and power efficiency of a typical Cu/graphene composite anode device reach 6.1 cd/A and 7.6 lm/W, respectively, which are markedly higher than those of the control devices with a graphene anode, a Cu anode or an ITO anode. The low sheet resistance of the composite electrode, the high quality of graphene without any transfer process and the avoidance of wave guiding loss in glass or polyethylene terephthalate substrates result in the improvements of light emission efficiencies.

1. Introduction

Organic light-emitting diodes (OLEDs) have been extensively researched in the last two decades because of their amazing light emission properties and huge potential in display and illumination. As an efficient transparent and conductive material, indium tin oxide (ITO) is widely used as the transparent anode of OLEDs. However, ITO has some disadvantages in serving as the anode, such as high cost, limited use for flexible substrates, and degradation of device performance over time due to indium diffusion.[1] So far, many materials have been used to replace ITO as electrodes, such as Ag nanowire film,[2] thin polycrystalline *p*-Si film,[3] carbon nanotubes (CNTs),[4] and graphene.[5–7]

Graphene is a two-dimensional monolayer with sp^2-hybridized carbon structure, and has been demonstrated as a promising transparent and conductive electrode in solar cells,[8] photodetectors,[9] and light-emitting diodes.[10] However, compared to ITO, the graphene usually has higher sheet resistance and lower work function, which will result in high series resistance and large injection barrier, respectively, when serving as the anode of an OLED.[11] In addition, so far, the fabrication of graphene based devices usually involves complicated graphene transfer process, which inevitably introduces contamination, and may cause performance degradation of the devices. It is reported that graphene synthesized by the chemical vapor deposition (CVD) method usually has higher conductivity (ca. several hundred Ω/□) compared to that synthesized by other methods. Han et al. reported that the sheet resistance of the CVD grown graphene could further be reduced to 30 Ω/□ by *p*-doping with HNO_3 or $AuCl_3$. With that approach, they demonstrated high luminous efficiency bottom-emission OLEDs with graphene anodes.[11] In this paper, we propose a novel Cu/graphene composite electrode, and apply it as the anode to top-emission organic light-emitting diode (TEOLED). The Cu/graphene composite electrode is fabricated by growing a graphene film on a Cu foil via the CVD method. Herein, the graphene contributes to hole injection into organic layers, and the underlying Cu helps to decrease the series resistance and increase the light reflection. Significantly, the device fabrication is free from graphene transfer process. Besides, compared to the reported graphene based OLEDs which are usually bottom-emitting from graphene covered glass or polyethylene terephthalate (PET) substrates, the TEOLEDs have much less optical absorption and wave guiding loss, enhanced light outcoupling, larger aperture ratio, and easier integration with the active-matrix control circuits. Furthermore, the high heat dissipation coefficient of Cu may help to enhance the lifetime and stability of the as-fabricated TEOLEDs.[12]

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2. Results and Discussion

Before device fabrication, the properties of the CVD grown graphene were investigated. The optical microscope image of graphene transferred on a Si/300 nm SiO_2 substrate is shown

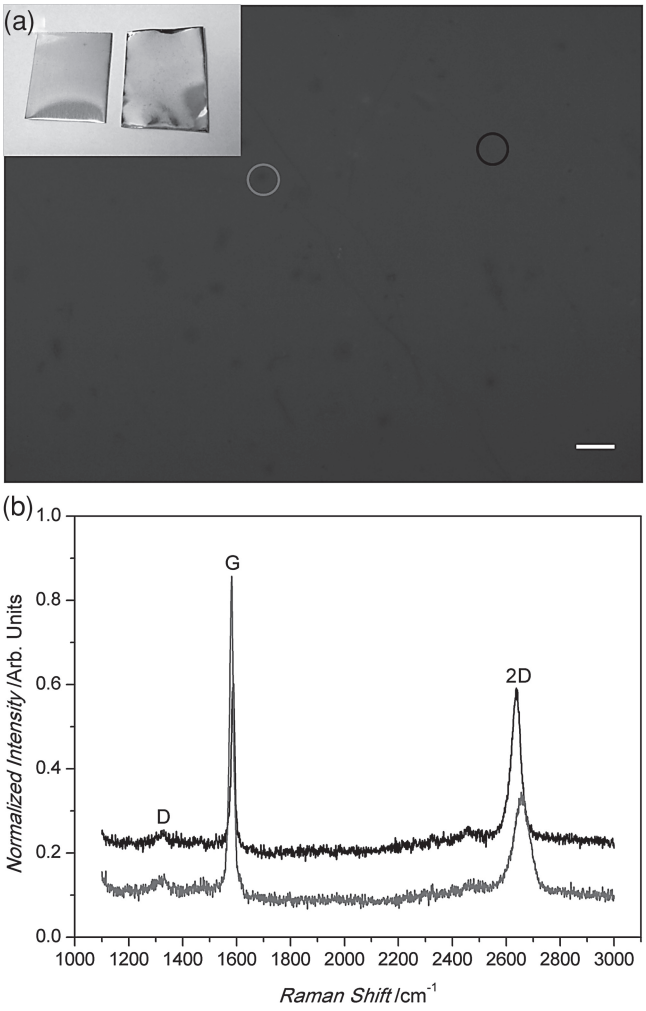

Figure 1. Characterization of the graphene grown on Cu. a) The optical microscope image of graphene transferred on a Si/300 nm SiO_2 substrate. Gray circle and black circle represent the dark and light region, respectively. Scale bar: 10 μm. The inset: the images of an as received Cu substrate (left) and a Cu/graphene composite electrode after CVD growth (right). b) Raman spectrum of graphene transferred on a Si/300 nm SiO_2 substrate. The gray line represents a typical Raman spectrum detected in the dark region (gray circle), and the black line gives a typical result measured in the light region (black circle).

in **Figure 1**a. The as-prepared graphene is continuous and with large area. A small percentage of dark flakes and wrinkles associated with the thermal expansion coefficient difference between Cu and graphene can be clearly found, which is consistent with previous reports.[13] The inset of Figure 1a shows an as received Cu substrate (left) and a Cu/graphene composite electrode (right) after CVD growth of graphene, respectively. It is clearly seen that the surface of Cu is shinier after CVD growth, which indicates that the surface is covered by graphene because graphene can block the oxidation of Cu surface.[14] A typical Raman spectrum of graphene transferred on a Si/300 nm SiO_2 substrate is shown in Figure 1b. The D band (centered at ≈1330 cm^{-1}) is almost negligible, indicating the low defect density of the graphene. The intensity ratio of the G band (centered at ≈1596 cm^{-1}) and the 2D band (centered at ≈2648 cm^{-1}) detected in the light region (black circle) is close to 1:1, suggesting the formation of bilayer graphene.[15] The Raman spectrum in the dark region (gray circle) has the 2D band with lower intensity and larger full-width at half-maximum (FWHM), corresponding to few-layer graphene with a small percentage.

To fabricate a TEOLED with a Cu/graphene composite anode, different organic materials and metal cathode are subsequently evaporated on a Cu/graphene substrate away from the Ni/Au ohmic contact electrode in high vacuum layer by layer. Herein, V_2O_5 is used to enhance hole injection ability of anode. N, N-bis-1-naphthl-diphenyl-1, 1-biphenyl-4, 4-diamine (NPB) is used as the hole transport layer. 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1) benzopyrano (6,7,8-ij) quinolizin-11-one (C545T) doped in the tris (8-hydroxyquinoline) aluminum (Alq_3) is used as the emission source. Alq_3 also serves as the electron transport layer. 4, 7-diphenyl-1, 10-phenanthroline (Bphen) doped with Cs_2CO_3 (Bphen: Cs_2CO_3) is used as the electron injection and transport layer, and a stacked Sm (15 nm)/Au (15 nm) is used as the semitransparent cathode for top emission. The resulting TEOLED with the structure of Cu/Graphene/V_2O_5 (5nm)/NPB (60 nm)/Alq_3: C545T (30 nm)/Alq_3 (15 nm)/Bphen: Cs_2CO_3 (15 nm)/Sm (15 nm)/Au (15 nm), which is referred to as the Cu/Graphene composite anode device in the following text, is depicted in **Figure 2**a. Figure 2b shows the electroluminescence spectra of a TEOLED at different forward biases. The center wavelength of light emission is about 530 nm, corresponding to green light emitted from C545T.

Figure 3a shows a typical current density–voltage relation of the Cu/graphene composite anode TEOLED together with those of other two control devices. As can be seen, the device with graphene anode has the lowest current density compared to the other two devices under identical voltages. This may be due to the big series resistance resulting from the high sheet resistance of graphene. It is worth noting that, under identical voltage, the current of the Cu/graphene composite anode device is lower than that of the ITO anode device, although the sheet resistance of the Cu/graphene composite electrode is smaller than that of ITO. We think that this phenomenon can be understood as follows: because the sheet resistances of Cu/graphene and ITO are both relatively low, herein, the currents are mainly determined by resistances of the barriers for hole injection. In our case, the measured work function of Cu/Graphene composite anode is about 4.46 eV, which is lower than that of oxygen plasma treated ITO (~ 5.0 eV). This may result in a higher hole injection barrier and lower current. Typical luminance vs voltage characteristics of the three types of devices are shown in Figure 3b. The turn-on voltage at luminance of 1cd/m^2 is about 2.4 V for the Cu/Graphene composite anode device. Besides, at the forward bias of 8 V, the luminances of both Cu/graphene composite anode and ITO anode devices exceed 10000 cd/m^2, about one order of magnitude higher than that of the graphene anode device at 8 V. Figure 3c and Figure 3d are current and power efficiencies vs. voltage relations, respectively, for the three types of TEOLEDs. It is clear that the Cu/graphene composite anode device, with the maximum of current and power efficiencies of about 6.1 cd/A and 7.6 lm/W respectively, exhibits the best performance compared to the other two types of devices.

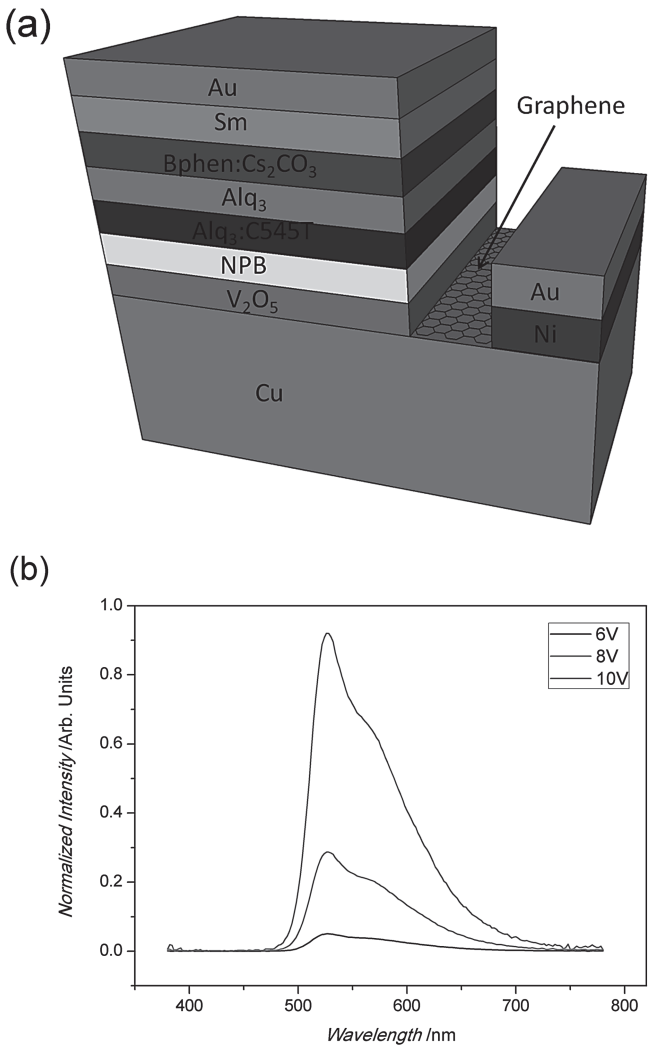

Figure 2. a) A schematic diagram of the structure of TEOLEDs with Cu/graphene composite anodes. b) The electroluminescence spectrum of a typical TEOLED with a Cu/graphene composite anode at different forward voltages.

We attribute the high efficiencies of Cu/graphene composite anode devices to the following aspects: First, the sheet resistance of a typical Cu/graphene composite anode is several orders of magnitude lower (≈0.0039 Ω/□) than that of graphene (≈several hundred Ω/□) and ITO (10–80 Ω/□), which decreases the power loss on series resistance and contributes to higher power efficiency. Second, compared to the ITO anode control device, the Cu/graphene composite anode device has better carrier balance, i.e., the higher internal quantum efficiency, which results from reduced hole current injection from the anode.[16] It is noted that both ITO anode devices and Cu/graphene composite anode devices have low sheet resistances and the same cathodes and electron injection and transport layers, the electron currents are similar. The lower total current of Cu/graphene composite anode devices implies the better carrier balance in these devices. This will contribute to the improved current efficiency. In addition, the generated bottom emission light has to pass through the glass substrate at least twice times before outcoupling to the top semitransparent cathode in either ITO anode or graphene anode devices, which results in much energy loss via waveguide effect and absorption. In comparison, there is almost no such waveguide loss in the Cu/graphene composite anode devices, which benefits light extraction efficiency for top emission.

In order to examine the role of graphene in the Cu/graphene composite anode, Cu anode control devices were investigated. **Figure 4**a–c show the current vs voltage relation, current efficiencies and power efficiencies vs voltage relations, respectively, for a typical Cu/graphene composite anode device and a typical Cu anode control device. The current and power efficiencies for a typical Cu anode control TEOLED are usually quite low with large turn-on voltage, which implies that the injection barrier exists for hole. We think that this phenomenon may result from the interfacial dipole and the related chemical interactions at the interfaces. It has been demonstrated that the vacuum levels of organic material and metal (such as Ni, Au, etc.) do not align at the organic/metal interface as the result of the formation of an electric dipole layer, which tends to increase the barrier height for hole.[17] To overcome this problem, one approach is to insert a layer of transition metal oxides, such as MoO_3,[18] V_2O_5,[19] and WO_3 between the anode and the hole transport layer.[20] However, it is found that in a Cu/MoO_3 structure, contrast to the interfaces between MoO_3 and Au, Ni, and Mo, Cu is easy to diffuse throughout MoO_3 film to form a Cu-Mo-O alloy regardless of MoO_3 film thickness, and thus hinders MoO_3's ability of lowering hole barrier due to the reduction of Mo^{6+} to Mo^{5+}.[21] We think that similar physical and chemical processes may exist in a Cu/V_2O_5 structure, because of the strong diffusion ability of Cu in V_2O_5 and the spontaneous chemical reaction: $2Cu+V_2O_5 \rightarrow 2VO_2+Cu_2O$ $\Delta G = -112.86$ kJ mol^{-1}.[21,22] To verify this, surface work functions are measured for comparisons. The work function of 5 nm V_2O_5/Cu is only about 5.03 eV, which is lower than that of 5 nm V_2O_5/graphene/Cu (≈5.32 eV). In other words, in our Cu anode control device, the high hole barrier still exists even with 5 nm V_2O_5 deposited on Cu, which accordingly results in a poor luminous efficiency. Therefore, we can ascribe the role of graphene in the Cu/graphene composite anode to the following two aspects: On one hand, graphene is an effective anode and is able to inject hole to organic layers. On the other hand, the graphene on Cu may prevent the diffusion of Cu into V_2O_5, and favor the hole injection. Together with the underlying Cu, it is believed that the Cu/graphene composite anode will find its applications in future TEOLED display.

3. Conclusions

A novel Cu/graphene composite electrode is employed as the anode for TEOLED. The Cu/graphene composite electrodes are fabricated by growing graphene directly on Cu substrates via the CVD method. The maxima of current efficiency and power efficiency of a typical Cu/graphene composite anode device are markedly higher than those of the control devices. We attribute the high efficiencies of the Cu/graphene composite anode device to the low series resistance of anode, better carrier balance, the high quality of graphene without any transfer process, and nearly no waveguide loss in the substrate. The role

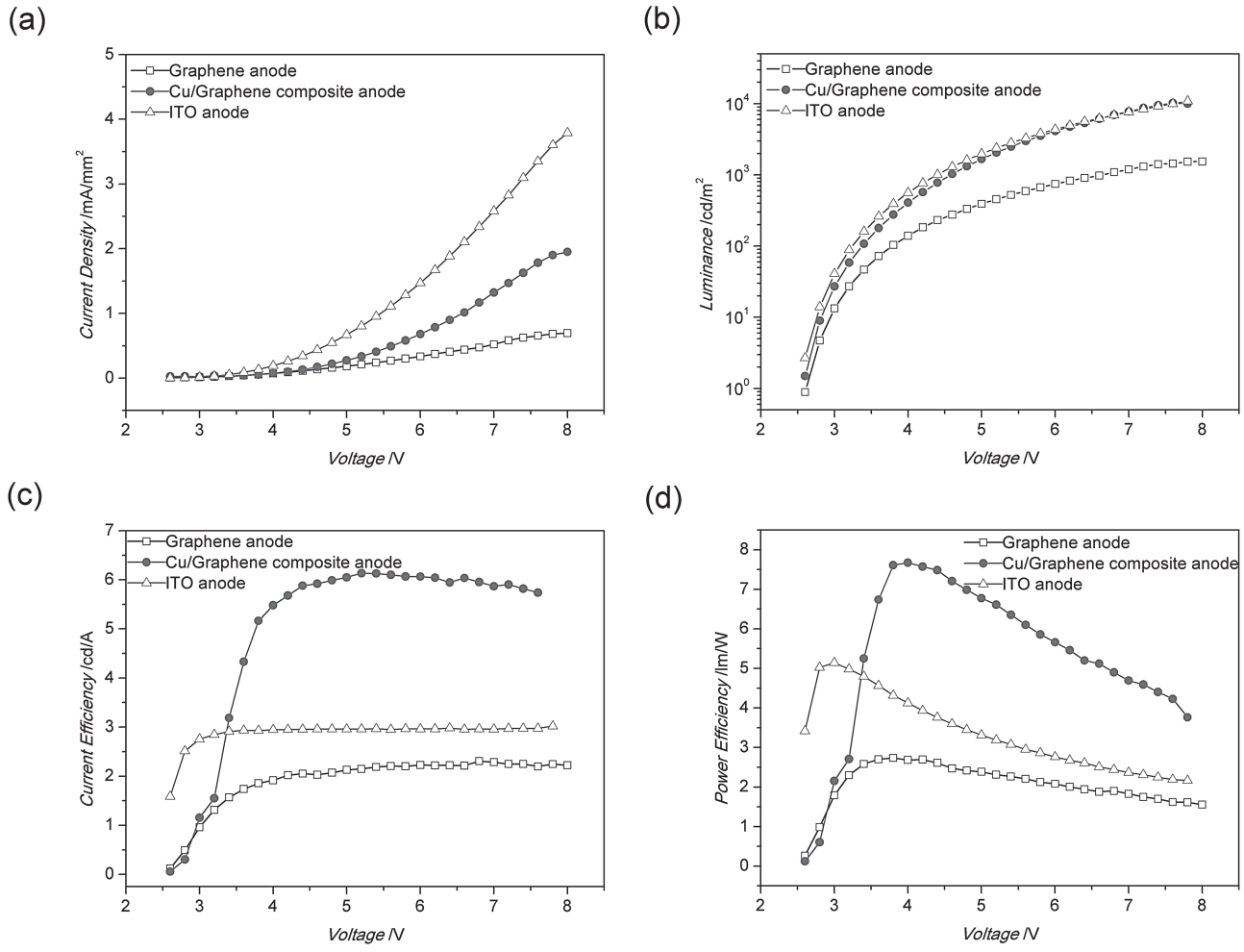

Figure 3. a) The current density-voltage characteristics of TEOLEDs with a Cu/graphene composite anode, a Cu anode and an ITO anode. b) The typical luminance vs voltage characteristics of a Cu/graphene composite anode device, a graphene anode device and an ITO anode device. c) The current efficiency vs voltage characteristics of the three types of TEOLEDs. d) The power efficiency vs. voltage characteristics of the three types of TEOLEDs.

of graphene in the Cu/graphene composite anode is also discussed. We believe that Cu/graphene composite anode will find applications in future TEOLEDs.

4. Experimental Section

Synthesis and Characterization of Graphene for Cu/Graphene Composite Anode: The large-area graphene used in this work was synthesized via the CVD method.[13] In this method, pieces of 125-μm-thick Cu foils were placed in a quartz tube in the center of a tube furnace. Then the chamber of the furnace was pumped down to 0.02 Torr. After that, the furnace was heated to 1000 °C under a H_2 flow rate of 20 SCCM. At 1000 °C, the Cu foils were annealed for 30 min to remove the copper oxide and increase the Cu grain size. Later, 25 SCCM CH_4 and 10 SCCM H_2 were introduced in the tube with a growth pressure of 0.5 Torr. The synthesis duration was 30 min. Finally, the samples were cooled down to room temperature without changing the chamber pressure and gas flow rates.

The as-synthesized graphene samples were transferred to Si/300 nm SiO_2 substrates for Raman characterization via the stamp method with the help of poly methyl methacrylate (PMMA).[23] The optical images of the graphenes were taken by an optical microscope (Olympus BX51M). The Raman spectra of the graphenes were measured with a microzone confocal Raman spectroscope (HORIBA Jobin Yvon, LabRam HR 800) equipped with a color charge coupled device. The excitation wavelength was 632.8 nm. A Hall measurement system (Accent HL5500) was used to investigate the electrical properties of the graphene and Cu/graphene composite electrode.

Fabrication and Measurement of Cu/graphene Composite Anode Teoleds and Control Devices: To fabricate a TEOLED with Cu/graphene composite anode, a Ni/Au (10 nm/100 nm) ohmic contact electrode was first deposited on Cu/graphene for later-on measuring purpose by thermal evaporation with a mask. After that, organic materials and metal cathode were thermally evaporated on Cu/graphene away from the Ni/Au pad in high vacuum (5.0×10^{-4} Pa) layer by layer. The emission area of the devices was 2×2 mm^2. For electroluminescence (EL) measurement, the voltage bias was supplied by a computer controlled source meter (Keithley 2400). EL spectra and luminance of the TEOLEDs were measured by a calibrated spectrometer (PR-705). The devices were unencapsulated and measured in air ambient at room temperature.

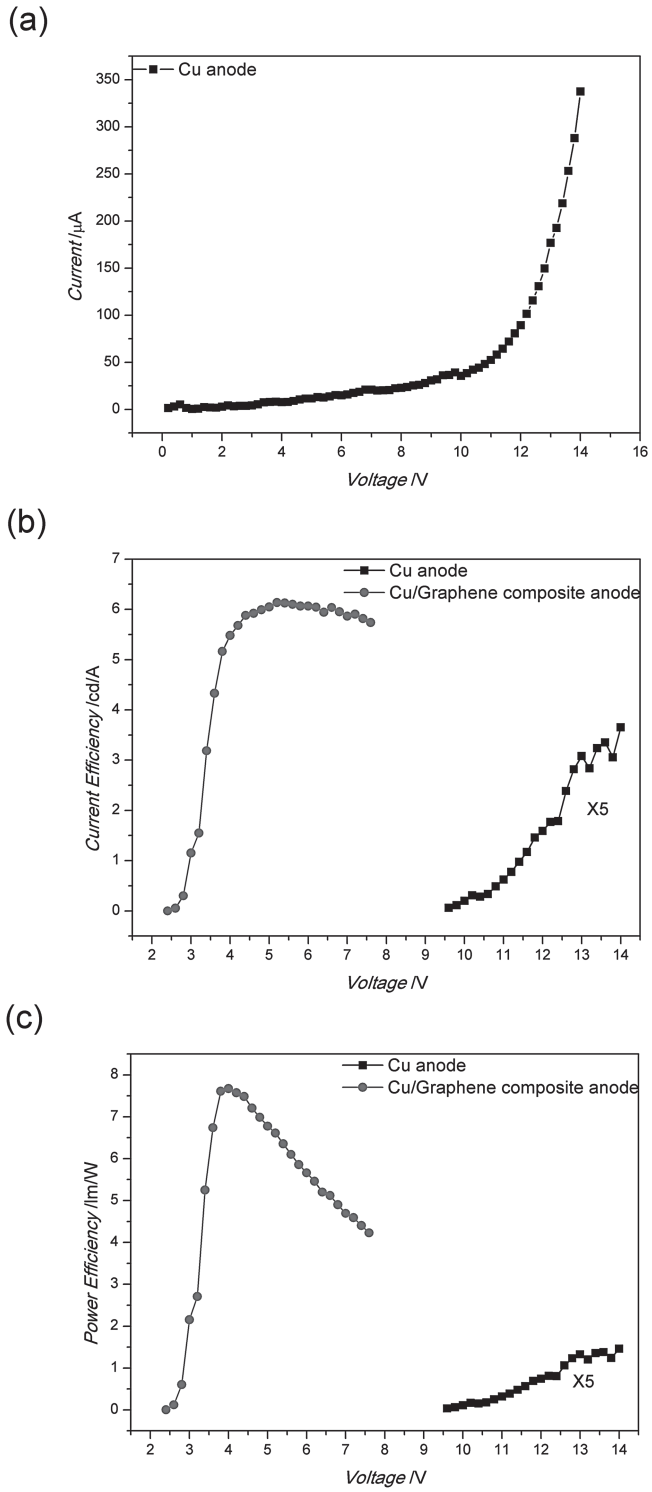

Figure 4. a) The current-voltage characteristics of a TEOLED with a Cu anode. b) The current efficiency vs voltage characteristics of TEOLEDs with a Cu anode and a Cu/graphene composite anode. c) The power efficiency vs voltage characteristics of TEOLEDs with a Cu anode and a Cu/graphene composite anode.

Three control devices, which had identical structures for the organic materials and cathodes except that the anodes were graphene-on-glass, ITO-on-glass, and Cu foil, respectively, were also fabricated for comparison. The rear surfaces of the glasses were thermally evaporated 100 nm Cu films for light reflection. The surface work function values of different anodes are measured by a photoelectron spectrometer (Riken Keiki AC-2).

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